



Nanoscopic vibrating structures at nonequilibrium

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by

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Abstract

This thesis derives the equilibrium state equation and fluctuation expressions of monodimensional chains of oscillators under fixed-length and fixed-force boundary conditions, proves the equivalence of the two boundaries, generalises the equilibrium expressions to nonequilibrium single oscillator relations by assuming a factorised nonequilibrium distribution, and verifies all the conclusions by simulating monodimensional Lennard-Jones chains of oscillators. This thesis also discusses the properties of coupled chains, based on a coupled chain model combining Lennard-Jones interactions and harmonic interactions.

Monodimensional oscillator systems discussed here contain nearest-neighbor interactions only, which makes it numerically possible to compute the state equation in equilibrium using statistical mechanics. In nonequilibrium steady states, monodimensional systems often violate the locality condition required by the local thermodynamics equilibrium, because correlations can persist over long distances and times. This can result in mechanical and thermodynamical properties that are peculiar and anomalous.

Firstly, using appropriate approximations, we derive microscopic equivalent for the van der Waals and Tonks equations, for Lennard-Jones chains. The validity of these equations is analysed, with a discussion on their applicability across different thermodynamic regimes. It is shown that the microscopic van der Waals equation provides a better description at elevated temperatures and that, in the high-temperature limit, it asymptotically reduces to the microscopic Tonks equation.

Secondly, we concentrate on single oscillator relations that represent the average length and length fluctuation as functions of average kinetic energy and average force, which are interpreted as microscopic pressure and temperature. Using simulations and factorised distributions from statistical mechanics, we show that these single-oscillator relations perform remarkably well across a broad and physically relevant range of nonequilibrium states, and their validity is intrinsically related to the decay of correlations.

Furthermore, we propose some considerations about the similarities of these systems with other known solvable models, for example the Tonks gas or harmonic systems. After these insights, we use the same framework to analyse state equations, fluctuations, and nonequilibrium relations of coupled chain models that bind a Lennard-Jones chain with an harmonic chain. By cutting the coupled model into repeated cells, we derive the statistical mechanics expression for the equilibrium state equations and fluctuations, approximate them in high temperature and low temperature limits and verify our results using simulations. We also generalise those equilibrium expressions to nonequilibrium single-cell relations, which are valid as long as the correlation among different cells decays.

Some final remarks on possible extensions of the present work finally conclude the thesis.

Dedicated to my father and mother.

Acknowledgements

This thesis is a summary of my study in the past ten years. It is devoted to a very classic, perhaps even “outdated” problem. The statistical mechanics method I have employed is also well-known and lacks novelty. Nevertheless, I still feel glad and a little proud to have had the opportunity to apply it to solve a problem, however simple it might be. I first encountered Thermodynamics and Statistical mechanics during my undergraduate years. The exams were difficult but I achieved good marks. At that time, I believed I understood thermodynamics. Later, during my graduate studies, I read some classic texts in the field and came to realize that I was merely familiar with the terminology. Now, during my PhD candidature, as I try to apply this knowledge, I immediately realize how little I actually know. “What is ‘familiarily known’ is not ‘properly known’”, still less “not so familiarily known”. “Know I don’t know”, that’s the core of the journey I’ve been on.

Along this journey, I have been fortunate to receive support and guidance from many people to whom I owe my sincere gratitude.

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孙瑞祺

Ruiqi Sun, 12/03/2026

Declaration

I, hereby declare that the Thesis entitled “Nanoscopic vibrating structures at nonequilibrium”, and submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Science Computing and Emerging Technologies of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the Thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the Thesis.

Ruiqi Sun, [Ruiqi Sun](#)

12/03/2026

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Introduction

Monodimensional systems, because of their simple and concise characters, have been considered as useful theoretical thinking tools. The “Monodimensional system” considered in this thesis is defined as a system composed of particles, which has only one degree of freedom. The most famous monodimensional model is the monodimensional Ising model, which Lenz proposed to understand magnetisation. The Ising model is a discrete model, consisting of scalar spins with only two states denoted by $+1$ and -1 , which correspond to “up” and “down” arrows in Fig. 1.1. An external field is imposed to push all the arrows to point, for example, upward. Energies of interactions among spins exist to favour a parallel alignment. Both external and inter-spin interactions tend to make the system “in order”. There also exists a dynamics due to thermal exchange that makes the spin system change its state and increase the system “disorder”. The interplay between “in order” and “disorder” makes it possible to use statistical mechanics methods to compute the properties of this system. When one considers a special case with a homogeneous external field and nearest-neighbour interactions, the system is exactly solvable via transfer matrix methods and the exact solution shows no spontaneous magnetisation at any nonvanishing temperature [Chowdhury and Stauffer, 2000].

Another monodimensional model frequently researched is the Fermi-Pasta-Ulam-Tsingou

(FPUT) chain. This model was initially designed to realise and explore the equipartition of energy in dynamical systems. Unlike the Ising model, the Fermi-Pasta-Ulam-Tsingou chain is a continuous model with an established dynamics. As shown in Fig. 1.1 it contains oscillators of equal masses connected by elastic springs with each oscillator moving continuously via Newton's laws. In the first simulation run by Fermi, Pasta, Ulam and Tsingou, the energy accumulates among the lowest few normal modes. This result leads to a series of theoretical and numerical findings on ergodicity, integrability, chaos and stability of motion [Berman and Izrailev, 2005], initiating new areas in the study of mono-dimensional chains of oscillators. This is also the main topic of this thesis: a line of oscillators moving one-dimensionally and connected one-by-one constitutes a monodi-mensional chain, which is characterised by the potential of each oscillator [Ford, 1992]. According to the potentials, chains can be classified into two categories: 1) indissociable chains, when potentials increase to infinity if being infinitely stretched. Typical examples include harmonic chains, where nearest neighbors interact via a harmonic potential and FPUT chains with non-harmonic potential up to quartic order. Case 2) is instead given by dissociable chains: potentials approach a finite value when being infinitely stretched. A key example in that sense is the Lennard-Jones chain, which is the focus of this thesis.

The Ising model was designed to understand phase transition, but no transition is found

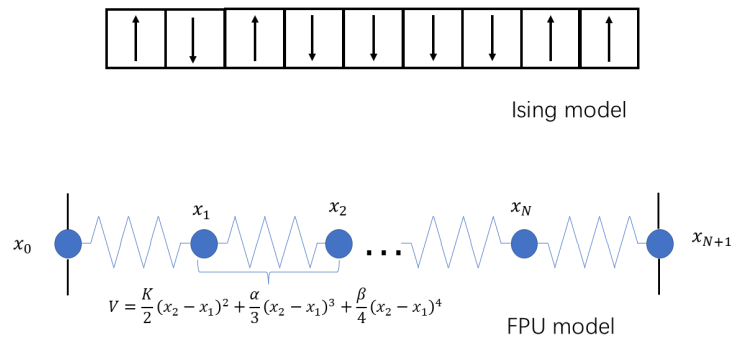


Figure 1.1: Sketch of Ising model and FPUT model.

there. FPUT chains with constant energy were simulated to validate equipartition of energy, but the long-time dynamics has proved to be “periodic, with almost perfect returns

to the initial conditions” [Berman and Izrailev, 2005]. The inability of monodimensional models to capture real-world behavior is unsurprising: the world is three-dimensional and a monodimensional model seems overly simplistic. However, with progress in miniaturization, the discovery of graphene [Novoselov et al., 2004] and advances in nanofabrication [Iijima, 1991, Iijima and Ichihashi, 1993], monodimensional systems - such as particles confined in one or several layers and further rolled into strings or nanotubes, have transitioned from theory to reality. As a result, statistical mechanics computation on monodimensional system are no longer just convenient testing cases or educational tools; they have become increasingly relevant to real physical phenomena and hold potential for practical application.

The driver of this thesis is to use tools borrowed from dynamical systems and from molecular dynamics simulations on monodimensional chains of oscillators. These are often used to represent and investigate structures as different as nanotubes [Fucetola et al., 2024, Kostoglou et al., 2020], nanoactuators [Hartbaum et al., 2011] and nanocantilevers [Ghosh et al., 2019] and often they are also used to cast some light on the thermodynamics and statistical mechanics of low-dimensional systems. To begin the discussion, we will first review some basic conclusions of thermodynamics and statistical mechanics for monodimensional chains of oscillators. We will also introduce molecular dynamics methods and concepts we apply in this work, including thermostats.

1.1 Monodimensional thermodynamics

1.1.1 Equilibrium

A typical model employed in monodimensional thermodynamics is a rod of length L and mass M , infinitely contracted in its radial dimensions. The monodimensional thermodynamics of such objects is constructed on the following assumptions, as discussed in [Callen, 1991].

Assumption I: There exist particular states of monodimensional objects that are characterised completely by the extensive parameters such as internal energy U , and the length L .

Assumption II: The entropy S is a function of those parameters. The equilibrium states correspond to the maximization of entropy.

Assumption III: The entropy is extensive, so that for any $\lambda \in \mathbb{R}$:

$$S(\lambda U, \lambda L) = \lambda S(U, L)$$

and also continuous and monotonically increasing with respect to the internal energy, that is:

$$\left(\frac{\partial S}{\partial U} \right)_L = \frac{1}{T} > 0. \quad (1.1.1)$$

We define the positive quantity as the inverse of temperature. The pressure is also defined via the partial derivative of entropy, but the value could be either positive or negative:

$$\left(\frac{\partial S}{\partial L} \right)_U = \frac{P}{T}.$$

Using those assumptions above we get the basic differential:

$$dS = \frac{1}{T} dU + \frac{P}{T} dL \quad (1.1.2)$$

and the expression of entropy:

$$S(U, L) = \int \frac{1}{T(U, L)} dU + \int \frac{P(U, L)}{T(U, L)} dL. \quad (1.1.3)$$

Assumption IV: The entropy vanishes in the state for which

$$\left(\frac{\partial U}{\partial S} \right)_L = 0 \quad (1.1.4)$$

where the temperature defined in Eq. (1.1.1) is zero.

One important inference drawn from the assumptions above is the equivalence of maximum entropy and the minimum energy principle. A detailed proof is given in the Appendix A.1. Here we give the conclusion: the equilibrium state is the one that has maximum entropy for given energy, and, at the same time, the minimum energy for given entropy. The “energy” here is the internal energy U and its Legendre transform:

$$\begin{aligned}\delta S(U, L) &= 0 \quad \delta^2 S < 0 \\ \delta U(S, L) &= 0 \quad \delta^2 U > 0\end{aligned}\tag{1.1.5}$$

The value of U is computed by solving Eq. (1.1.2) for dU and integrating:

$$U(S, L) = \int_0^S T(S, L) dS - \int_0^L P(S, L) dL,\tag{1.1.6}$$

where the T and P above are functions of the entropy S and length L . These are functions that we call “state equation”, e.g. general relations that are valid for selected system observables.

These state equations with entropy as a variable are abstract and difficult to measure by experiment, so it is more convenient to replace entropy S with the partial derivative for S i.e. the temperature $\partial U / \partial S = T$. Using a Legendre transform, the result is the free energy written as:

$$F(T, L) = U(S(T, L), L) - TS(T, L) = - \int_0^T S(T, L) dT - \int_0^L P(T, L) dL.\tag{1.1.7}$$

The state equations for $P(T, L)$ and $S(T, L)$ are required to compute $F(T, L)$; the latter could be computed using the heat capacity at constant length $C_L = (\partial U / \partial T)_L$, as well

as the postulation in Eq. (1.1.4):

$$S(T, L) = \int_0^T \frac{C_L}{T} dT \quad (1.1.8)$$

We can also replace the length with pressure via $P = -(\partial F / \partial L)_T$. Using the Legendre transform again, we get the Gibbs free energy:

$$G(T, P) = F(T, L(T, P)) + PL(T, P) = - \int_0^T S(T, P) dT + \int_0^P L(T, P) dP, \quad (1.1.9)$$

which requires the state equation $L(T, P)$ and $S(T, P)$. The $S(T, P)$ is found via the isobaric heat capacity $C_P = (\partial U / \partial T)_P$

$$S(T, P) = \int_0^T \frac{C_P}{T} dT.$$

The form of the state equations above is not arbitrary: any thermodynamically stable state equation must satisfy the following two conditions. Firstly, Maxwell relation must hold, so that the integrals in Eq. (1.1.6), (1.1.7) and (1.1.9) are all path independent.

$$\begin{aligned} \left(\frac{\partial T}{\partial L} \right)_S &= - \left(\frac{\partial P}{\partial S} \right)_L \\ \left(\frac{\partial S}{\partial L} \right)_T &= \left(\frac{\partial P}{\partial T} \right)_L \\ \left(\frac{\partial S}{\partial P} \right)_T &= - \left(\frac{\partial L}{\partial T} \right)_P. \end{aligned}$$

Secondly, a so-called stability condition must be present. Combining Eq. (1.1.6) into the $\delta^2 U > 0$ in Eq. (1.1.5), using the definition of C_L in Eq. (1.1.8) and employing the Maxwell relation above gives the stability conditions:

$$\begin{aligned} C_L &> 0 \\ \left(\frac{\partial P}{\partial L} \right)_T &< 0, \end{aligned}$$

the derivation of which has been worked out in the Appendix A.2.

By referring to the density as $\rho = \frac{M}{L}$, the second inequality can also be written as:

$$\left(\frac{\partial P}{\partial \rho}\right)_T > 0. \quad (1.1.10)$$

Note that, by this condition, the ideal gas is thermodynamically stable everywhere, because

$$P = \frac{MRT}{L} = \rho RT \rightarrow \left(\frac{\partial P}{\partial \rho}\right)_T = RT > 0,$$

but, on the other hand, the van der Waals gas is thermodynamically unstable in a region defined by the cubic expression resulting from $(\partial P / \partial \rho)_T$:

$$\begin{aligned} P &= \frac{MRT}{L - Mb} - \frac{aM^2}{L^2} \\ &= \frac{RT}{\rho^{-1} - b} - a\rho^2 \\ &\rightarrow \left(\frac{\partial P}{\partial \rho}\right)_T \\ &= \frac{-2ab^2\rho^3 + 4ab\rho^2 - 2a\rho + RT}{(1 - \rho b)^2} < 0. \end{aligned}$$

In the region where the cubic curve in the numerator is lower than zero, the van der Waals gas loses its stability and a phase transition occurs. These examples will be important when we discuss the behaviors of monodimensional chains and when we provide single-particle microscopic equations that are related to these.

1.1.2 Non-equilibrium

Non-equilibrium thermodynamics is strongly dependent upon the local thermodynamic equilibrium (LTE). In the context of monodimensional system, LTE could be interpreted as the following statements: a) Conserved quantities continuously distribute along the system. For example, the mass density $\rho(x, t)$, momentum density $\rho(x, t)v(x, t)$, and energy density $\rho u(x, t)$ are continuously distributed. There also exist continuous temperature distributions $T(x, t)$ and pressure distributions $P(x, t)$; b) all conclusions in equilib-

rium thermodynamics are applicable to these distributions. From LTE, we can derive the time dependence of entropy in Eq. (1.1.3) by using the time dependence of density and energy. We first apply Eq. (1.1.3) locally:

$$\rho(x, t)s(x, t)dx = \rho(x, t) \left(\int_0^{u(x, t)} \frac{1}{T(x, t)} du + \int_{\rho(x, t)}^{+\infty} \frac{P(x, t)}{T(x, t)\rho^2} d\rho \right) dx;$$

then using the additive condition based on LTE, we write the nonequilibrium entropy as:

$$\begin{aligned} S(t) &= \int_0^L \rho(x, t)s(x, t)dx \\ &= \int_0^L \rho(x, t) \left(\int_0^{u(x, t)} \frac{1}{T(x, t)} du + \int_{\rho(x, t)}^{+\infty} \frac{P(x, t)}{T(x, t)\rho^2} d\rho \right) dx. \end{aligned}$$

The time derivative of the nonequilibrium entropy depends on time derivative of mass density and energy density [Evans and Morriss, 2008]:

$$\begin{aligned} \frac{dS}{dt} &= \int_0^L \frac{\partial \rho(x, t)s(x, t)}{\partial t} dx \\ &= \int_0^L \frac{d\rho(x, t)s(x, t)}{dt} - v(x, t) \frac{\partial \rho(x, t)s(x, t)}{\partial x} dx \\ &= \int_0^L \rho(x, t) \frac{ds(x, t)}{dt} + s(x, t) \frac{d\rho(x, t)}{dt} - v(x, t) \frac{\partial \rho(x, t)s(x, t)}{\partial x} dx \quad (1.1.11) \\ &= \int_0^L \frac{\rho(x, t)}{T(x, t)} \frac{du(x, t)}{dt} - \frac{P(x, t)}{T(x, t)\rho(x, t)} \frac{d\rho(x, t)}{dt} dx \\ &\quad + \int_0^L s(x, t) \frac{d\rho(x, t)}{dt} - v(x, t) \frac{\partial \rho(x, t)s(x, t)}{\partial x} dx, \end{aligned}$$

where in the second equality we have used the relation $\frac{d}{dt} = \frac{\partial}{\partial t} + v \frac{\partial}{\partial x}$.

The $d\rho/dt$, du/dt , and the time derivative of momentum density $d\rho v/dt$ also satisfy a conservation law [Todd and Daivis, 2017]:

$$\frac{d\rho(x, t)}{dt} = -\rho(x, t) \frac{\partial v(x, t)}{\partial x} \quad (1.1.12)$$

$$\rho(x, t) \frac{dv(x, t)}{dt} = -\frac{\partial}{\partial x} (P(x, t) + \Pi(x, t)) \quad (1.1.13)$$

$$\rho(x, t) \frac{du(x, t)}{dt} = -\frac{\partial}{\partial x} J_Q(x, t) - (P(x, t) + \Pi(x, t)) \frac{\partial}{\partial x} v(x, t) \quad (1.1.14)$$

where J_Q is the heat flux and $\Pi(x, t)$ defines nonequilibrium pressure, distinguished from the equilibrium pressure $P(x, t)$.

Substituting the Eq. (1.1.12) and Eq. (1.1.14) into Eq. (1.1.11) gives

$$\begin{aligned} \frac{dS}{dt} &= \int_0^L -\frac{1}{T(x, t)} \frac{\partial}{\partial x} J_Q(x, t) - \frac{\Pi(x, t)}{T(x, t)} \frac{\partial}{\partial x} v(x, t) dx - \int \frac{\partial \rho(x, t) v(x, t) s(x, t)}{\partial x} dx \\ &= \int_0^L \sigma(x, t) dx - \int_0^L \frac{\partial}{\partial x} J_s(x, t) dx \end{aligned}$$

where the $\sigma(x, t)$ is the entropy production and $J_s(x, t)$ is the entropy flux. To make it consistent with equilibrium thermodynamics, the entropy production must be non-negative. When entropy production vanishes throughout the system, it indicates that the entropy has reached a maximum and the system has attained thermodynamic equilibrium. Similar general conclusions can be explicitly formed for the systems we consider in this thesis.

1.2 Monodimensional statistical mechanics

1.2.1 Equilibrium case

As remarked, thermodynamics assumes that matter is continuous and does not immediately consider its microscopic structure. A microscopic foundation of thermodynamics is instead provided by Statistical mechanics. In the context of the one-dimensional system discussed in the preceding Section, statistical mechanics can be interpreted as follows.

The microscopic structure for a monodimensional rod as considered in Section 1.1, shown in Fig. 1.2, is considered as a monodimensional chain of oscillators: N replicated oscillators with potential V and mass m connect end to end. Each oscillator vibrates one-dimensionally, hence a $2N$ dimensional vector $\Gamma = (q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N)$ embedding all the N oscillator lengths and N momenta fully describes the microscopic state.

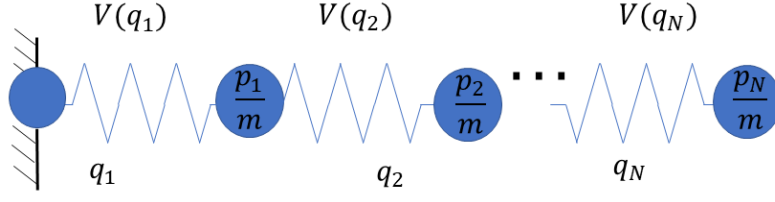


Figure 1.2: Sketch of a monodimensional chain of oscillators.

There exist phase variables $A(\Gamma)$ that depend on the phase space vector and correspond to the instantaneous value of thermodynamic quantities introduced above. Phase variables often used in this thesis are the length, i.e. the sum of all the lengths of all oscillators:

$$\mathbf{L}(\Gamma) = \sum_{k=1}^N q_k \quad (1.2.1)$$

and the Hamiltonian:

$$\mathbf{H}(\Gamma) = \sum_{k=1}^N \frac{p_k^2}{2m} + V(q_k). \quad (1.2.2)$$

At equilibrium and under specific potentials V , the motion of Γ can be chaotic and ergodic, which means that the steady distribution $f(\Gamma)$ spanned by Γ is independent of the initial states. Let us restrict our discussion to cases where the two conditions above are verified.

An equilibrium thermodynamic measurement is the average of instantaneous values over an ensemble distribution. Statistical mechanics assumes that the ensemble distribution is the one that maximises the entropy, which is in this context defined as:

$$S = - \int f(\Gamma) \ln f(\Gamma) d\Gamma$$

If we maximise S over the iso-length and iso-Hamiltonian surface of the Γ space, with the subsidiary condition that $f(\Gamma)$ is normalised, we have

$$S(U, L) = - \int f(\Gamma) \ln f(\Gamma) \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - (\lambda_1 - 1) \left(\int f(\Gamma) \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - 1 \right), \quad (1.2.3)$$

which is the continuous version of the entropy expression given in [Bricmont, 2022]. It turns out that the maximisation gives the micro-canonical distribution

$$f_{micr}(\Gamma) \propto e^{-\lambda_1},$$

where the value of the Lagrangian multiplier λ_1 is determined by the normalisation condition

$$\int e^{-\lambda_1} \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma = 1.$$

Then we also have:

$$f_{micr}(\Gamma) \propto e^{-\lambda_1} = \frac{1}{\int \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma}.$$

Using the equation above in Eq. (1.2.3), we also find that the value of the Lagrangian multiplier is identical to the entropy of the micro-canonical distribution:

$$\lambda_1 = S(U, L) = \ln \int \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma.$$

If we allow the Hamiltonian to fluctuate around its average value, we can replace the Dirac function depending on U in Eq. (1.2.3) with a Lagrangian term:

$$\begin{aligned} S(U, L) = & - \int f(\Gamma) \ln f(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - \\ & (\lambda_1 - 1) \left(\int f(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - 1 \right) - \\ & \lambda_2 \left(\int f(\Gamma) \mathbf{H}(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - U \right). \end{aligned}$$

Maximising it now gives the canonical distribution:

$$f_{cano}(\Gamma) \propto e^{-\lambda_1} e^{-\lambda_2 \mathbf{H}(\Gamma)}.$$

The multipliers λ_1 and λ_2 above are also determined by the relevant Lagrangian terms: λ_1 is proved to be the opposite of the free energy divided by temperature, or the Massieu

function $S \left[\frac{1}{T} \right]$

$$\lambda_1 = S \left[\frac{1}{T} \right] = -\frac{F(T, L)}{T}$$

and λ_2 is the inverse temperature $1/T$ (more details are given in the Appendix A.3)

$$\lambda_2 = \frac{1}{T}.$$

Finally, the normalised canonical distribution is given by

$$f_{cano}(\Gamma) = e^{\frac{F}{T}} e^{-\frac{\mathbf{H}(\Gamma)}{T}} \delta(\mathbf{L}(\Gamma) - L),$$

and the statistical expression of free energy becomes

$$F(T, L) = -T \ln \int e^{-\frac{\mathbf{H}(\Gamma)}{T}} \delta(\mathbf{L}(\Gamma) - L) d\Gamma.$$

Combining the $F(T, L)$ above with Eq. (1.1.7), we have the statistical expression of the $P(T, L)$ state equation, which we will use in this thesis:

$$P(T, L) = - \left(\frac{\partial F}{\partial L} \right)_T = T \frac{\int e^{-\frac{\mathbf{H}(\Gamma)}{T}} \frac{\partial}{\partial L} \delta(\mathbf{L}(\Gamma) - L) d\Gamma}{\int e^{-\frac{\mathbf{H}(\Gamma)}{T}} \delta(\mathbf{L}(\Gamma) - L) d\Gamma}.$$

Using the monodimensional length and Hamiltonian defined in Eq. (1.2.1) and Eq. (1.2.2), the equation above becomes

$$\begin{aligned} P(T, L) &= T \frac{\int \prod_{k=1}^N e^{-\frac{p_k^2}{2mT}} dp_k \int e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \frac{\partial}{\partial L} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k}{\int \prod_{k=1}^N e^{-\frac{p_k^2}{2mT}} dp_k \int e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k} \\ &= -T \frac{\int e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \frac{\partial}{\partial q_1} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k}{\int e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k} \\ &= - \frac{\int \frac{\partial V(q_1)}{\partial q_1} e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k}{\int e^{-\frac{\sum_{k=1}^N V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) \prod_{k=1}^N dq_k} \end{aligned}$$

where the second equality is obtained by using $\frac{\partial}{\partial L} = -\frac{\partial}{\partial \mathbf{L}(\Gamma)} = -\frac{\partial}{\partial \mathbf{L}(\Gamma)} \frac{d\mathbf{L}(\Gamma)}{dq_1} = -\frac{\partial}{\partial q_1}$ because $\frac{d\mathbf{L}(\Gamma)}{dq_1} = \sum_{k=1}^N \frac{\partial \mathbf{L}(\Gamma)}{\partial q_k} \frac{\partial q_k}{\partial q_1} = 1$, and the third equality is the result of integration by parts. Finally, we simplify the Dirac function by using $q_N = L - \sum_{k=1}^{N-1} q_k$. The final version of $P(T, L)$ that is particularly relevant for chains is:

$$P(T, L) = \frac{\int_{-\infty}^{+\infty} -\frac{\partial V(q_1)}{\partial q_1} e^{-\frac{\sum_{k=1}^{N-1} V(q_k)}{T}} e^{-\frac{V(L - \sum_{k=1}^{N-1} q_k)}{T}} \prod_{k=1}^{N-1} dq_k}{\int_{-\infty}^{+\infty} e^{-\frac{V(q_1)}{T}} e^{-\frac{\sum_{k=1}^{N-1} V(q_k)}{T}} e^{-\frac{V(L - \sum_{k=1}^{N-1} q_k)}{T}} \prod_{k=1}^{N-1} dq_k}. \quad (1.2.4)$$

By replacing the length L with the inverse density N/ρ for oscillators, we can also write it as:

$$P(T, \rho) = \frac{\int_{-\infty}^{+\infty} -\frac{\partial V(q_1)}{\partial q_1} e^{-\frac{V(q_1)}{T}} dq_1 \int_{-\infty}^{+\infty} e^{-\frac{V(q_k)}{T}} e^{-\frac{V(\frac{N}{\rho} - \sum_{k=1}^{N-1} q_k)}{T}} \prod_{k=2}^{N-1} dq_k}{\int_{-\infty}^{+\infty} e^{-\frac{V(q_1)}{T}} dq_1 \int_{-\infty}^{+\infty} e^{-\frac{V(q_k)}{T}} e^{-\frac{V(\frac{N}{\rho} - \sum_{k=1}^{N-1} q_k)}{T}} \prod_{k=2}^{N-1} dq_k}. \quad (1.2.5)$$

If we further allow the length to fluctuate but constrain its average, then the entropy is defined over all the Γ space as

$$\begin{aligned} S(U, L) = & - \int f(\Gamma) \ln f(\Gamma) d\Gamma - \\ & (\lambda_1 - 1) \left(\int f(\Gamma) d\Gamma - 1 \right) - \lambda_2 \left(\int f(\Gamma) \mathbf{U}(\Gamma) d\Gamma - U \right) - \\ & \lambda_3 \left(\int f(\Gamma) \mathbf{L}(\Gamma) d\Gamma - L \right). \end{aligned} \quad (1.2.6)$$

and the resultant maximum distribution is the Gibbs distribution,

$$f_{Gibbs}(\Gamma) \propto e^{-\lambda_1} e^{-\lambda_2 \mathbf{H}(\Gamma)} e^{-\lambda_3 \mathbf{L}(\Gamma)}.$$

Putting the equation above into Eq. (1.2.6) and simplifying all the Lagrangian terms, we find that the multiplier λ_1 is the negative of the Gibbs free energy divided by temperature, or the Massieu function $S \left[\frac{1}{T}, \frac{P}{T} \right]$, λ_2 is the inverse temperature, and λ_3 is the pressure

divided by temperature (details are discussed in the Appendix A.3)

$$\begin{aligned}\lambda_1 &= S \left[\frac{1}{T}, \frac{P}{T} \right] = -\frac{G(T, P)}{T} \\ \lambda_2 &= \frac{1}{T} \\ \lambda_3 &= \frac{P}{T}.\end{aligned}$$

Then the normalised Gibbs distribution becomes:

$$f_{Gibbs}(\Gamma) = e^{\frac{G}{T}} e^{-\frac{H(\Gamma) + PL(\Gamma)}{T}}, \quad (1.2.7)$$

from which we have the statistical expression of Gibbs free energy:

$$G(T, P) = -T \ln \int e^{-\frac{H(\Gamma) + PL(\Gamma)}{T}} d\Gamma. \quad (1.2.8)$$

By using the differential in Eq. (1.1.9), we obtain the statistical expression for the length $L(T, P)$ state equation.

$$L(T, P) = \frac{\int \mathbf{L}(\Gamma) e^{-\frac{H(\Gamma) + PL(\Gamma)}{T}} d\Gamma}{\int e^{-\frac{H(\Gamma) + PL(\Gamma)}{T}} d\Gamma}.$$

Using the $\mathbf{H}(\Gamma)$ in Eq. (1.2.2) and $\mathbf{L}(\Gamma)$ in Eq. (1.2.1), the equation above becomes:

$$\begin{aligned}L(T, P) &= \frac{\int \sum_{k=1}^N q_k e^{-\frac{\sum_{j=1}^N \frac{p_j^2}{2m} + V(q_j) + Pq_j}{T}} \prod_{j=1}^N dp_j dq_j}{\int e^{-\frac{\sum_{j=1}^N \frac{p_j^2}{2m} + V(q_j) + Pq_j}{T}} \prod_{j=1}^N dp_j dq_j} \\ &= \frac{\int e^{-\frac{\sum_{j=1}^N \frac{p_j^2}{2m}}{T}} \prod_{j=1}^N dp_j \sum_{k=1}^N \int q_k \prod_{j=1}^N e^{-\frac{V(q_j) + Pq_j}{T}} dq_j}{\int e^{-\frac{\sum_{j=1}^N \frac{p_j^2}{2m}}{T}} \prod_{j=1}^N dp_j \int \prod_{j=1}^N e^{-\frac{V(q_j) + Pq_j}{T}} dq_j} \\ &= \sum_{k=1}^N \frac{\int q_k e^{-\frac{V(q_k) + Pq_k}{T}} dq_k}{\int e^{-\frac{V(q_k) + Pq_k}{T}} dq_k} \\ &= N \frac{\int q e^{-\frac{V(q) + Pq}{T}} dq}{\int e^{-\frac{V(q) + Pq}{T}} dq},\end{aligned}$$

where the third equality reduces the momentum terms involving p_j and cancels all the crossing terms with $j \neq k$ and the fourth equality considers that every term behind the summation is identical. Replacing the ratio of L/N with the inverse density ρ^{-1} , we have an equivalent form that we will also use in this thesis:

$$\rho^{-1}(T, P) = \frac{\int q e^{-\frac{V(q)+Pq}{T}} dq}{\int e^{-\frac{V(q)+Pq}{T}} dq}. \quad (1.2.9)$$

Finally, we note that we can also solve the equation above for P to get the $P(T, L)$ state equation using integration by parts (more details in the Appendix A.4), and the result is :

$$P(T, L) = \frac{\int -\frac{\partial V(q)}{\partial q} e^{-\frac{V(q)+Pq}{T}} dq}{\int e^{-\frac{V(q)+Pq}{T}} dq}. \quad (1.2.10)$$

This equation indicates that pressure is the average force of the Gibbs distribution. On the other hand, the $P(T, L)$ equation in Eq. (1.2.4) gives pressure as the average force of canonical distribution. This inconsistency will be fixed in the limit at $N \rightarrow +\infty$ with constant (T, P) . A rigorous proof could be found in the Appendix A.4. Here we give a phenomenological argument: the canonical distribution gives rise to no length fluctuations while the Gibbs distribution allows length to fluctuate. For the Gibbs distribution, there is a linear scaling between length and number of oscillators N and a square root scaling for the length fluctuations. The ratio of them becomes negligible in the limit $N \rightarrow +\infty$, where the Gibbs distribution converges to the canonical distribution, and the state equations derived from both of them become equivalent. The derivation of the two scaling regimes is as follows.

The Gibbs distribution of monodimensional chains comes from the product of the single-oscillator distributions, and each one of them can be decomposed into the product of

kinetic part $\phi(p_k, T)$ and potential part $\psi(q_k, T, P)$:

$$f_{Gibbs}(\Gamma) = \prod_{k=1}^N \phi(p_k, T) \psi(q_k, T, P) = \prod_{k=1}^N \frac{e^{-\frac{p_k^2}{2mT}}}{\int e^{-\frac{p_k^2}{2mT}} dp_k} \frac{e^{-\frac{V(q_k)+Pq_k}{T}}}{\int e^{-\frac{V(q_k)+Pq_k}{T}} dq_k}, \quad (1.2.11)$$

which is derived by combining Eq. (1.2.2), Eq. (1.2.1), Eq. (1.2.7) and Eq. (1.2.8).

The average length is N times $\kappa_1(T, P)$, the first order cumulant of $\psi(q_k, T, P)$:

$$\begin{aligned} L(T, P) &= \int \mathbf{L}(\Gamma) f_{Gibbs}(\Gamma) d\Gamma \\ &= \int \prod_{k=1}^N dp_k dq_k \sum_{k=1}^N q_k \prod_{j=1}^N \phi(p_j, T) \psi(q_j, T, P) \\ &= \sum_{k=1}^N \int q_k \psi(q_k, T, P) dq_k \\ &= \sum_{k=1}^N \frac{\int q_k e^{-\frac{V(q_k)+Pq_k}{T}} dq_k}{\int e^{-\frac{V(q_k)+Pq_k}{T}} dq_k}, \end{aligned}$$

considering that every term under the summation are identical, the last line above could be rewritten as

$$\begin{aligned} L(T, P) &= N \frac{\int q e^{-\frac{V(q)+Pq}{T}} dq}{\int e^{-\frac{V(q)+Pq}{T}} dq} \\ &= N \frac{\Phi_1}{\Phi_0} = \kappa_1(T, P). \end{aligned} \quad (1.2.12)$$

The fluctuation is $\sqrt{N}$ times $\sqrt{\kappa_2(T, P)}$, the second order cumulant:

$$\begin{aligned} \Delta L &= \sqrt{\int f_{Gibbs}(\Gamma) \mathbf{L}(\Gamma)^2 d\Gamma - \left(\int f_{Gibbs}(\Gamma) \mathbf{L}(\Gamma) d\Gamma \right)^2} \\ &= \sqrt{\sum_{k,j=1}^N \int \prod_{i=1}^N dq_i \psi(q_i, T, P) q_k q_j - \left(\int \prod_{i=1}^N dq_i \psi(q_i, T, P) q_k \right) \left(\int \prod_{s=1}^N dq_s \psi(q_s, T, P) q_j \right)} \\ &= \sqrt{\sum_{k=1}^N \int dq_k \psi(q_k, T, P) q_k^2 - \left(\int dq_k \psi(q_k, T, P) q_k \right)^2}. \end{aligned}$$

The last line above reduces all the cross terms to zero because all variables are independent, and we can further simplify this to N times the identical term

$$\Delta L = \sqrt{N \left(\int dq \psi(q, T, P) q^2 - \left(\int dq \psi(q, T, P) q \right)^2 \right)} = \sqrt{N \left(\frac{\Phi_2}{\Phi_0} - \left(\frac{\Phi_1}{\Phi_0} \right)^2 \right)},$$

which is interpreted as the square root of the second order cumulant:

$$\Delta L = \sqrt{N \kappa_2(T, P)}. \quad (1.2.13)$$

Note that both Eq. (1.2.12) and Eq. (1.2.13) use the Gibbs distribution in Eq. (1.2.11), take the potential part ψ only and introduce equations Φ_n as:

$$\Phi_n(T, P) = \int q^n \psi(q, T, P) dq.$$

The ratio between Eq. (1.2.12) and Eq. (1.2.13) denotes the relative deviation of the average length, which tends to zero at the limit $N \rightarrow +\infty$ with constant (T, P) :

$$\lim_{N \rightarrow +\infty} \frac{\Delta L}{L} = \lim_{N \rightarrow +\infty} \frac{1}{\sqrt{N}} \frac{\sqrt{\kappa_2(T, P)}}{\kappa_1(T, P)} = 0. \quad (1.2.14)$$

In this limit, the Gibbs distribution becomes indistinguishable from the canonical distribution and the Gibbs free energy also converges to the free energy. As expected, statistical mechanics is consistent with thermodynamics in the large N limit, which is why we call it the “thermodynamics limit”.

1.2.2 Non-equilibrium regimes

Generally speaking, non-equilibrium statistical mechanics is a developing discipline with different branches and a full introduction is beyond the scope of this thesis. Here we only discuss the microscopic foundation of local thermodynamic equilibrium (LTE) in terms of monodimensional systems, because it is relevant to the results presented in this thesis.

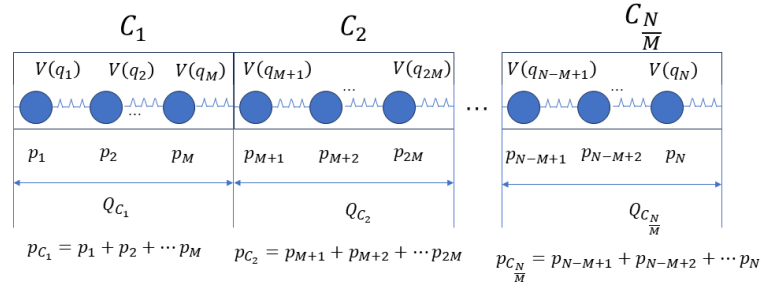


Figure 1.3: A chain subdivided into cells.

LTE is a “strong” condition. As clear in a number of texts and journal articles such as Refs. [Landau and Lifshitz, 1980] Section 9, [Kondepudi and Prigogine, 2014] Section 15.1, [Spohn, 1991] Section 2.3, and finally [Falcioni et al., 2007, Rondoni and Pigolotti, 2012]), LTE is characterised by three strict requirements. In the context of a monodimensional system, they are interpreted as follows. Firstly, subdivide the chain of N oscillators into cells. Each cell contains M oscillators, as shown in Fig. 1.3. Secondly, the correlation among the cells is negligible and lastly, thermalisation is fast within each cell, in practice “as short as an instant” at the time scale of measurement. When these conditions are met, the chain in Fig. 1.3 satisfies the following nonequilibrium distribution :

$$f = \prod_{k=1}^{N/M} f_{C_k} \propto \prod_{k=1}^{N/M} \exp \left[-\frac{p_{C_k}^2}{2m_{C_k} T_{C_k}} \right] \exp \left[-\frac{V_{C_k}(Q_{C_k}) + P Q_{C_k}}{T_{C_k}} \right], \quad (1.2.15)$$

where the whole distribution is factorised as the product of cell distributions. Each cell distribution has the form of a Gibbs distribution. The Q_{C_k} and p_{C_k} are the length and total momentum of the cell, whereas the cell temperature should be proportional to the average kinetic energy because

$$\int \frac{p_{C_k}^2}{m_{C_k}} f \prod dp_{C_j} dQ_{C_j} \propto \int \frac{p_{C_k}^2}{m_{C_k}} \exp \left[-\frac{p_{C_k}^2}{2m_{C_k} T_{C_k}} \right] dp_{C_k} \propto T_{C_k}.$$

The parameter P , according to Eq. (1.2.10), is the average force related to the cell poten-

tial:

$$P = \int -f \frac{\partial V_{C_k}(Q_{C_k})}{\partial Q_{C_k}} \prod dQ_{C_j} dp_{C_j} \\ \propto \int -\frac{\partial V_{C_k}(Q_{C_k})}{\partial Q_{C_k}} \exp \left[-\frac{V_{C_k}(Q_{C_k}) + PQ_{C_k}}{T_{C_k}} \right] dQ_{C_k},$$

where the form of cell potential V_{C_k} depends on the correlation within the cell and is different from the oscillator potential V when $M \neq 1$. Let us now discuss the limit case with $M = 1$, where the cell potential is reduced to the oscillator potential V and the nonequilibrium distribution becomes the product of single-oscillator distributions

$$f \propto \prod_{k=1}^N \exp \left[-\frac{H_k + Pq_k}{T_k} \right] = \prod_{k=1}^N \exp \left[-\frac{p_k^2}{2mT_k} - \frac{V(q_k) + Pq_k}{T_k} \right]. \quad (1.2.16)$$

Here, T_k is proportional to the average kinetic energy of the k^{th} oscillator, and P , as shown in Eq. (1.2.10), is the homogeneous average force:

$$T_k = \int -f \frac{p_k^2}{m} \prod dp_j dq_j \\ P = \int -f \frac{\partial V(q_k)}{\partial q_k} \prod dp_j dq_j \quad k = 1, 2, \dots, N.$$

From the factorised distribution in Eq. (1.2.16), we can relate the average length of the k^{th} oscillator and its square fluctuation to its kinetic energy T_k and average force P :

$$\langle q_k \rangle = \kappa_1(T_k, P) \\ \langle q_k^2 \rangle - \langle q_k \rangle^2 = \kappa_2(T_k, P), \quad (1.2.17)$$

which constitute two nonequilibrium single-oscillator relations. They also share the same mathematical formula of the equilibrium state equation in Eq. (1.2.12) and the fluctuation expression in Eq. (1.2.13), but with a different nature: Eq. (1.2.12) and Eq. (1.2.13) relate thermodynamic quantities that pertain to practically isolated mesoscopic cells, containing a large number of particles in equilibrium; on the other hand, Eq. (1.2.17) applies to a single oscillator. The validity of Eq. (1.2.17) depends on the factorised distribution in

Eq. (1.2.16), which is characterised by the following correlation index:

$$C = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sigma^2}{\sum_{k=1}^N \sigma_k^2} - 1}, \quad (1.2.18)$$

where σ^2 is defined as the square fluctuation of the sum of an arbitrary single-oscillator quantity A_k :

$$\sigma^2 = \sum_{k=1}^N \sum_{m=1}^N \langle A_k A_m \rangle - \sum_{k=1}^N \langle A_k \rangle \sum_{m=1}^N \langle A_m \rangle \quad (1.2.19)$$

and $\sum_{k=1}^N \sigma_k^2$ is the sum of square fluctuation of the same quantity:

$$\sum_{k=1}^N \sigma_k^2 = \sum_{k=1}^N \left(\langle A_k^2 \rangle - \langle A_k \rangle^2 \right).$$

Here A_k is an arbitrary quantity that depends on a single oscillator only. For example, it could be the single oscillator length q_k , single oscillator momentum p_k , or the single-oscillator Hamiltonian $H_k = \frac{p_k^2}{2m} + V(q_k)$. In the extreme case where all oscillators fully correlate, i.e., they move coherently, each oscillator will have the same A_k at any time:

$$A_1 = A_2 = \dots A_N = A,$$

and display the same fluctuations:

$$\sigma_1^2 = \sigma_2^2 = \dots \sigma_N^2 = \left(\langle A^2 \rangle - \langle A \rangle^2 \right).$$

On the other hand, the total square fluctuation is N^2 times of the single one:

$$\begin{aligned} \sigma^2 &= \sum_{k=1}^N \sum_{m=1}^N \langle A_k A_m \rangle - \sum_{k=1}^N \langle A_k \rangle \sum_{m=1}^N \langle A_m \rangle \\ &= N^2 \left(\langle A^2 \rangle - \langle A \rangle^2 \right), \end{aligned}$$

so that substituting the equations above into Eq. (1.2.18), we find $C = 1$ in the fully correlated case. The factorised distribution in Eq. (1.2.16) denotes the other extreme,

each oscillator moves independently and we have:

$$\langle A_k A_m \rangle - \langle A_k \rangle \langle A_m \rangle = \left(\langle A_k^2 \rangle - \langle A_k \rangle^2 \right) \delta_{km}.$$

Substituting this equation into Eq. (1.2.19), we find that

$$\sigma^2 = \sum_{k=1}^N \sigma_k^2,$$

and thus we have $C = 0$ for the completely factorised distribution. As we will see shortly, our systems show interesting correlations for a number of observables.

1.3 Molecular dynamics and monodimensional chains

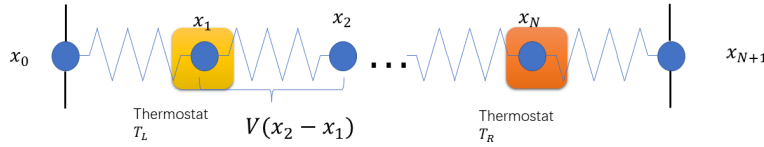


Figure 1.4: Sketch of the model simulated by monodimensional molecular dynamics.

Generally speaking, thermodynamics provides the relationship between measurable observables, where the dependency on the structure of matter is not explicit. Statistical mechanics allows computing these observables by statistical distributions based instead on that microscopic structure. Molecular dynamics, among its many diverse scopes and objectives also provides a way to generate distributions by directly simulating the motion of molecules. As power of computation has been increasing, molecular dynamics (MD) simulations have extended their applications from simple models such as hard-sphere system [Wainweight and Alder, 1958], to more complicated Lennard-Jones fluids [Rahman, 1964], and more sophisticated systems including synthetic polymers with complex structure [Encinar et al., 2008], mixtures of polymer and small molecules [Eslami et al., 2012] and lipid bilayers [Marrink et al., 2004] in biological systems. Molecular dynamics serves as the bridge connecting theory and experiment. To the end of experiments, with

finely tuned potential functions and molecular structures, MD method can simulate real systems and reproduce experimental observations in the laboratory. Furthermore, many parameters that are difficult to vary in laboratory experiments, such as inter-molecular interaction, are continuously changeable in MD simulations. Researchers can also design a totally virtual system or study a more realistic model in unphysical limits. This advantage makes MD a powerful tool for theoretical researchers (see, as an example, results in Ref. [Evans et al., 1993]). This thesis simulates one of the simplest MD model: a monodimensional chain of thousands of oscillators varying in a wide range of temperatures, as sketched in Fig. 1.4. The work in this thesis is a combination of theoretical computation and MD simulation, where the simulation is based on the following terms that capture the interaction among the constituents of the model:

$$\frac{dx_i}{dt} = v_i \quad i = 1, \dots, N \quad (1.3.1)$$

$$m_i \frac{dv_i}{dt} = -\frac{\partial V(x_i - x_{i-1})}{\partial x_i} + \frac{\partial V(x_{i+1} - x_i)}{\partial x_{i+1}} \quad i = 2, \dots, N-1$$

$$m_1 \frac{dv_1}{dt} = -\frac{\partial V(x_1 - x_0)}{\partial x_1} + \frac{\partial V(x_2 - x_1)}{\partial x_2} - f_{T_L} \quad (1.3.2)$$

$$m_N \frac{dv_N}{dt} = -\frac{\partial V(x_N - x_{N-1})}{\partial x_N} + \frac{\partial V(x_{N+1} - x_N)}{\partial x_{N+1}} - f_{T_R}, \quad (1.3.3)$$

where the partial differential of the potential can also be written as minus force

$$F_{i,i-1} = -\frac{\partial V(x_i - x_{i-1})}{\partial x_i}.$$

Three components are central in this formulation: the interaction V , the thermostat forces f_{T_L}, f_{T_R} in Eq. (1.3.2) and Eq. (1.3.3), and the boundary condition of the edges of the chain. i.e. the dynamics of x_0 and x_{N+1} . Also, it is important to discuss the numeric method used to solve the equation. In the following four Sections, we will introduce them one by one and pay attention to their roles.

1.3.1 Interactions and Lennard-Jones potential

The structure of matter is influenced, among various variables, in particular way by the geometric arrangement of and the interactions among the particles. Given the simplicity of monodimensional systems, there is only one possible geometric arrangement and what essentially distinguishes different monodimensional systems is the interaction. Historically, researchers first considered integrable interactions such as harmonic, hardcore and Takahashi-like potential among others [Chowdhury and Stauffer, 2000]. With developments in computers and more powerful numerical methods, a wide range of non-integrable potentials came into consideration. Some of them are perturbations of the integrable ones, the most famous being the Fermi-Pasta-Ulam-Tsingou potential. Others are direct imitations of real-world interactions and one of the most common in physical chemistry is the Lennard-Jones potential studied in this thesis, discussed and employed in a number of references in the literature [Morris and Rondoni, 1999, Casas-Vázquez and Jou, 2003, Jou and Restuccia, 2016, Criado-Sancho et al., 2006, Cao and He, 2015, Puglisi et al., 2017, Giberti et al., 2019b,a].

In all simulations presented in this work, we apply a revised version of Lennard-Jones potential:

$$V_{LJ}(r) = \begin{cases} \epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - 2 \left(\frac{\sigma}{r}\right)^6 \right] & r > 0 \\ +\infty & r \leq 0 \end{cases} \quad (1.3.4)$$

where the interaction distance is $r = x_i - x_{i-1} > 0$, ϵ is the well depth and σ is the value at which the Lennard-Jones potential is at its minimum. The Lennard-Jones potential consists of two parts: the repulsive part dominates for $r < \sigma$ and the attractive part for $r > \sigma$. The repulsive part tends to infinity at $r \rightarrow 0$ and this enforces $r > 0$ in monodimensional systems, so that the order of oscillators is kept. The attractive part tends to zero at $r \rightarrow \infty$, making the chain dissociable, contrary, for example, to the harmonic chain that is not dissociable and has alterable order. The contrast of these two interactions shown in Fig. 1.5 becomes noticeable in a coupled chain model with both interactions,

which will be discussed in Chapter 4.

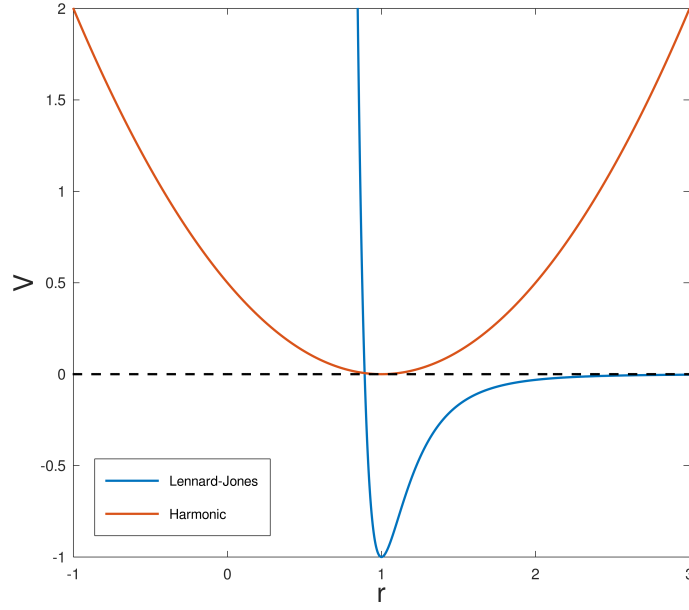


Figure 1.5: The comparison between typical Lennard-Jones and harmonic potentials for reduced units, where r is in multiples of σ .

In this thesis, all real physical units are replaced with units reduced by the Lennard-Jones parameters, given by the following dimensionless quantities:

$$\begin{aligned}
 x_i^* &= \frac{x_i}{\sigma} \\
 T^* &= \frac{T}{\epsilon} \\
 P^* &= \frac{P\sigma}{\epsilon} \\
 \rho^* &= \frac{\rho}{\sigma} \\
 t^* &= \frac{t}{\sigma\sqrt{m/\epsilon}}
 \end{aligned} \tag{1.3.5}$$

where the asterisk indicates reduced quantities. Note that from now on the asterisks will be dropped for convenience of notation and that $\sigma = m = \epsilon = 1.0$ in all the simulations and numerical results considered here.

1.3.2 Temperature and thermostats

Thermostats are means to simulate thermalisation processes and steady states. They play a crucial role in molecular dynamics, and will be important for our own models too.

There are many ways to formulate a thermostat. Here we introduce two of them: one is to control the total kinetic energy (the Gaussian thermostat), the other is to generate a distribution proportional to $\exp \left[-\frac{\mathbf{H}}{T} \right]$ (the Nosé Hoover thermostat).

According to the law of energy equipartition, the average total kinetic energy equals NT for a monodimensional chain of N oscillators equilibrium at temperature T , which could also be proved by using the Gibbs distribution in Eq. (1.2.11):

$$\begin{aligned}
 & \int \sum_{j=1}^N \frac{p_j^2}{2m} f_{Gibbs}(\Gamma, T, P) d\Gamma \\
 &= \int \sum_{j=1}^N \frac{p_j^2}{2m} \prod_{k=1}^N \phi(p_k, T) dp_k \\
 &= N \int \frac{p^2}{2m} \sqrt{\frac{mT}{2\pi}} \exp \left[-\frac{p^2}{2mT} \right] dp \\
 &= NT
 \end{aligned}$$

where the third and fourth lines use the following results for Gaussian integrals :

$$\begin{aligned}
 \int x^2 e^{-\frac{1}{2}ax^2} dx &= \sqrt{2\pi a}^{-\frac{3}{2}} \\
 \int e^{-\frac{1}{2}ax^2} dx &= \sqrt{\frac{2\pi}{a}}.
 \end{aligned}$$

Based on the equality between average kinetic energy and temperature, we can control the temperature by solving the dynamics under an “iso-kinetic-energy” constraint. Following the Lagrangian method referred in Chapter IV of Ref. [Courant and Hilbert, 1962], the

constrained action of the system in Fig. 1.4 is written as

$$\begin{aligned}\mathcal{L} &= \int dt K(t) - V(t) + \lambda(t)G \\ &= \int \frac{1}{2} \sum_{i=1}^N m_i \dot{x}_i^2 - \sum_{i=1}^N V(x_i - x_{i-1}) + \lambda(t) \sum_{i=1}^N (m_i \dot{x}_i^2 - Nk_B T),\end{aligned}$$

where the $K(t) - V(t)$ is the Lagrangian without constraint and G denotes the “constant kinetic energy constraint”. Then the case $\delta\mathcal{L} = 0$ corresponds to the constrained dynamics:

$$\frac{d}{dt} \left[(1 + 2\lambda(t)) m_i \frac{dx_i}{dt} \right] = F_i = -\frac{\partial V(x_i - x_{i-1})}{\partial x_i} + \frac{\partial V(x_{i+1} - x_i)}{\partial x_{i+1}} \quad i = 1, 2, \dots, N.$$

Considering the left-hand side as the generalised momentum $\mathbf{p}$ and taking $\mathbf{M}$ as the diagonal inertial matrix, we can formulate the thermostatted dynamics in vector form as follows:

$$\begin{aligned}\dot{\mathbf{q}} &= \frac{\mathbf{M}^{-1}}{1 + 2\lambda(t)} \mathbf{p} \\ \dot{\mathbf{p}} &= \mathbf{F} \\ Nk_B T (1 + 2\lambda(t))^2 &= \mathbf{p}^T \mathbf{M} \mathbf{p}.\end{aligned}$$

The $\lambda(t)$ above is a rescaling factor that maps the momentum onto the iso-kinetic energy surface: this formulation constitutes a rescaling thermostat (see Fig. 1.6a) and will be reduced to a Gaussian thermostat [Todd and Daivis, 2017] when the inertial matrix is proportional to the unitary matrix $m_{ij} = m\delta_{ij}$ and the iso-kinetic-energy surface is reduced to a sphere. As shown by Fig. 1.6b. The velocity vector $\mathbf{v}(t - \Delta t)$ is altered by an impulse $\frac{\mathbf{F}}{m}\Delta t = \frac{\mathbf{F}_{\parallel}}{m}\Delta t + \frac{\mathbf{F}_{\perp}}{m}\Delta t$, being decomposed into $\frac{\mathbf{F}_{\parallel}}{m}\Delta t$ parallel and $\frac{\mathbf{F}_{\perp}}{m}\Delta t$ perpendicular to $\mathbf{v}(t - \Delta t)$. Gaussian thermostats introduce a fictitious friction force to cancel out the parallel component $\frac{\mathbf{F}_{\parallel}}{m}\Delta t$. In the limit when the time step Δt is sufficiently close to zero, the resultant vector $\mathbf{v}(t) = \mathbf{v}(t - \Delta t) + \frac{\mathbf{F}_{\perp}}{m}\Delta t$ is still on the iso-kinetic-energy sphere and will be identical to the result of rescaling thermostat. The corresponding differential

vector formula is written as:

$$\dot{\mathbf{q}} = \mathbf{M}^{-1}\mathbf{p}$$

$$\dot{\mathbf{p}} = \mathbf{F} - \alpha\mathbf{p}$$

$$\alpha = \frac{\mathbf{F}^T \mathbf{M}^{-1} \mathbf{p}}{\mathbf{p}^T \mathbf{M}^{-1} \mathbf{p}}.$$

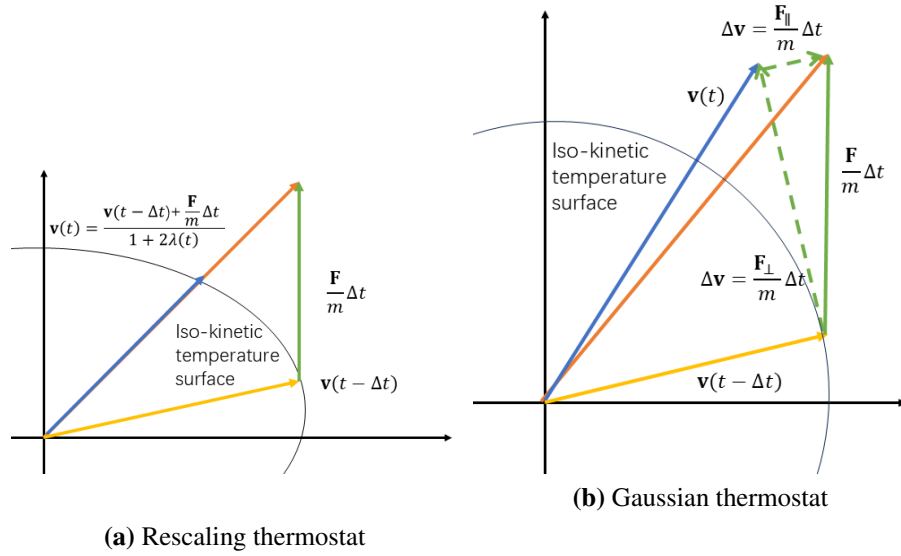


Figure 1.6: Scheme for rescaling thermostat (left) and Gaussian thermostat (right).

Note that the friction coefficient α in the Gaussian thermostat does not represent a new degree of freedom because its varying rate $\dot{\alpha}$ is determined by the other variables. So, if we make the friction coefficient a new degree of freedom ζ and define $\dot{\zeta}$ in a proper way, we will get the so-called Nosé-Hoover thermostat with the following definition:

$$\dot{\mathbf{q}} = \mathbf{M}^{-1}\mathbf{p}$$

$$\dot{\mathbf{p}} = \mathbf{F} - \zeta\mathbf{p}$$

$$\dot{\zeta} = \frac{1}{Q} \left[\mathbf{p}^T \mathbf{M}^{-1} \mathbf{p} - Nk_B T \right].$$

If we assume ergodicity, this system will generate a canonical distribution in the extended

phase space including ξ [Morris and Dettmann, 1998]:

$$f_c(\Gamma, \xi) \propto \exp \left[-\frac{1}{T} (H(\Gamma) + \frac{1}{2} Q \xi^2) \right].$$

When the system is small or stiff, the ergodic assumption may fail [Legoll et al., 2009, Fillipov et al., 1998] but the non-ergodicity effect is almost always negligible in our simulation, because in this thesis most simulations here are run over very long ($N \geq 1000$) chains.

1.3.3 Boundary conditions for linear chains

How the oscillators at the edges behave, e.g. the motion of x_0 and x_{N+1} , represents the boundary conditions for monodimensional chains. Among various options, two mostly used are fixed-length boundary and fixed-force boundary: in the first case, the positions of the very left and right oscillators are set at the very beginning and never change in the subsequent steps, with the corresponding formula given by:

$$x_0 = 0 \quad x_{N+1} = L \quad v_0 = v_{N+1} = 0.$$

In the fixed-force boundary condition, the very right (or left) oscillator is instead movable, but constrained by a constant force f_p :

$$x_0 = 0 \quad v_0 = 0 \quad \frac{dv_{N+1}}{dt} = -\frac{\partial V(x_{N+1} - x_N)}{\partial x_{N+1}} - f_p.$$

For dissociable chains such as LJ chains, the effect of f_p is to compress the chain, but, for unbounded potentials like harmonic or FPUT chains, f_p could either compress or stretch the chain. When f_p is set equal to zero, this condition is referred to as a “free boundary”, since one of the edges moves freely.

Another boundary condition commonly used is the periodic boundary case, as represented in Fig. 1.7. In this condition, we consider a ring where the zeroth oscillator is a copy of the

N^{th} oscillator and the $(N + 1)^{th}$ oscillator is a copy of the first oscillator. Equivalently, the zeroth oscillator, together with the N^{th} oscillator can be thought of being embedded in a rigid box of length L . The dynamics at the boundary is given by:

$$\begin{aligned} x_0 &= x_N - L & v_0 &= v_N \\ x_{N+1} &= x_1 + L & v_{N+1} &= v_1. \end{aligned}$$

Periodic boundary

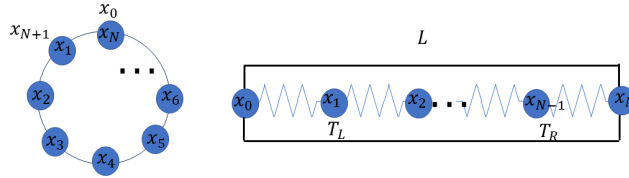


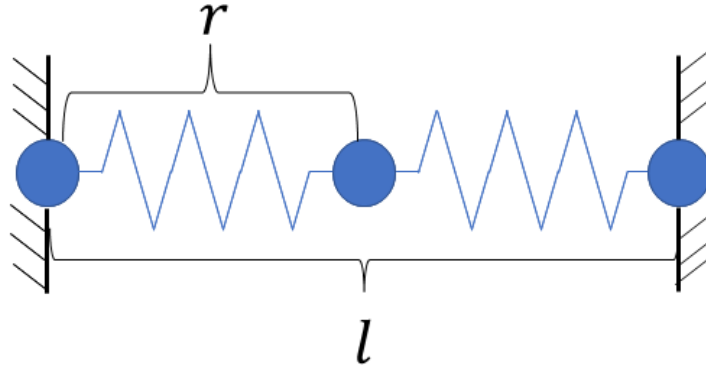
Figure 1.7: Sketch of the periodic boundary. It could be interpreted either as a ring or as a rigid box.

1.3.4 Methods of integration

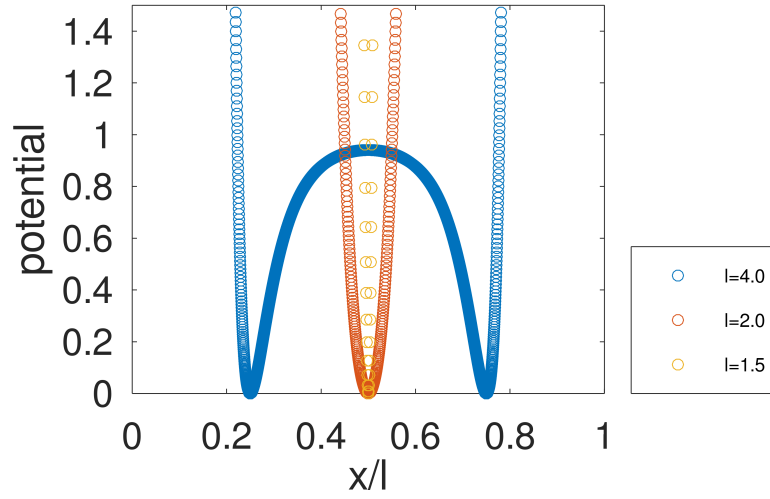
From the viewpoint of numerical computation, an integrator is a method to change a differential equation into a discrete map [Cencini et al., 2010]. Given a differential equation $\frac{dy(t)}{dt} = f(y(t))$, the most direct form of integration is the Eulerian method, as shown in Eq. (1.3.6): it replaces the differential on the left-hand side with a difference $\frac{y(t+h) - y(t)}{h}$ and computes the values on the right-hand side at $t = t + \phi h$, where h is the step size and the ϕ is an arbitrary value between 0 and 1. The easiest choice is $\phi = 0$, corresponding to the explicit Eulerian integrator. Note also that $\phi = 1.0$ is the implicit integrator, which is numerically more stable than the case $\phi = 0.0$ because it is symplectic [Cencini et al., 2010].

$$\frac{y(t+h) - y(t)}{h} = k$$

$$k = f(y(t+h\phi)).$$
(1.3.6)



(a) oscillator



(b) potential

Figure 1.8: (a) Sketch of a single Lennard-Jones oscillator. The distance l determines the form of the potential well in the right panel. (b) Potential profile under different l , where the bottom of the potential well has been translated to the same horizontal line.

Both implicit and explicit Eulerian integrators are approximations of straight segments, with an error of second-order given by $h^2 \frac{d^2 f}{dy^2}$. The integrator applied in this thesis is a fourth-order Runge-Kutta (RK4), whose discrete map form of step size h is given by

[Atkinson et al., 2009]:

$$\begin{aligned}\frac{y(t+h) - y(t)}{h} &= k \\ k &= \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \\ k_1 &= f(y(t)) \\ k_2 &= f(y(t) + k_1 \frac{h}{2}) \\ k_3 &= f(y(t) + k_2 \frac{h}{2}) \\ k_4 &= f(y(t) + k_3 h),\end{aligned}$$

The advantage and the precision of the RK4 integrator could be illustrated by applying

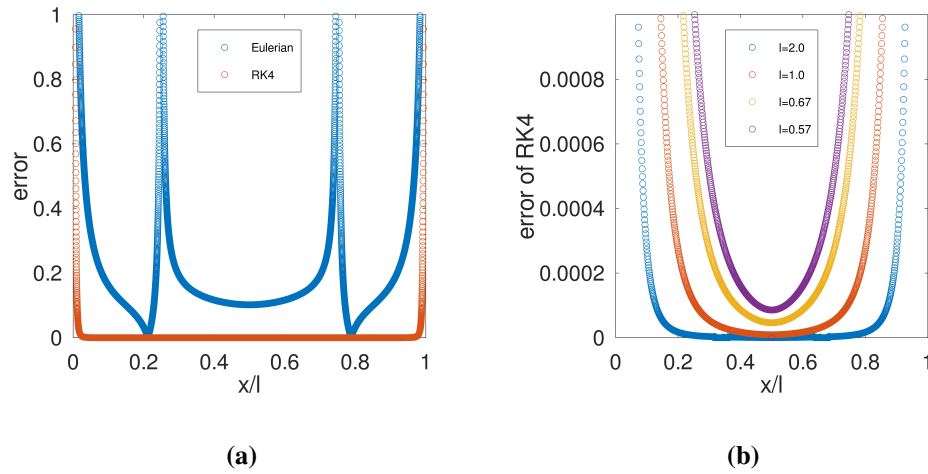


Figure 1.9: (a) Comparison of the error of Eulerian method and RK4 method for the single oscillator at $l = 2.0$. (b) Error of RK4 for smaller l .

it to an isolated single Lennard-Jones oscillator illustrated in Fig. 1.8a. The form of the potential well is written in Eq. (1.3.7) below, which contains a parameter l (the length of the oscillator). From Fig. 1.8b we could see that the shorter the length l is, the steeper the potential well, making it the more challenging to integrate accurately.

$$V = \frac{1.0}{x^{12}} - \frac{2.0}{x^6} + \frac{1.0}{(l-x)^{12}} - \frac{2.0}{(l-x)^6} \quad (1.3.7)$$

Fig. 1.9a illustrates that even for a relatively long length $l = 2.0$, the error in the Eulerian

integrator with a step size $h = 0.001$ is significant, exceeding 0.1 in the central region. This indicates that the Eulerian integrator is unsuitable even for low-temperature cases, where the range of motion remains restricted to the central region. In contrast, the RK4 method maintains high precision also at extremely short lengths (see Fig. 1.9b), which makes it a reliable choice.

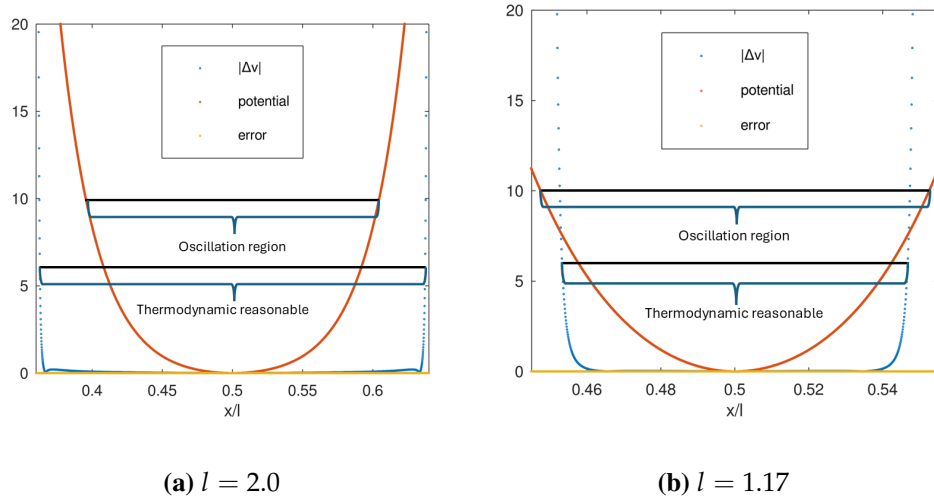


Figure 1.10: Oscillation range of a single Lennard-Jones oscillator at $T = 10.0$ and variation of velocity for $l = 2.0$ (left panel) and $l = 1.17$ (right panel).

Note also that high precision alone is insufficient for a simulation to be physically correct: a physically meaningful simulation must also ensure that the velocity change at each step is, at the least, of the same order as the intrinsic fluctuations. For an oscillator at temperature $T = 10.0$, the oscillation range roughly corresponds to the region where the potential energy is below $T = 10.0$. However, the thermodynamically reasonable region is where the change in velocity $|\Delta v|$ is smaller than the fluctuation $2\sqrt{T} \approx 6.3246$. Fig. 1.10 shows that the same time step $h = 0.001$ maintains the error small for both $l = 2.0$ and $l = 1.17$ within the range of oscillation. However, for $l = 1.17$, the range of oscillations exceeds the thermodynamically reasonable region, which indicates that the simulation for $l = 1.17$ with $h = 0.001$ will give numerically stable but thermodynamically incorrect results. Fig. 1.11 gives one example. simulating chains of $\rho = 1.15$ and $\rho = 1.55$ with $h = 0.001$ and $T_L = T_R = 10.0$, the resultant density and temperature profile for $\rho = 1.55$ (see the red circles in Fig. 1.11) oscillates with huge amplitude and

narrow period, making it look like multiple points plotted for each i value. On the other hand, $\rho = 1.15$ gives homogeneous distributions (blue circles in Fig. 1.11) as expected. This example illustrates how improper time steps result in a nonphysical profile.

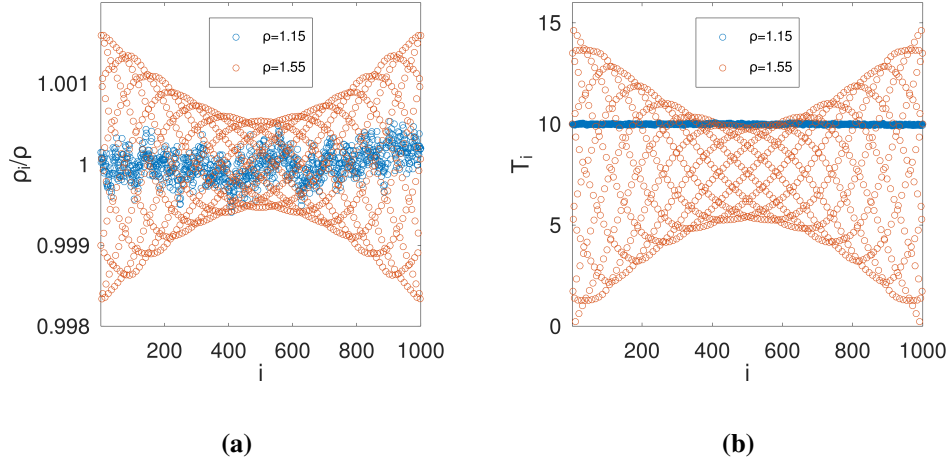


Figure 1.11: Unphysical profile made by improper but stable time step.

1.3.5 Equilibrium and nonequilibrium simulation

Thermostatted dynamical systems numerically integrated under a proper boundary condition give rise to steady states characterised by a steady state distribution. The steady state could be either at nonequilibrium or equilibrium. It is important to specify that the term “equilibrium”, in the context of thermodynamics, contains three essential components [Callen, 1991]: no macroscopic velocity field, which corresponds to mechanical equilibrium; no diffusion and chemical reaction, which accounts to chemical equilibrium; and, most importantly, no heat flux and maintenance of thermal equilibrium. Both fixed-force and fixed-length boundaries agree with the first component. Our system contains identical oscillators, validating the second component. The final component is determined by the temperatures at boundaries: equilibrium states with temperature T are produced by simulations with $T_L = T_R = T$ and nonquilibrium states with heat flux are produced by non-equilibrium simulation with $T_L \neq T_R$. Note that there are other approaches to run nonequilibrium simulations. For example, the SLLOD equation [Todd and Daivis, 2017] introduces nonequilibrium by modifying the dynamical equations, which provides

another way to introduce a temperature gradient in simulations under periodic boundary conditions. In that scenario, the average velocity of the system in simulation is non-zero and there are random directional movement. Systems as such are labeled as “random heat engines” [Iida et al., 2022, Sheng et al., 2021, Ruben Gomez-Solano, 2021]: their efficiency may exceed the thermodynamic limit in the low-dimensional case, considering the anomalous low-dimensional heat conduction [Lepri et al., 2010, Dhar, 2008].

1.3.6 Phase variables

Statistical mechanics treats thermodynamic variables as averages over the ensemble distribution (see Section 1.2). Under the ergodic assumption [Cencini et al., 2010], the ensemble distribution could be produced by integrating the differential equations Eq. (1.3.1)-(1.3.3). As a final step, let us define the phase variables corresponding to the thermodynamic variables that interest us.

An equilibrium simulation produces homogeneous states and the corresponding phase variables are defined globally, including the chain’s total length, which is defined as the average distance between the first and last oscillator (see Fig. 1.4):

$$L = \langle x_{N+1} - x_0 \rangle.$$

Its fluctuation is defined as the square deviation:

$$\sqrt{\sigma^2} = \sqrt{\langle (x_{N+1} - x_0)^2 \rangle - \langle x_{N+1} - x_0 \rangle^2}$$

and dividing the total length by the number of oscillators N produces the inverse density:

$$\rho^{-1} = \frac{L}{N}.$$

The total kinetic energy divided by N is proportional to temperature, as per our discussion

above on temperature and thermostats:

$$T = \frac{1}{N} \sum_{k=1}^N \frac{p_k^2}{m}.$$

The expression for pressure is derived by following the momentum conservation of the i^{th} particle. In steady states, the average momentum should be conserved, then we have:

$$\begin{aligned} m \left\langle \frac{dv_i}{dt} \right\rangle &= \langle F_{i,i-1} \rangle - \langle F_{i+1,i} \rangle \\ &= -(P_{i+1,i} - P_{i,i-1}) = 0 \end{aligned}$$

which indicates that the pressure is the average force imposed from the $(i-1)^{th}$ oscillator on the i^{th} oscillator:

$$P_{i,i-1} = \langle F_{i,i-1} \rangle. \quad (1.3.8)$$

The equation above is the pressure in Lagrangian form or the pressure computed by following a moving mass element. We can also define the pressure in Eulerian form by computing the momentum flowing through a given threshold in space, based on the momentum density in atomic representation [Todd and Daivis, 2017]

$$\rho(x, t)v(x, t) = \sum_{i=1}^N m_i v_i \delta(x - x_i)$$

and more details have been attached in the Appendix B.1. The pressure in Lagrangian and Eulerian form can be shown to be equivalent, which has been fully discussed in [Mejía-Monasterio et al., 2019].

Pressure, or momentum flux, remains homogeneous in non-equilibrium states due to the very simple geometry of monodimensional chains and the corresponding phase variable is the same. On the other hand, inverse density and temperature are inhomogeneous in nonequilibrium states. Despite the complexities involved in the definition of nonequilibrium thermodynamic quantities [Giberti et al., 2019b, Rugh, 1997, Morriss and Rondoni, 1999, Casas-Vázquez and Jou, 2003, Jou and Restuccia, 2016, Criado-Sancho et al., 2006,

Puglisi et al., 2017], here we interpret the single-oscillator kinetic energy as its “temperature” and the length as its “inverse density”:

$$T_k = \left\langle \frac{p_k^2}{m_k} \right\rangle$$

$$\rho_k^{-1} = \langle x_k - x_{k-1} \rangle.$$

1.4 Objective and overview of the thesis

Sections 1.1 and 1.2 have given a general discussion on the main assumptions of thermodynamics and statistical mechanics regarding chains of oscillators. This thesis wants to investigate the validity of those assumptions by exploring the properties of a specific example, the Lennard-Jones (LJ) chain. This model has been studied in a number of references in the literature [Morris and Rondoni, 1999, Casas-Vázquez and Jou, 2003, Jou and Restuccia, 2016, Criado-Sancho et al., 2006, Cao and He, 2015, Puglisi et al., 2017, Giberti et al., 2019b,a, Lee-Dadswell et al., 2017, Zhong et al., 2012, Chen et al., 2016]. Many properties of LJ chains have been discussed using computer simulations: for example, [Zhong et al., 2012, Savin and Kosevich, 2014] report normal heat conduction along LJ chains, [Lepri et al., 2005] show an unusual width of the dynamical correlation spectrum which signals the breakdown of linearized hydrodynamics, and [Giberti et al., 2019b,a] systematically study the length fluctuation of LJ chains with both nearest and second nearest interactions. Lennard-Jones chains are dissociable and stretching will ultimately break them. [Welland et al., 1992] simulate a LJ chain being stretched and report an exponential dependence of the fracture-site probability with distance from the end. Statistical mechanics methods have as well been applied: for example, [Lee-Dadswell et al., 2017] use a statistical mechanics approach to compute the cluster sizes in a LJ chain. The characteristic of this thesis is combining simulations with statistical mechanics methods and comparing the results to look deeper into both equilibrium and nonequilibrium properties. This includes state equations involving temperature, pressure and density, non-equilibrium single-oscillator relations and correlations of interesting quantities, such

as oscillator length, overall energy, and speed (the absolute value of velocity).

The first original results in this thesis is the study of the state equations of Lennard-Jones chains involving temperature, pressure and density ($PT\rho$ equation). Comparing the prediction made by statistical mechanics in Section 1.2.1 with the measurement made by molecular dynamics, we present new insights on microscopic relations in LJ chains in Chapter 2.

The second novel contribution is a generalisation of the equilibrium state equation to nonequilibrium states. Chapter 3 will discuss the validity of the two nonequilibrium single-oscillator relations in Eq. (1.2.17) and their basis, analysing the validity of factorised nonequilibrium distributions in Eq. (1.2.16) by nonequilibrium simulation.

The last finding is the discussion of more complicated systems. Chapter 4 couples Lennard-Jones chains with harmonic chains, computes equilibrium state equations and fluctuations by statistical mechanics, compares them to the equilibrium simulation and generalises to nonequilibrium.

Equilibrium State equation of Lennard-Jones chains

This Chapter is devoted to the state equations of Lennard-Jones chains, involving temperature, pressure and density ($PT\rho$ equation). Among the three quantities, P and ρ are conjugate, i.e. the dimension of P/ρ is that of an energy. Henceforth, there are two kinds of representations of a $PT\rho$ equation: $P(T, \rho)$, the pressure P represented as a function of T and ρ , or $\rho^{-1}(T, P)$, the inverse density ρ^{-1} represented as a function of T and P . Section 2.1 discusses the pressure state equation of $P = P(T, \rho)$ and Section 2.2 discusses the inverse density state equation of $\rho^{-1} = \rho^{-1}(T, P)$. In both Sections, we first compute the state equation predicted by statistical mechanics, i.e. Eq. (1.2.5) and Eq. (1.2.9), approximate them in analytic form by using properties of the Lennard-Jones potential and describe the range of validity of those approximations using a phase diagram. Finally, we compare all the results with an equilibrium simulation. Note also that, at the end of Chapter 2.2, we discuss the equivalence between $P(T, \rho)$ and $\rho^{-1}(T, P)$ state equations as well.

2.1 State equation for pressure in a Lennard-Jones chain

2.1.1 Statistical mechanics and phase diagram for isolated oscillators

Eq. (1.2.5) in Section 1.2.1 is a general expression of the $P(T, \rho)$ state equation for monodimensional chains of arbitrary potential. Applying the Lennard-Jones potential in Eq. (1.3.4) and using reduced units in Eq. (1.3.5), we get the following expression:

$$P(T, \rho) = \frac{\int_0^{\frac{N}{\rho}} -\frac{\partial V_{LJ}(q_1)}{\partial q_1} e^{-\frac{V_{LJ}(q_1)}{T}} dq_1 \prod_{k=2}^{N-1} \int_0^{\frac{N}{\rho}} e^{-\frac{V_{LJ}(q_k)}{T}} dq_k e^{-\frac{V_{LJ}(\frac{N}{\rho} - \sum_{k=1}^{N-1} q_k)}{T}}}{\int_0^{\frac{N}{\rho}} e^{-\frac{V_{LJ}(q_1)}{T}} dq_1 \prod_{k=2}^{N-1} \int_0^{\frac{N}{\rho}} e^{-\frac{V_{LJ}(q_k)}{T}} dq_k e^{-\frac{V_{LJ}(\frac{N}{\rho} - \sum_{k=1}^{N-1} q_k)}{T}}}.$$

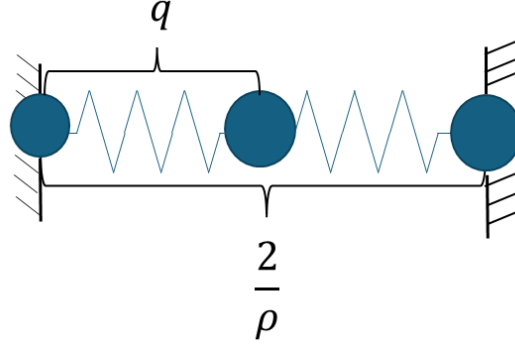
The integral terms are high-dimensional, making an analytical solution impossible to achieve. However, we can get some insights by analysing the simplest case $N = 2$, where the equation above is reduced to:

$$\begin{aligned} P(T, \rho) &= \frac{\int_0^{\frac{2}{\rho}} -\frac{\partial V_{LJ}(q_1)}{\partial q_1} e^{-\frac{V_{LJ}(q_1) + V_{LJ}(\frac{2}{\rho} - q_1)}{T}} dq_1}{\int_0^{\frac{2}{\rho}} e^{-\frac{V_{LJ}(q_1) + V_{LJ}(\frac{2}{\rho} - q_1)}{T}} dq_1} \\ &= \frac{\int_0^{\frac{2}{\rho}} \frac{\rho^2}{2} \frac{\partial V^*(\rho, q)}{\partial \rho} e^{-\frac{V^*(\rho, q)}{T}} dq}{\int_0^{\frac{2}{\rho}} e^{-\frac{V^*(\rho, q)}{T}} dq} \\ &= -T \frac{\rho^2}{2} \frac{\partial}{\partial \rho} \ln \int_0^{\frac{2}{\rho}} e^{-\frac{V^*(\rho, q)}{T}} dq. \end{aligned} \quad (2.1.1)$$

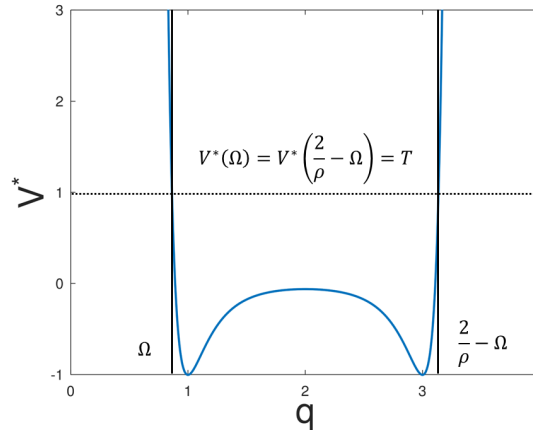
In the second line above, we have defined the equivalent potential field V^* and used the equality $\frac{\partial V_{LJ}}{\partial q_1} = \frac{\partial V^*}{\partial \frac{2}{\rho}} = -\frac{\rho^2}{2} \frac{\partial V^*}{\partial \rho}$. The V^* is written as:

$$\begin{aligned} V^* &= V_{LJ}(q) + V_{LJ}\left(\frac{2}{\rho} - q\right) \\ &= \left[\left(\frac{1}{q}\right)^{12} - 2 \left(\frac{1}{q}\right)^6 + \left(\frac{\rho}{2 - \rho q}\right)^{12} - 2 \left(\frac{\rho}{2 - \rho q}\right)^6 \right], \end{aligned} \quad (2.1.2)$$

which corresponds to an isolated oscillator, oscillating between two fixed particles with distance $2/\rho$ (see Fig. 2.1a) and is “tuned” by the density ρ , where Fig. 2.1b gives an example of V^* of $\rho = 0.5$.



(a) single oscillator



(b) potential

Figure 2.1: a) Sketch of the single oscillator of density ρ . b) The potential V^* of $\rho = 0.5$ and the definition of the parameter Ω .

Linear approximation of the exponent $e^{-V^*/T}$ in Eq. (2.1.1) interestingly provides the microscopic van der Waals (mvdW) equation in linear form:

$$\begin{aligned}
 P^{\text{Van}}(T, \rho) &= -T \frac{\rho^2}{2} \frac{\partial}{\partial \rho} \ln \int_0^{2/\rho} e^{-V^*/T} dr \\
 &\approx -T \frac{\rho^2}{2} \frac{\partial}{\partial \rho} \ln \int_{\Omega(\rho, T)}^{2/\rho - \Omega(\rho, T)} \left(1 - \frac{V^*}{T}\right) dq \\
 &= -T \frac{\rho^2}{2} \frac{\partial}{\partial \rho} \ln \left(1 + \frac{v}{T}\right) \left(\frac{2}{\rho} - 2\Omega\right),
 \end{aligned}$$

where the term $\Omega(\rho, T)$ in the second line, as shown in Fig. 2.1b, is the truncation of

the integral to make a first order approximation $1 - V^*/T$ positive and consistent with $e^{-V^*/T}$ being positive. Term v in the third line is the negative average potential defined as:

$$\begin{aligned} v(\rho, T) &= -\frac{1}{\frac{2}{\rho} - 2\Omega(\rho, T)} \int_{\Omega(\rho, T)}^{2/\rho - \Omega(\rho, T)} V^* dq \\ &= \frac{\frac{4}{5}(\Omega^{-5} - (\frac{2}{\rho} - \Omega)^{-5}) + \frac{2}{11}((\frac{2}{\rho} - \Omega)^{-11} - \Omega^{-11})}{\frac{2}{\rho} - 2\Omega}, \end{aligned}$$

If we treat both Ω and v as constant, we get the mvdW equation in linear form

$$P^{\text{Van}}(T, \rho) = \frac{T}{(1 + \frac{v}{T}) \left(\frac{2}{\rho} - 2\Omega \right)} \sim \frac{T\rho}{(1 + a)(1 - \rho b)}, \quad (2.1.3)$$

which is based on the same approximation of the classic van der Waals equation. Both describe the hard core repulsion with parameter b and use parameter a to describe the attraction [Kardar, 2007]. In fact, if we consider the density dependence of the term v we can get the mvdW equation in standard form, which is identical to the microscopic relation proposed in Ref. [Sun et al., 2025]:

$$\begin{aligned} P^{\text{Van}}(T, \rho) &= -T \frac{\rho^2}{2} \frac{\partial}{\partial \rho} \ln\left(1 + \frac{v}{T}\right) \left(\frac{2}{\rho} - 2\Omega \right) \\ &= -T \frac{\rho^2}{2} \frac{\left(1 + \frac{v}{T}\right) \left(-\frac{2}{\rho^2}\right) + \frac{1}{T} \frac{\partial v}{\partial \rho} \left(\frac{2}{\rho} - 2\Omega\right)}{\left(1 + \frac{v}{T}\right) \left(\frac{2}{\rho} - 2\Omega\right)} \\ &\sim \frac{T}{\rho^{-1} - \Omega} - \frac{\frac{\partial v}{\partial \rho}}{1 + \frac{v}{T}} \rho^2 \\ &= \frac{T}{\rho^{-1} - b} - a\rho^2, \end{aligned} \quad (2.1.4)$$

but here we stress that both Eq. (2.1.3) and Eq. (2.1.4) describe an isolated monodimensional oscillator while the classic van der Waals equation is for the equilibrium of gases made by large number of particles moving and interacting in three-dimensional space. This difference makes the parameter a and b in classic van der Waals equation almost constants. For temperature lower than the critical value $T < \frac{8a}{27b}$, it will make $(\partial P / \partial \rho)_T < 0$, in contradiction to the stability condition referred in Eq. (1.1.10). This contradiction im-

plies that the system undergoes a phase transition, which violates the general theorem of Van Hove [Chowdhury and Stauffer, 2000]: a one-dimensional model with short-range inter-particle interactions (including the Lennard-Jones chain we studied) cannot exhibit a phase transition at any non-zero temperature. In contrast, the mvdW equation in both linear form in Eq. (2.1.3) and standard form in Eq. (2.1.4) has $(\partial P / \partial \rho)_T > 0$, in alignment with the Van Hove theorem. In this sense, both forms are physically correct but here we exclusively use the linear form in Eq. (2.1.3) because its solution for inverse density ρ^{-1} fits with the state equation for inverse density of chains, which will be shown in the next Section. Discussion on the standard form Eq. (2.1.4) is added in Appendix B.2 and an analysis of how this equation for single particles can explain a phenomenological law for thermal transport in LJ chains is discussed in Ref. [Sun et al., 2025].

At high temperatures, the mvdW equation in Eq. (2.1.3) is reduced to a simpler form:

$$\begin{aligned}
 & \lim_{T \rightarrow +\infty} P^{\text{Van}}(T, \rho) \\
 &= \lim_{T \rightarrow +\infty} \frac{T}{(1 + \frac{v}{T})(\frac{2}{\rho} - 2\Omega)} \\
 &= \frac{T}{\frac{2}{\rho} - 2\Omega} \\
 &\sim \frac{T\rho}{1 - \rho b} = P^{\text{Tonks}}(T, \rho).
 \end{aligned}$$

We name it as the “microscopic Tonks” (mTonks) equation because it is identical to the state equation of Tonks gas, but again, the Tonks gas is made of hard-core particles [Chowdhury and Stauffer, 2000], while the mTonks equation is based on a single, isolated monodimensional oscillator and refers to single-particle properties only. This equation could also be deduced by a physical argument: the force between hardcore particles of diameter b is affected only by collisions. Hence, the average force is the product of exchanged momentum with the frequency of collisions. The characteristic momentum exchanged is proportional to $\sqrt{Tm}$, because of the definition $T = \langle p^2/m \rangle$. The frequency is the inverse of the mean free time, the ratio between the mean free length $\frac{2}{\rho} - 2b$ and the characteristic velocity $\sqrt{T/m}$. Putting all together we get the Tonks equation:

$$p^{\text{Tonks}} \propto \frac{T}{\frac{2}{\rho} - 2b} \sim \frac{T\rho}{1 - b\rho}. \quad (2.1.5)$$

Both mTonks and mvdW equations are approximations of the term $P(T, \rho)$ in Eq. (2.1.1). Fig. 2.2a shows that, under constant temperature, the mTonks equation is a good approximation for $0 < \rho < \rho_1$ and the mvdW equation is for $\rho_1 < \rho < \rho_2$. Varying the temperature, limits ρ_1 and ρ_2 also vary, as shown in the four panels of Fig. 2.2. Finding ρ_1 and ρ_2 for different temperatures, we get Fig. 2.3, which is a sort of “phase diagram” on the (ρ, T) plane. Note that the phase diagram referred here is not the thermodynamics phase diagram because there is no phase transition in this system: it solely represents the geometry of the $P(T, \rho)$ surface. Also, all these relations are to be seen as for single particles only and cannot be considered thermodynamically rigorous.

In Fig. 2.3, the region above the blue circles has:

$$\left| \frac{P - P^{\text{Van}}}{P} \right| < 0.02,$$

and the region over the red circles has:

$$\left| \frac{P - p^{\text{Tonks}}}{P} \right| < 0.02,$$

where P is computed by integration from Eq. (2.1.1). These regions show the range of validity of the mvdW equation and mTonks equation, which will be qualitatively verified by simulation in the following Section. Quantitative verification is difficult because Fig. 2.3 is the phase diagram of an isolated single oscillator and the simulation is for chains with large number of particles. Simulating a single oscillator is challenging also because the Nosé Hoover thermostat is non-ergodic in small systems [Fillipov et al., 1998].

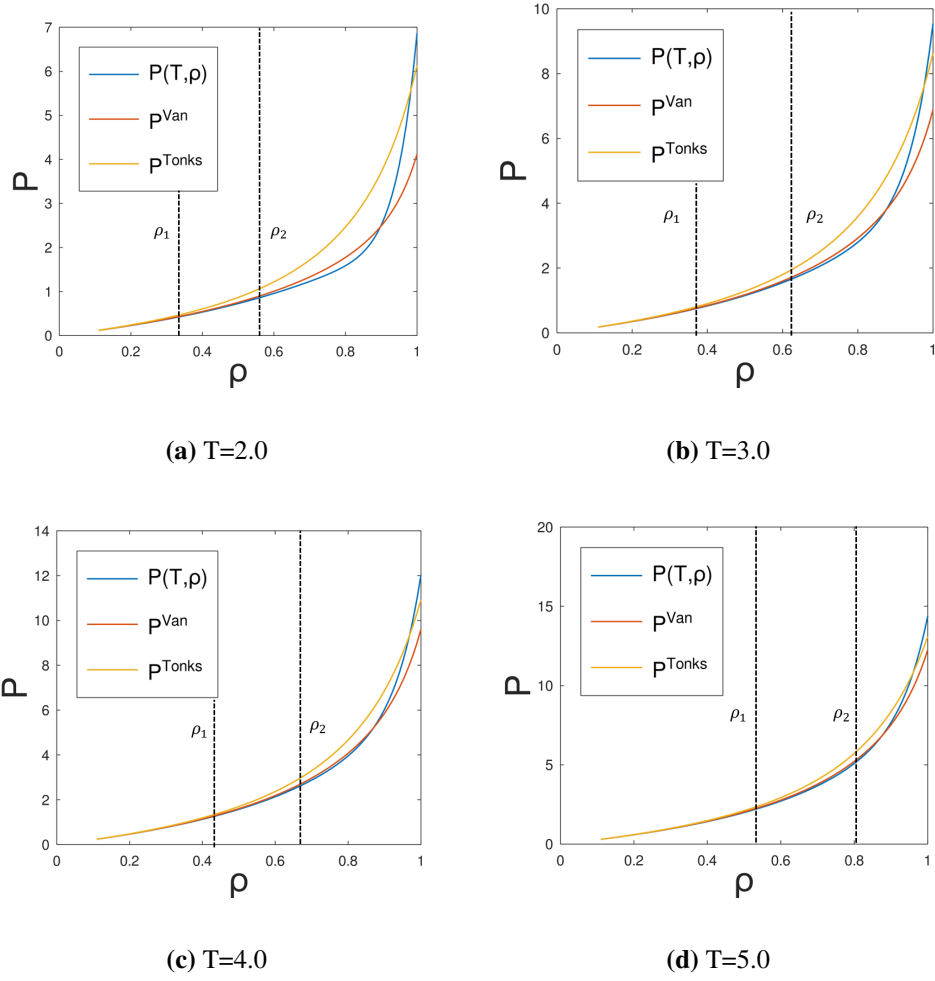


Figure 2.2: An example of four profiles of Eq. (2.1.1) compared with the mvdW equation in Eq. (2.1.3) and the mTonks equation in Eq. (2.1.5). Verticals lines $\rho = \rho_1$ and $\rho = \rho_2$ denote where the best fits occur.

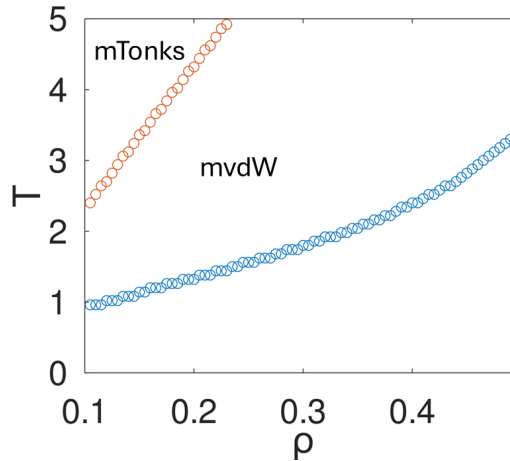


Figure 2.3: The isolated single oscillator phase diagram.

2.1.2 Comparison with equilibrium simulation

We now look at the results that can be obtained via direct simulations. Fig. 2.4 presents the sketch of the system simulated in this Section.

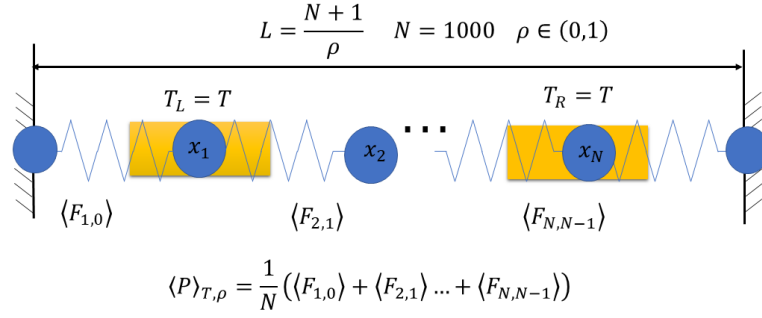


Figure 2.4: Equilibrium simulation under fixed-length boundary.

We use a monodimensional chain of $N = 1000$ identical particles of the same mass, where their instantaneous positions are denoted by $x_1, \dots, x_k, \dots, x_N$, and the momenta by $p_1, \dots, p_k, \dots, p_N$. Each particle interacts with its nearest neighbour in between via a Lennard-Jones (LJ) potential

$$V_{LJ}(x_{k+1} - x_k) = \frac{1}{(x_{k+1} - x_k)^{12}} - 2 \frac{1}{(x_{k+1} - x_k)^6} \quad \text{for } k = 0, 1, \dots, N.$$

Besides the force exerted by Lennard-Jones interactions as discussed above, the first and the last particle in the chain are also subject to two separate Nosé-Hoover (NH) thermostats, at the same temperature via the relaxation time θ . The following $2N + 2$ equa-

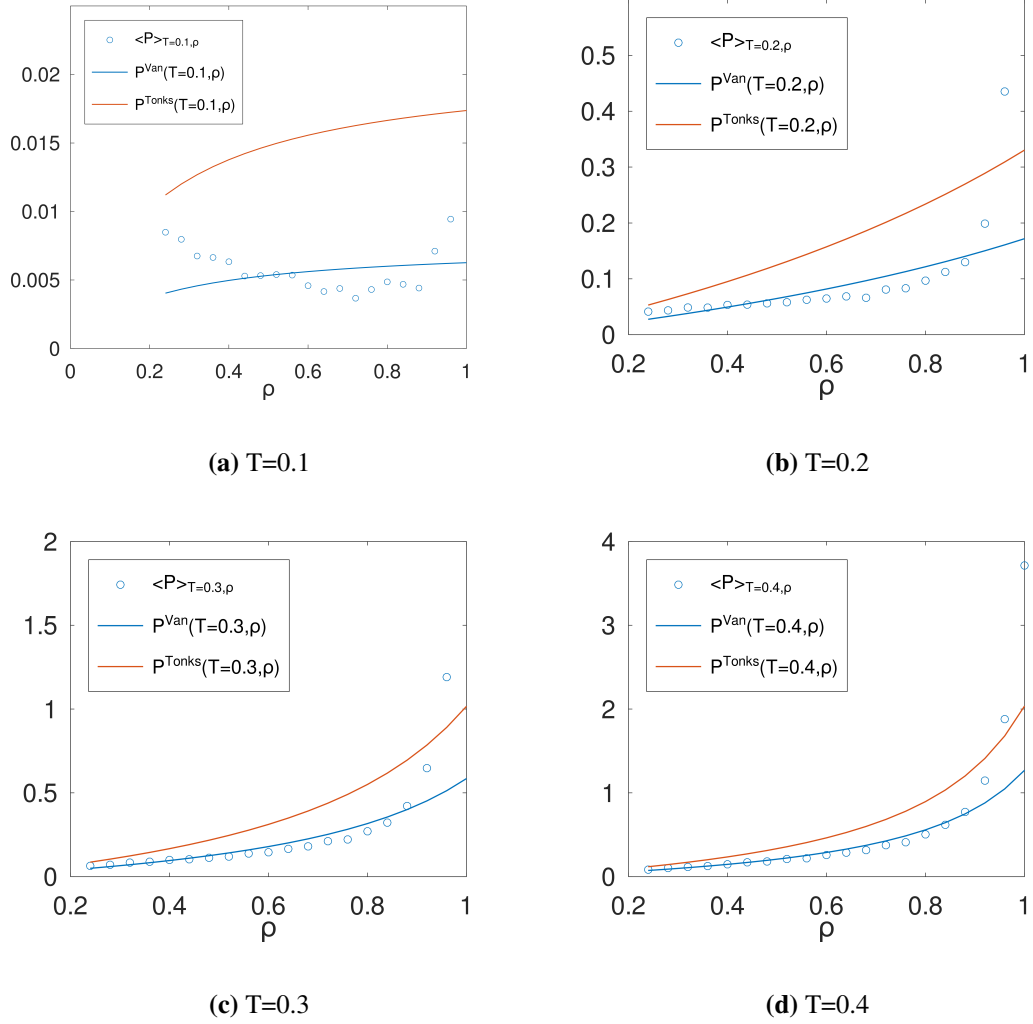


Figure 2.5: An example of four profiles of $\langle P \rangle_{T,\rho}$ as per Eq. (2.1.6), at increasing but low temperatures. (a) At $T_L = T_R = 0.1$ the microscopic van der Waals equation fails everywhere, but as the temperature is risen to (b) $T_L = T_R = 0.2$, (c) $T_L = T_R = 0.3$ and (d) $T_L = T_R = 0.4$ the agreement gradually improves and becomes almost complete, except for very high densities.

tions of motion thus hold:

$$\begin{aligned}
\frac{dx_k}{dt} &= \frac{p_k}{m} & k = 1, \dots, N = 1000 \\
x_0 &= 0.0 \\
x_{N+1} &= L = \frac{N+1}{\rho} \\
\frac{dp_k}{dt} &= F_{k,k-1} - F_{k+1,k} & k = 2, \dots, N-1 \\
\frac{dp_1}{dt} &= F_{1,0} - F_{2,1} - \xi_1 p_1 \\
\frac{dp_N}{dt} &= F_{N,N-1} - F_{N+1,N} - \xi_N p_N \\
F_{k,k-1} &= -\frac{\partial V_{LJ}(x_k - x_{k-1})}{\partial x_k} = \frac{\partial V_{LJ}(x_k - x_{k-1})}{\partial x_{k-1}} & k = 1, 2, \dots, N, N+1 \\
\dot{\xi}_1 &= \frac{1}{\theta^2} \left(\frac{p_1^2}{mT} - 1 \right) \\
\dot{\xi}_N &= \frac{1}{\theta^2} \left(\frac{p_N^2}{mT} - 1 \right).
\end{aligned}$$

In the equation above, units of all variables are assumed to be reduced, with the Boltzmann constant k_B set to unity. The mass of every particle is also given by $m = 1$, as well as the relaxation times of the thermostats, i.e. $\theta = 1$. During the simulation, we numerically integrate the equation with reduced units and specific values of $(T, \rho = \frac{N+1}{L})$ via a fourth-order Runge-Kutta method with step size $\Delta t = 0.001$. Time averages are typically taken after equilibration, over the time interval $[1 \cdot 10^8, 4 \cdot 10^8]$ to evaluate the state equation for pressure by calculating the average force along the chain, e.g.:

$$\langle P \rangle_{T,\rho} = \frac{1}{N} (\langle F_{1,0} \rangle + \langle F_{2,1} \rangle + \dots \langle F_{N+1,N} \rangle), \quad (2.1.6)$$

where the angular brackets $\langle \cdot \rangle_{T,\rho}$ indicate the average value given by the simulation with temperature and length fixed at $(T, \rho = \frac{N+1}{L})$. The results are in line with the conclusions drawn from statistical mechanics in the previous Sections. We find that the mvdW equation is not adequate to describe the behaviour of equilibrium chains at low temperature (see Fig. 2.5a and 2.5b). As temperature rises, mvdW equation becomes a good model of the chain's behaviour, especially in the low density regime (as can be seen in Fig. 2.5c

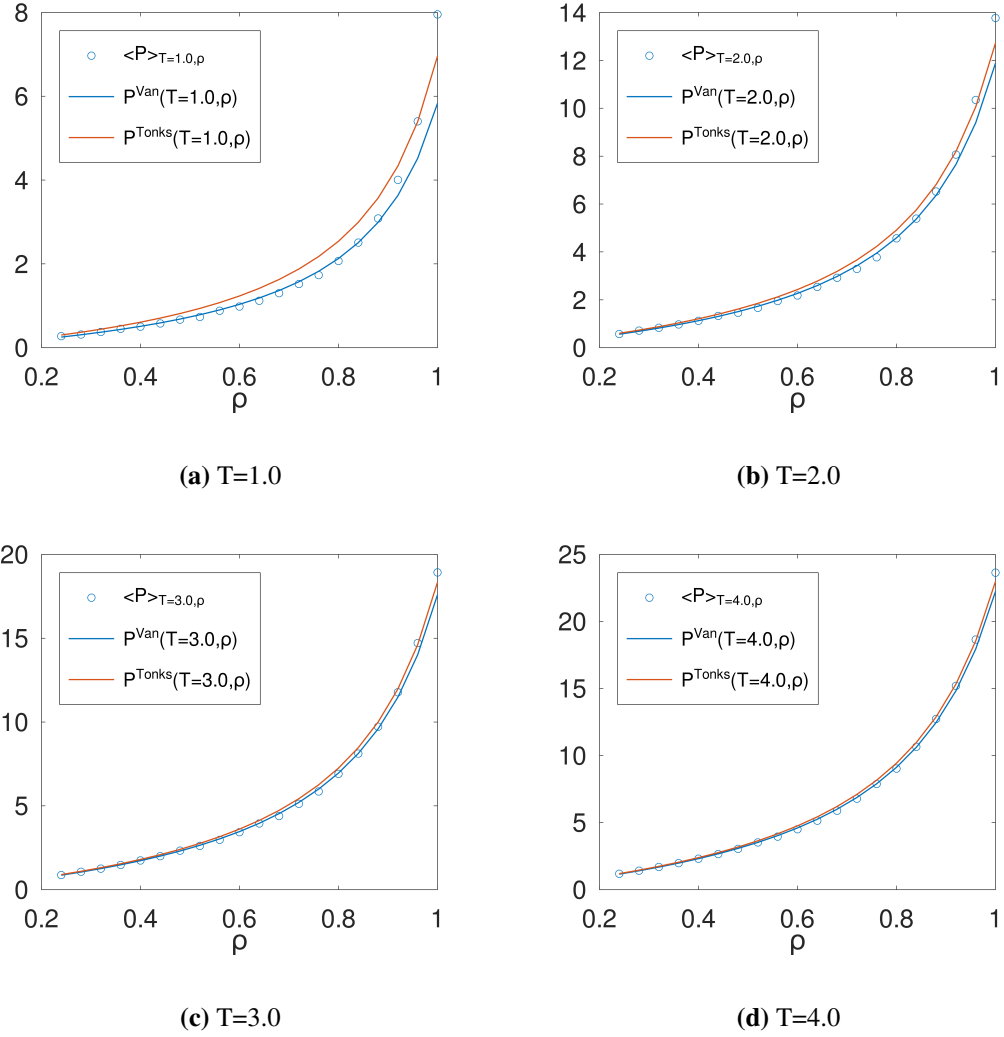


Figure 2.6: An example of four profiles of $\langle P \rangle_{T,\rho}$ as per Eq. (2.1.6), at moderate to high temperatures. (a) At $T_L = T_R = 1.0$, the microscopic van der Waals equation works quite well for almost every density considered, except for high ones. The accuracy increases for higher temperatures such as (b) $T_L = T_R = 2.0$, (c) $T_L = T_R = 3.0$ and (d) $T_L = T_R = 4.0$. The microscopic Tonks equation, Eq. (2.1.5), increases its accuracy as temperature increases and is generally an overestimation of the actual data for moderate temperatures, as shown in panels (a) and (b).

and 2.5d). The mvdW equation is a very good predictor of chain's observables as the temperature is increased to values such as $T = 1.0$, as shown in Fig. 2.6a. This agreement is maintained throughout every higher temperature we have considered, as shown in the remaining panels of the Figure 2.6, with an improvement for higher densities as T increases. It is interesting to note that, at high temperatures, mTonks equation describes the chain's behaviour as well as mvdW Equation does. Indeed, they are indistinguishable, indicating that these two equations converge to a common expression. Note that here we use the mvdW equation in linear form in Eq. (2.1.3). Appendix B.2 also provides fits as per Fig. 2.5 and Fig. 2.6 by using the mvdW equation in standard form in Eq. (2.1.4), with identical trends, in line with results provided also in Ref. [Sun et al., 2025].

To sum up, the landscape of the $P(T, \rho)$ surface drawn by equilibrium simulation $\langle P \rangle_{T, \rho}$ could be qualitatively described by an isolated single oscillator phase diagram in Fig. 2.3. The quantitative description instead fails: Fig. 2.3 shows that mTonks cannot work globally for $T < 6.0$ while the simulation conforms to the mTonks equation only at $T = 3.0, 4.0$ (see Fig. 2.6c and 2.6d). Such a disagreement stems from the difference between isolated single oscillators and chains of a large number of oscillators. In the next Section, we will find a phase diagram for chains and make a finer comparison between simulations and statistical mechanics by focusing on the $\rho^{-1}(T, P)$ landscape.

2.2 State equation for inverse density in a monodimensional chain

2.2.1 Statistical mechanics and phase diagram for chains

We now turn to the inverse density: Section 1.2.1 gives a general formula Eq. (1.2.12), which argues that the inverse density, defined as $\rho^{-1} = L/N$, equals the first order cumulant κ_1 of the potential part of the Gibbs distribution. Substituting the Lennard-Jones

interaction V_{LJ} into the general formula Eq. (1.2.12), we have:

$$\rho^{-1}(T, P) = \kappa_1(T, P) = \frac{\int_0^{+\infty} q e^{-\frac{V_{LJ}(q) + Pq}{T}} dq}{\int_0^{+\infty} e^{-\frac{V_{LJ}(q) + Pq}{T}} dq}. \quad (2.2.1)$$

It can also be approximated by the microscopic van der Waals (mvdW) equation, as we did in Section 2.1.1. We use $e^{-\frac{V_{LJ}}{T}} \approx 1 - \frac{V_{LJ}}{T}$ and truncate the potential V_{LJ} at $\Omega(T)$ with $V_{LJ}(\Omega(T)) = T$ (see Fig. 2.7).

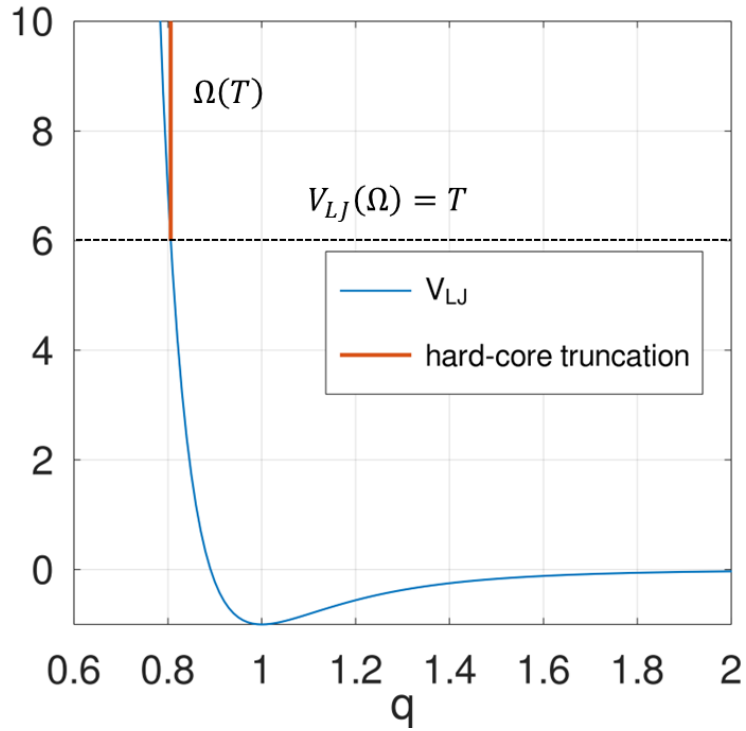


Figure 2.7: The truncated Lennard-Jones potential that we use for approximating $\rho^{-1}(T, P)$ by the microscopic van der Waals equation.

The resultant truncated integral is given by:

$$\begin{aligned} \rho^{-1}(T, P) = \kappa_1(T, P) &= \frac{\int_{\Omega(T)}^{+\infty} q e^{-\frac{Pq}{T} - \frac{V_{LJ}(q)}{T}} dq}{\int_{\Omega(T)}^{+\infty} e^{-\frac{Pq}{T} - \frac{V_{LJ}(q)}{T}} dq} \approx \frac{\int_{\Omega}^{+\infty} q e^{-\frac{Pq}{T}} (1 - \frac{V_{LJ}(q)}{T}) dq}{\int_{\Omega}^{+\infty} e^{-\frac{Pq}{T}} (1 - \frac{V_{LJ}(q)}{T}) dq} \\ &= \frac{\frac{\Omega^2}{P} e^{-\frac{P\Omega}{T}} + \frac{T^2}{P^2} e^{-\frac{P\Omega}{T}} + \int_{\Omega}^{+\infty} -q \frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq}{\frac{T}{P} e^{-\frac{P\Omega}{T}} + \int_{\Omega}^{+\infty} -\frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq} \\ &= \frac{T}{P(1+a)} + b. \end{aligned}$$

Solving the equation above for P gives:

$$P = \frac{T\rho(T, P)}{(1+a)(1-\rho b)},$$

which has the same form as the mvdW equation in linear form in Eq. (2.1.3) for the isolated single-oscillator. But here the parameters a and b are defined in a different way

$$a = \frac{P}{T} e^{\frac{P\Omega}{T}} \int_{\Omega}^{+\infty} -\frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq$$

$$b = \frac{1}{1+a} \left(\Omega + \frac{P}{T} e^{\frac{P\Omega}{T}} \int_{\Omega}^{+\infty} -q \frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq \right),$$

and can be now computed from first principles.

Expanding the V_{LJ} above by Eq. (1.3.4), the integral could be evaluated by observing:

$$a = \frac{P}{T} e^{\frac{P\Omega}{T}} \int_{\Omega}^{+\infty} -\frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq$$

$$= \frac{P}{T} e^{\frac{P\Omega}{T}} \frac{\epsilon}{T} \left(\int_{\Omega}^{+\infty} 2 \left(\frac{\sigma}{q} \right)^6 e^{-\frac{Pq}{T}} dq - \int_{\Omega}^{+\infty} \left(\frac{\sigma}{q} \right)^{12} e^{-\frac{Pq}{T}} dq \right)$$

$$= \frac{P\Omega}{T} e^{\frac{P\Omega}{T}} \frac{\epsilon}{T} \left(\int_1^{+\infty} 2 \left(\frac{\sigma}{\Omega} \right)^6 \frac{e^{-\frac{P\Omega}{T}t}}{t^6} dt - \int_1^{+\infty} \left(\frac{\sigma}{\Omega} \right)^{12} \frac{e^{-\frac{P\Omega}{T}t}}{t^{12}} dt \right)$$

$$= \frac{\epsilon}{T} \left(2 \left(\frac{\sigma}{\Omega} \right)^6 E_6(\gamma) \gamma e^{\gamma} - \left(\frac{\sigma}{\Omega} \right)^{12} E_{12}(\gamma) \gamma e^{\gamma} \right),$$

$$b = \frac{1}{1+a} \left(\Omega + \frac{P}{T} e^{\frac{P\Omega}{T}} \int_{\Omega}^{+\infty} -q \frac{V_{LJ}(q)}{T} e^{-\frac{Pq}{T}} dq \right)$$

$$= \frac{1}{1+a} \left(\Omega + \frac{P}{T} e^{\frac{P\Omega}{T}} \frac{\epsilon\sigma}{T} \left(\int_{\Omega}^{+\infty} 2 \left(\frac{\sigma}{q} \right)^5 e^{-\frac{Pq}{T}} dq - \int_{\Omega}^{+\infty} \left(\frac{\sigma}{q} \right)^{11} e^{-\frac{Pq}{T}} dq \right) \right)$$

$$= \frac{1}{1+a} \left(\Omega + \frac{P\Omega}{T} e^{\frac{P\Omega}{T}} \frac{\epsilon\sigma}{T} \left(\int_1^{+\infty} 2 \left(\frac{\sigma}{\Omega} \right)^5 \frac{e^{-\frac{P\Omega}{T}t}}{t^5} dt - \int_1^{+\infty} \left(\frac{\sigma}{\Omega} \right)^{11} \frac{e^{-\frac{P\Omega}{T}t}}{t^{11}} dt \right) \right)$$

$$= \frac{1}{1+a} \left(\Omega + \frac{\epsilon\sigma}{T} \left(2 \left(\frac{\sigma}{\Omega} \right)^5 E_5(\gamma) \gamma e^{\gamma} - \left(\frac{\sigma}{\Omega} \right)^{11} E_{11}(\gamma) \gamma e^{\gamma} \right) \right).$$

Here we use the substitution $q = t\Omega$ to get the generalised exponential integral as:

$$E_n(\gamma) = \int_1^{+\infty} \frac{e^{-\gamma t}}{t^n} dt,$$

where the γ is the rescaled pressure defined as

$$\gamma = \frac{P\Omega}{T}.$$

We now introduce the approximation

$$e^\gamma E_n(\gamma) \approx \frac{1}{\gamma + n - 1},$$

which is based on the following inequality:

$$\frac{1}{\gamma + n} < e^\gamma E_n(\gamma) \leq \frac{1}{\gamma + n - 1} \quad \text{for } n = 1, 2, 3, \dots$$

and the fact that in our case, we take $n = 5, 6, 11, 12$. So, the large integers make the upper bound and lower bound relatively close. Finally, considering that we can compute Ω by solving $V_{LJ}(\Omega(T)) = T$ for T via the substitution $x = \Omega^{-6}$, we can derive the mvdW equation from first principles without introducing any empirical parameter:

$$\begin{aligned} \rho_{Van}^{-1} &= \frac{T}{(1+a)P} + b \\ a &= \frac{\epsilon}{T} \left(2 \left(\frac{\sigma}{\Omega} \right)^6 \frac{\gamma}{\gamma+5} - \left(\frac{\sigma}{\Omega} \right)^{12} \frac{\gamma}{\gamma+11} \right) \\ b &= \frac{1}{1+a} \left(\Omega + \frac{\epsilon\sigma}{T} \left(2 \left(\frac{\sigma}{\Omega} \right)^5 \frac{\gamma}{\gamma+4} - \left(\frac{\sigma}{\Omega} \right)^{11} \frac{\gamma}{\gamma+10} \right) \right) \\ \gamma &= \frac{P\Omega}{T} \\ \Omega &= (1 + \sqrt{1+T})^{-\frac{1}{6}}. \end{aligned} \tag{2.2.2}$$

Note that in the high temperature limit, we have:

$$\lim_{T \rightarrow +\infty} \gamma = 0 \quad \lim_{T \rightarrow +\infty} a = 0 \quad \lim_{T \rightarrow +\infty} b = \Omega,$$

and the mvdW equation will be reduced to the mTonks equation:

$$\lim_{T \rightarrow +\infty} \rho_{Van}^{-1} \approx \rho_{Tonks}^{-1} = \frac{T}{P} + \Omega \tag{2.2.3}$$

To sum up, the mvdW equation ρ_{Van}^{-1} in Eq. (2.2.2) is the linear approximation of $\rho^{-1}(T, P) = \kappa_1(T, P)$, and the mTonks equation $\rho_{Tonks}^{-1}(T, P)$ in Eq. (2.2.3) is the high temperature approximation of the mvdW equation. Fig. 2.8a and 2.8b show that ρ_{Van}^{-1} captures the curvature of κ_1 at low temperature and converges at higher temperature. Fig. 2.8c and Fig. 2.8d denote that ρ_{Van}^{-1} fits with κ_1 approximately for $T_1 < T < T_2$ and ρ_{Tonks}^{-1} fits for $T > T_2$. Varying the pressure also changes the limits T_1 and T_2 . So, using T_1 and T_2 for different pressures, we obtain a “phase diagram” on the (P, T) plane which represents the geometry of the $\rho^{-1}(T, P)$ surface (see Fig. 2.9).

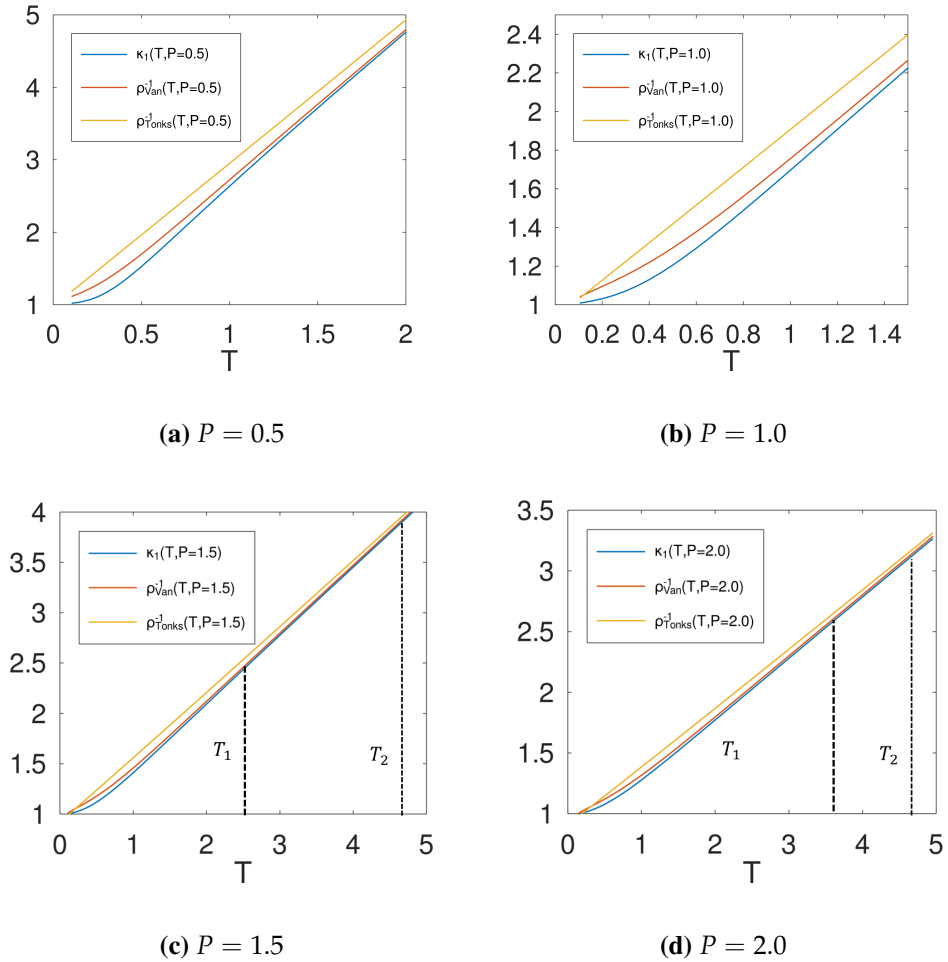


Figure 2.8: An example of four profiles of $\kappa_1(T, P)$ as per Eq. (2.2.1) compared with the microscopic van der Waals equation in Eq. (2.2.2) and the microscopic Tonks equation in Eq. (2.2.3). Vertical lines $T = T_1$ and $T = T_2$ denote where the best fits occur.

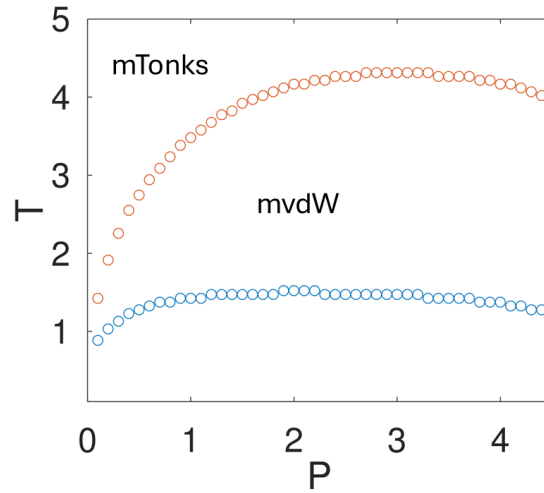


Figure 2.9: The diagram on the (P, T) plane for chains.

In Fig. 2.9, the region above the blue circles has:

$$\left| \frac{\kappa_1 - \rho_{Van}^{-1}}{\kappa_1} \right| < 0.02,$$

where the mvdW equation is a good approximation of κ_1 , and the region above the red circles has:

$$\left| \frac{\kappa_1 - \rho_{Tonks}^{-1}}{\kappa_1} \right| < 0.02.$$

where the mTonks equation finely approximates κ_1 . Note that this diagram is for chains of oscillators confined by a constant force. Contrary to the diagram for the isolated single oscillator in Fig. 2.3, the phase diagram for chains can be finely compared with simulation.

2.2.2 Comparison with equilibrium simulation

To maintain a constant pressure, this Section simulates a Lennard-Jones chain under fixed-force boundary, which is shown in Fig.2.10. The $2N + 2$ equations are given by:

$$\begin{aligned}
 \frac{dx_k}{dt} &= \frac{p_k}{m} & k = 1, \dots, N = 1000 \\
 x_0 &= 0.0 \\
 \frac{dp_k}{dt} &= F_{k,k-1} - F_{k+1,k} & k = 2, \dots, N-1 \\
 \frac{dp_1}{dt} &= F_{1,0} - F_{2,1} - \xi_1 p_1 \\
 \frac{dp_N}{dt} &= F_{N,N-1} - f_p - \xi_N p_N \\
 F_{k,k-1} &= -\frac{\partial V_{LJ}(x_k - x_{k-1})}{\partial x_k} = \frac{\partial V_{LJ}(x_k - x_{k-1})}{\partial x_{k-1}} & k = 1, 2, \dots, N \\
 \dot{\xi}_1 &= \frac{1}{\theta^2} \left(\frac{p_1^2}{mT} - 1 \right) \\
 \dot{\xi}_N &= \frac{1}{\theta^2} \left(\frac{p_N^2}{mT} - 1 \right).
 \end{aligned}$$

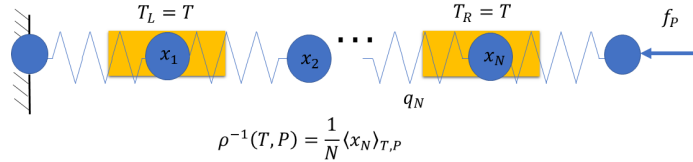


Figure 2.10: Equilibrium simulation under fixed-force boundary.

We control equal temperature on boundaries using Nosé-Hoover thermostats and the pressure along the chain by using a constant constraining force $f_p = P$. The equilibrium simulation allows us to obtain the average length L by evaluating the average position of the last particle

$$L = \langle x_N \rangle_{T,P},$$

here the $\langle \rangle_{T,P}$ denotes the time average by simulation under temperature T and constraining force $f_p = P$. In this way, the inverse density $\rho^{-1}(T, \rho)$ is the length divided by

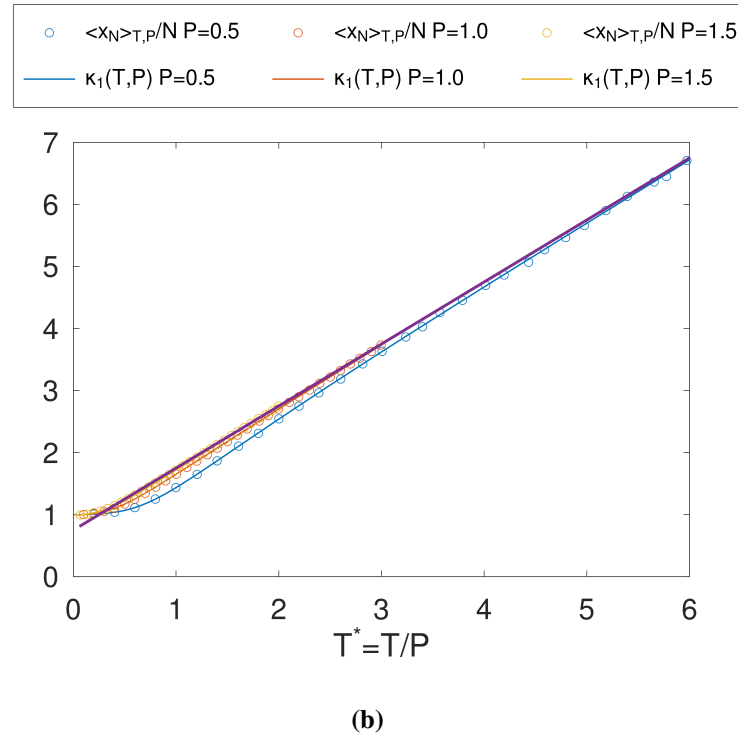
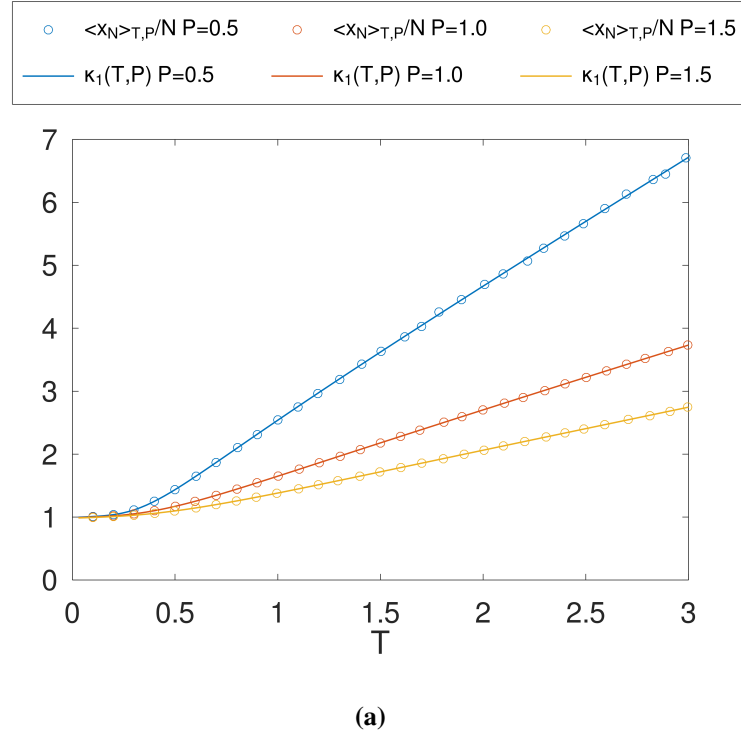


Figure 2.11: (a) The circles are profiles of $\langle x_N \rangle_{T,P}/N$ obtained from simulation, and the solid lines denote $\kappa_1(T,P)$ derived from an ensemble distribution. (b) Rescaling of panel (a) via $T^* = T/P$. All simulations are run for chains of $N = 1,000$ and with different temperature and pressure regimes considered.

N :

$$\rho^{-1}(T, \rho) = \frac{1}{N}L = \frac{1}{N} \langle x_N \rangle_{T,P} \quad (2.2.4)$$

and we can also evaluate the length fluctuation:

$$\Delta L = \sqrt{\langle x_N^2 \rangle_{T,P} - \langle x_N \rangle_{T,P}^2}. \quad (2.2.5)$$

We will now evaluate the validity and the agreement between the predictions by Eq. (2.2.1), and the simulation results by Eq. (2.2.4). Specifically, we aim to study the validity of the following relations in the Lennard-Jones monodimensional chains we are considering:

$$\frac{1}{N} \langle x_N \rangle_{T,P} = \kappa_1(T, P).$$

Fig. 2.11a shows that the cumulant $\kappa_1(T, P)$ does provide an accurate description of the behaviour of equilibrium chains over a broad range of temperatures and pressures as illustrated. This agreement confirms the validity of the phase diagram in Fig. 2.9 for the (P, T) plane, for a large range of temperatures T and pressure $P = f_p$. We also notice that, in the zero-temperature limit, κ_1 converges to unity without dependence on pressure. This is because, as $T \rightarrow 0$, the hard-core repulsive nature of the Lennard-Jones potential in Eq. (1.3.4) maintains the mechanical equilibrium length almost fixed at $\kappa_1 = 1.0$ with little dependence on pressure.

In the high temperature limit, the inverse density instead exhibits a linear dependence on temperature: by rescaling the temperature with pressure, $T^* = T/P$, most inverse density curves collapse onto a single straight line of the form $T/P + b$, as in Fig. 2.11b. This high temperature scaling behaviour is characteristic of the mTonks equation in Eq. (2.2.3) and aligns with the conclusion considered before: κ_1 converges to the mTonks equation in high temperature limit because LJ interaction is indistinguishable with the one from hard-core in this limit.

2.2.3 Comparison with the phase diagram for an isolated single oscillator

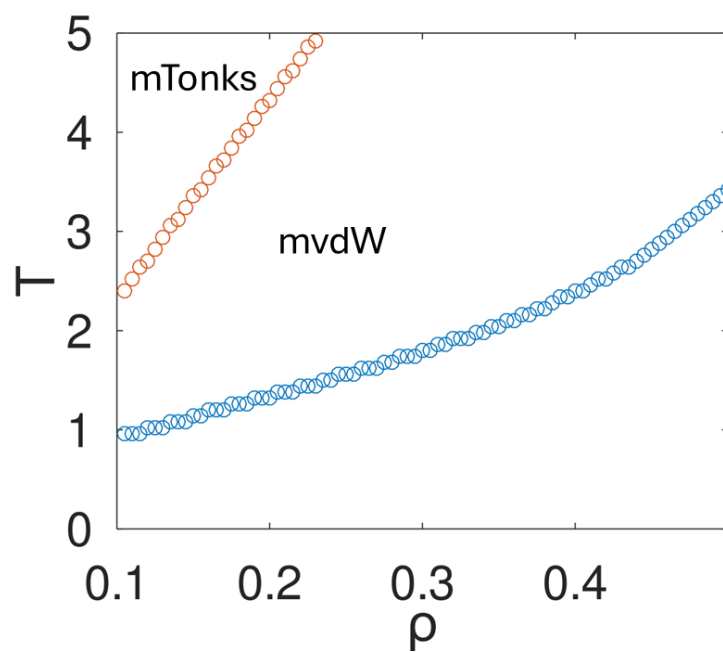
The (P, T) phase diagram shown in Fig. 2.9 could be referred to the (ρ, T) plane by the following transformation:

$$\rho = \kappa_1(T, P)^{-1},$$

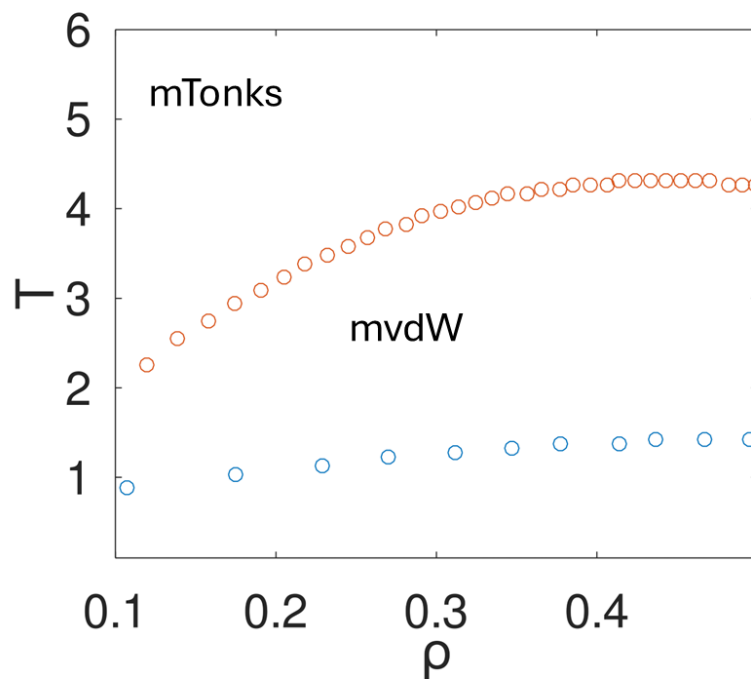
as shown in the lower panel of Fig. 2.12. Its validity is based on simulation under fixed-force boundary, while the phase diagram in the upper panel of Fig. 2.12 is based on the isolated single oscillators under fixed-length boundary. To make a meaningful comparison between them, we need to prove the equivalence of fixed-force and fixed-length boundaries. According to Section 1.2.1, the equivalence lies in thermodynamic limit when $N \rightarrow +\infty$ because of the square root regime of the length fluctuation $\Delta L = \sqrt{N\kappa_2(T, P)}$, as shown in Eq. (1.2.13). This can be verified from simulation via Eq. (2.2.5): using the two equations gives us a relation where the fluctuation per oscillator equals the second-order cumulant of the potential part of the Gibbs distribution:

$$\begin{aligned} \frac{\langle x_N^2 \rangle_{T,P} - \langle x_N \rangle_{T,P}^2}{N} &= \kappa_2(T, P) \\ &= \frac{\int_0^{+\infty} q^2 e^{-\frac{V_{LJ}+Pq}{T}} dq}{\int_0^{+\infty} e^{-\frac{V_{LJ}+Pq}{T}} dq} - \left(\frac{\int_0^{+\infty} q e^{-\frac{V_{LJ}+Pq}{T}} dq}{\int_0^{+\infty} e^{-\frac{V_{LJ}+Pq}{T}} dq} \right)^2. \end{aligned} \quad (2.2.6)$$

The second equality is the result of substituting the Lennard-Jones interaction V_{LJ} into the general formula Eq. (1.2.13). Fig. 2.13a shows that Eq. (2.2.6) is valid for a wide range of temperature and pressure. We also notice that, in the zero-temperature limit, the fluctuations vanish without dependence on pressure, since the mechanical equilibrium in this limit does not give rise to fluctuations. In the high temperature limit, all fluctuation curves follow a parabola $(T/P)^2$ (see Fig. 2.13b) when rescaling the temperature with pressure using $T^* = T/P$. Again, this stems from LJ interactions being indistinguishable



(a) single-oscillator phase diagram



(b) chain phase diagram

Figure 2.12: comparison of single-oscillator phase diagram and the phase diagram of Lennard-Jones chain.

from hard-core ones at high temperatures:

$$e^{-\frac{V_{LJ}(q)}{T}} \approx \begin{cases} 0 & 0 < q \leq b \\ 1 & q > b \end{cases}$$

where b acts as an effective hard-core diameter. Substituting this approximation in Eq. (2.2.6) gives

$$\lim_{T \rightarrow +\infty} \kappa_2(T, P) = \frac{\int_b^{+\infty} q^2 e^{-\frac{Pq}{T}} dq}{\int_b^{+\infty} e^{-\frac{Pq}{T}} dq} - \left(\frac{\int_b^{+\infty} q e^{-\frac{Pq}{T}} dq}{\int_b^{+\infty} e^{-\frac{Pq}{T}} dq} \right)^2.$$

Using the following integrals

$$\int_b^{+\infty} q^n e^{-\frac{Pq}{T}} dq = \frac{T}{P} \left(b^n e^{-\frac{Pb}{T}} + n \int_b^{+\infty} q^{n-1} e^{-\frac{Pq}{T}} dq \right), \quad \int_b^{+\infty} e^{-\frac{Pq}{T}} dq = \frac{T}{P} e^{-\frac{Pb}{T}},$$

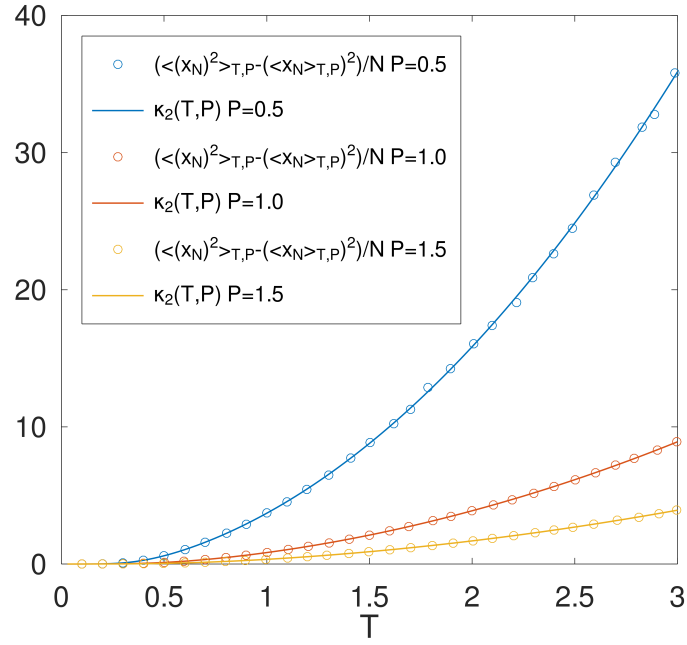
we get the parabola in Fig. 2.13b,

$$\lim_{T \rightarrow +\infty} \kappa_2(T, P) = \left(\frac{T}{P} \right)^2.$$

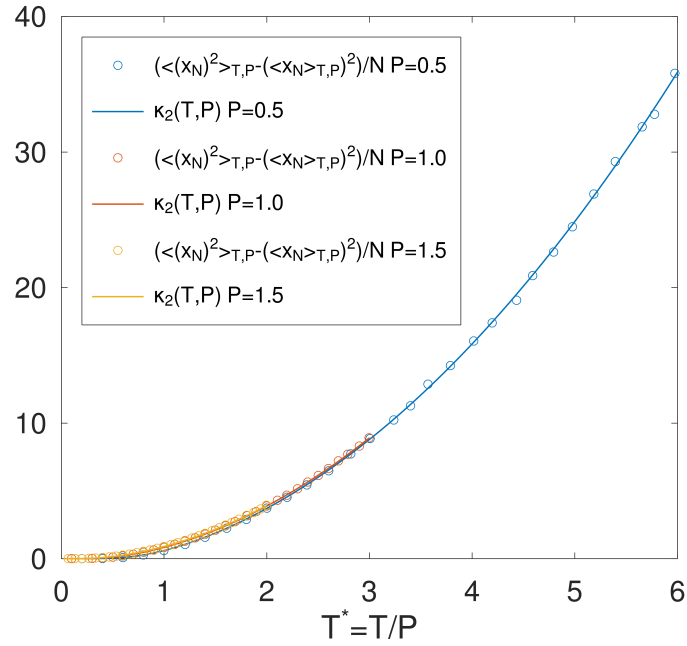
Now we can take Fig. 2.12b as the phase diagram for Lennard-Jones chains of infinitely many oscillators in equilibrium, without specifying the boundary condition. However, both the mvdW and mTonks equations exhibit an extended range of validity: at higher densities, specifically up to $\rho = 0.5$, chains require a lower temperature compared to the isolated single oscillator for these equations to remain applicable.

The nature of the “equivalent potential” V^* may help to explain the difference. The mvdW equation approximates $e^{-\frac{V^*}{T}} \approx 1 - \frac{V^*}{T}$, which is valid for V^* close to zero, whereas mTonks equation approximates V^* with a hard-core potential, which is valid for V^* being sufficiently “steep”. The V^* of an isolated single oscillator with two fixed boundaries of distance $2/\rho$, is given by :

$$V_{single}^* = \left(\frac{1}{q} \right)^{12} - 2 \left(\frac{1}{q} \right)^6 + \left(\frac{1}{\frac{2}{\rho} - q} \right)^{12} - 2 \left(\frac{1}{\frac{2}{\rho} - q} \right)^6.$$



(a)



(b)

Figure 2.13: (a) The circles are profiles of $\frac{\langle x_N^2 \rangle_{T,P} - \langle x_N \rangle_{T,P}^2}{N}$ obtained from simulation, and the solid lines denote $\kappa_2(T, P)$ derived from an ensemble distribution. (c) Rescaling of panel (a) via $T^* = T/P$. All simulations are run for chains of $N = 1,000$ and with different temperature and pressure regimes considered.

In contrast, no matter what the boundary condition is, the V^* for an oscillator in chains of the same density ρ is regulated by the pressure P as follows:

$$V_{chain}^* = \left(\frac{1}{q}\right)^{12} - 2\left(\frac{1}{q}\right)^6 + P(\rho, T)q, \quad (2.2.7)$$

where $P(\rho, T)$ is the solution of Eq. (2.2.1) for P .

Fig. 2.14 compares V_{single}^* and V_{chain}^* at $\rho = 0.5, T = 1.0$. V_{chain}^* is “shallower” and “steeper” than V_{single}^* , which better fits with the approximation of the two microscopic equations we use.

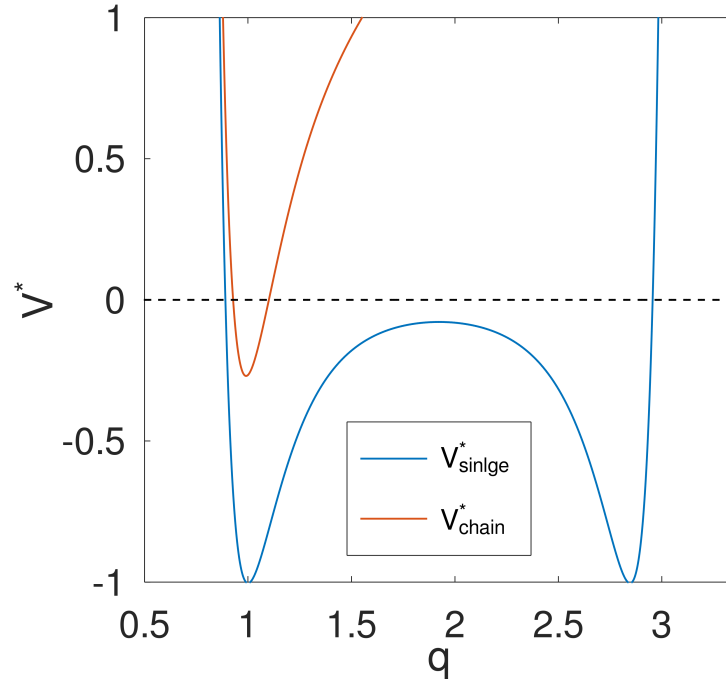


Figure 2.14: Comparison of the equivalent potential V_{single}^* for the isolated single oscillator, and V_{chain}^* for the chain of oscillators.

Non-equilibrium single-oscillator relations

In the previous Chapter, we have expressed the time-averaged inverse density of monodimensional Lennard-Jones chains at equilibrium as the first-order cumulant of the potential part of the Gibbs distribution and its fluctuation as the second-order cumulant. In this Chapter, we will apply the same expressions to non-equilibrium steady states and find two single-oscillator relations describing the single-oscillator length and fluctuations. The origin and validity of those relations are also discussed by comparing them to nonequilibrium simulation under a temperature gradient and when a fixed-force boundary is present.

3.1 Single-oscillator relations using statistical mechanics

The Gibbs distribution has been proven to fully describe the inverse density and length fluctuation of monodimensional Lennard-Jones chains at equilibrium, but the same distribution is no longer valid in non-equilibrium steady states. Using the fact that fluxes of conserved quantities remain homogeneous across the system, such as the average force (i.e., the flux of momentum) that yields the pressure, we assume that a factorised nonequilibrium distribution exists. As we discussed in Section 1.2.2, the nonequilibrium dis-

tribution Eq. (1.2.16) is factorised into the product of the single-oscillator distributions characterised by the average kinetic energy T_k and the homogeneous average force P . In Lennard-Jones chains, this is written as:

$$\begin{aligned}
 & \rho(p_1, q_1, \dots, p_N, q_N; T_1, \dots, T_N, P) \\
 &= \prod_{k=1}^N \phi(p_k, T_k) \psi(q_k, T_k, P) \\
 &= \prod_{k=1}^N \frac{e^{-\frac{p_k^2}{T_k}}}{\int e^{-\frac{p_k^2}{2mT_k}} dp_k} \frac{e^{-\frac{V_{LJ}(q_k) + Pq_k}{T_k}}}{\int e^{-\frac{V_{LJ}(q_k) + Pq_k}{T_k}} dq_k}.
 \end{aligned} \tag{3.1.1}$$

According to this, we get an expression for the average length per single oscillator:

$$\langle q_k \rangle = \kappa_1(T_k, P) = \frac{\Phi_1(T_k, P)}{\Phi_0(T_k, P)}, \tag{3.1.2}$$

which relates the average length per oscillator $\langle q_k \rangle$ to the average force P and kinetic energy T_k via the first-order cumulant $\kappa_1(T_k, P)$ of the term $\psi(q_k, T_k, P)$ in Eq. (3.1.1). Similarly, we find an expression for the length fluctuation per single oscillator as

$$\langle q_k^2 \rangle - \langle q_k \rangle^2 = \kappa_2(T_k, P) = \frac{\Phi_2(T_k, P)}{\Phi_0(T_k, P)} - \left(\frac{\Phi_1(T_k, P)}{\Phi_0(T_k, P)} \right)^2, \tag{3.1.3}$$

now relating the fluctuation per oscillator $\langle q_k^2 \rangle - \langle q_k \rangle^2$ to the average force P and local kinetic energy T_k . The Φ_n here is now defined as:

$$\Phi_n(T_k, P) = \int q^n e^{-\frac{V_{LJ}(q) + Pq}{T_k}} dq.$$

3.2 Comparison with non-equilibrium simulation

The single-oscillator relations in Eq. (3.1.2) and Eq. (3.1.3) can be investigated by comparing with direct measurement from simulation. Here we use a nonequilibrium Lennard-Jones chain subjected to a constraining force, as sketched in Fig. 3.1: this is similar to the

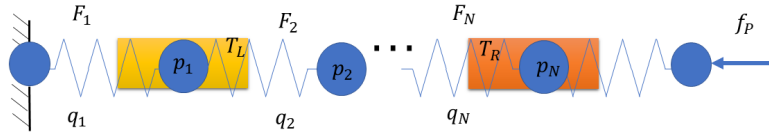


Figure 3.1: Sketch of the chain of Lennard-Jones oscillators with $T_R > T_L$, that are considered in this Chapter.

model we have discussed in Section 2.2.2, except that the variables are replaced with the distances between two consecutive oscillators denoted by $q_1, \dots, q_k, \dots, q_N$, and the thermostats on boundary are set at different temperatures $T_L < T_R$. Hence, the corresponding equations of motion become:

$$\begin{aligned}
 \frac{dq_1}{dt} &= \frac{p_1}{m} \\
 \frac{dq_k}{dt} &= \frac{p_k}{m} - \frac{p_{k-1}}{m} \quad k = 2, \dots, N \\
 \frac{dp_k}{dt} &= F(q_k) - F(q_{k+1}) \quad k = 2, \dots, N-1 \\
 \frac{dp_1}{dt} &= F(q_1) - F(q_2) - \xi_1 p_1 \\
 \frac{dp_N}{dt} &= F(q_N) - f_p - \xi_N p_N \\
 F(q_k) &= -\frac{dV_{LJ}(q_k)}{dq_k} \quad k = 1, 2, \dots, N \\
 \dot{\xi}_1 &= \frac{p_1^2}{T_L} - 1 \\
 \dot{\xi}_N &= \frac{p_N^2}{T_R} - 1 \\
 T_R &> T_L.
 \end{aligned}$$

Here we again set units of all variables as reduced, with Boltzman constant, mass and relaxation times equal to unity. We numerically integrate the equations still employing a fourth-order Runge-Kutta method with step size $\Delta t = 0.001$ and take time averages after equilibration, over the usual time interval $[1 \cdot 10^8, 4 \cdot 10^8]$ for quantities of interest. This is done for the average local length, the local length fluctuation and the local kinetic temperature as well. All microscopic quantities mentioned above are given, respectively, by:

$$l_k = \langle q_k \rangle$$

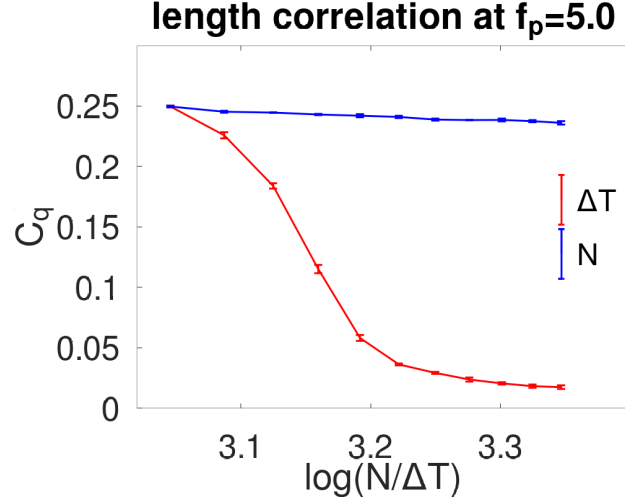


Figure 3.2: The correlation C_q defined in Eq. (3.2.3) referred to a decreasing temperature gradient, which is realised by increasing number of oscillators N with constant boundary temperatures $T_R = 1.0, T_L = 0.1$ (the blue line), or decreasing $\Delta T = T_R - T_L$ with constant $N = 1000$ (the red line). The error bars are obtained by averaging over four different initial states, each one over the time interval $[1 \cdot 10^8, 4 \cdot 10^8]$. For illustrative purposes, N is plotted on a logarithmic scale.

$$\sigma_k^2 = \langle q_k^2 \rangle - \langle q_k \rangle^2 \quad (3.2.1)$$

$$T_k = \frac{\langle p_k^2 \rangle}{m}.$$

As mentioned, the mechanical pressure along the chain in this work is interpreted as an average force that remains homogeneous at equilibrium and at steady states in non-equilibrium, given by:

$$P = \langle F(q_1) \rangle = \langle F(q_2) \rangle = \dots = \langle F(q_N) \rangle.$$

We can also compute the fluctuation of the total length

$$\sigma^2 = \sum_{k,m=1}^N \langle q_k q_m \rangle - \langle q_k \rangle \langle q_m \rangle \quad (3.2.2)$$

and the ratio between σ^2 and the sum $\sum \sigma_k^2$ gives a length correlation index C_q :

$$C_q = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sigma^2}{\sum_{k=1}^N \sigma_k^2} - 1}. \quad (3.2.3)$$

Here the term σ^2 is the total length fluctuation defined in Eq. (3.2.2) and σ_k^2 is the length fluctuation of the k^{th} oscillator defined in Eq. (3.2.1). As we discuss in Section 1.2.2, the correlation can also be defined via other variables. If we consider the speed, e.g., the absolute value of velocity, then we have the speed correlation:

$$C_v = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sum_{k=1}^N \sum_{m=1}^N \langle |p_k| |p_m| \rangle - \langle |p_k| \rangle \langle |p_m| \rangle}{\sum_{k=1}^N \langle p_k^2 \rangle - \langle |p_k| \rangle^2}} - 1 \quad (3.2.4)$$

or if we take the single oscillator energy:

$$E_k = \frac{p_k^2}{2} + V_{LJ}(q_k),$$

then we get the energy correlation:

$$C_E = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sum_{k=1}^N \sum_{m=1}^N \langle E_k E_m \rangle - \langle E_k \rangle \langle E_m \rangle}{\sum_{k=1}^N \langle E_k^2 \rangle - \langle E_k \rangle^2}} - 1. \quad (3.2.5)$$

Note that Eq. (3.2.3), (3.2.4) and (3.2.5) represent the overall correlation along the entire

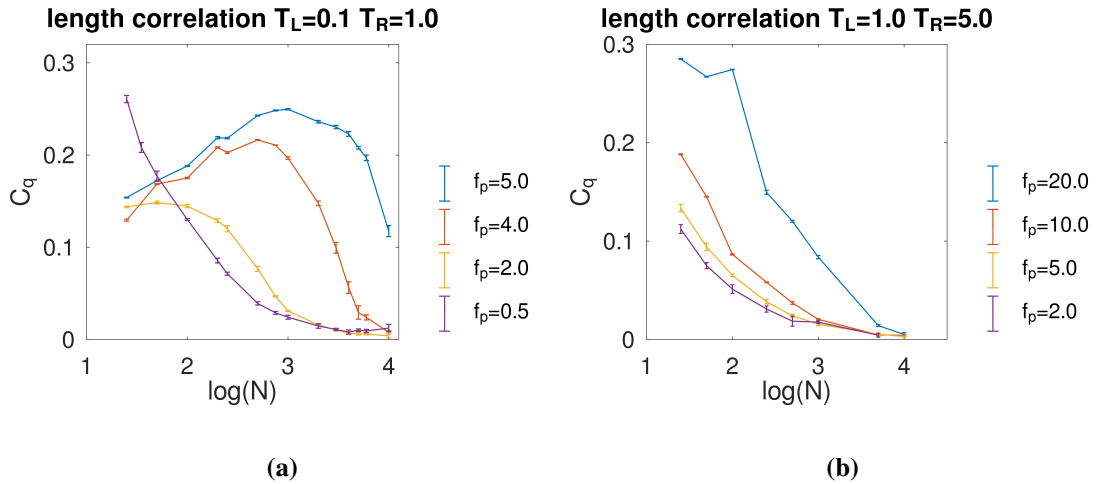


Figure 3.3: The correlation C_q defined in Eq. (3.2.3) concerning number of oscillators N , with fixed boundary temperature T_L, T_R and constraining force f_p . The error bars are obtained by averaging over four different initial states, each one over the time interval $[1 \cdot 10^8, 4 \cdot 10^8]$. For illustrative purposes, N is plotted on a logarithmic scale.

chain. The local correlation can be defined accordingly. For instance, the local length

correlation is given by

$$c_q(k, m) = \frac{\langle q_k q_m \rangle - \langle q_k \rangle \langle q_m \rangle}{\langle q_k^2 \rangle - \langle q_k \rangle^2}, \quad (3.2.6)$$

which, in the homogeneous case, is related to the overall correlation through

$$C_q = \sqrt{\frac{1}{N(N-1)}} \sqrt{\sum_{k,m}^N c_q(k, m) - N}.$$

Similarly, we define the local energy and speed correlation as

$$c_E(k, m) = \frac{\langle E_k E_m \rangle - \langle E_k \rangle \langle E_m \rangle}{\langle E_k^2 \rangle - \langle E_k \rangle^2}, \quad (3.2.7)$$

$$c_v(k, m) = \frac{\langle |p_k p_m| \rangle - \langle |p_k| \rangle \langle |p_m| \rangle}{\langle p_k^2 \rangle - \langle p_k \rangle^2}, \quad (3.2.8)$$

In the homogeneous case, analogous relations hold:

$$C_E = \sqrt{\frac{1}{N(N-1)}} \sqrt{\sum_{k,m}^N c_E(k, m) - N}$$

$$C_v = \sqrt{\frac{1}{N(N-1)}} \sqrt{\sum_{k,m}^N c_v(k, m) - N}$$

The correlations introduced above characterise inter-oscillator couplings. Additionally, we may introduce a measure c_{qv} for intra-oscillator coupling between length and velocity of the same oscillator:

$$c_{qv}(k) = \langle q_k p_k \rangle \quad (3.2.9)$$

When both inter- and intra- correlations are zero, we conclude that the motion of each degree of freedom is independent, and the overall distribution factorises into a product of single-freedom distributions, i.e., a product of single-cell distributions being factorised as the single-particle length distribution times single-particle velocity distribution. Section 1.2.2 has proved that, for an arbitrary single-oscillator quantity, we have $C = 1$ in the fully correlated case and $C = 0.0$ with the factorised distribution in Eq. (3.1.1).

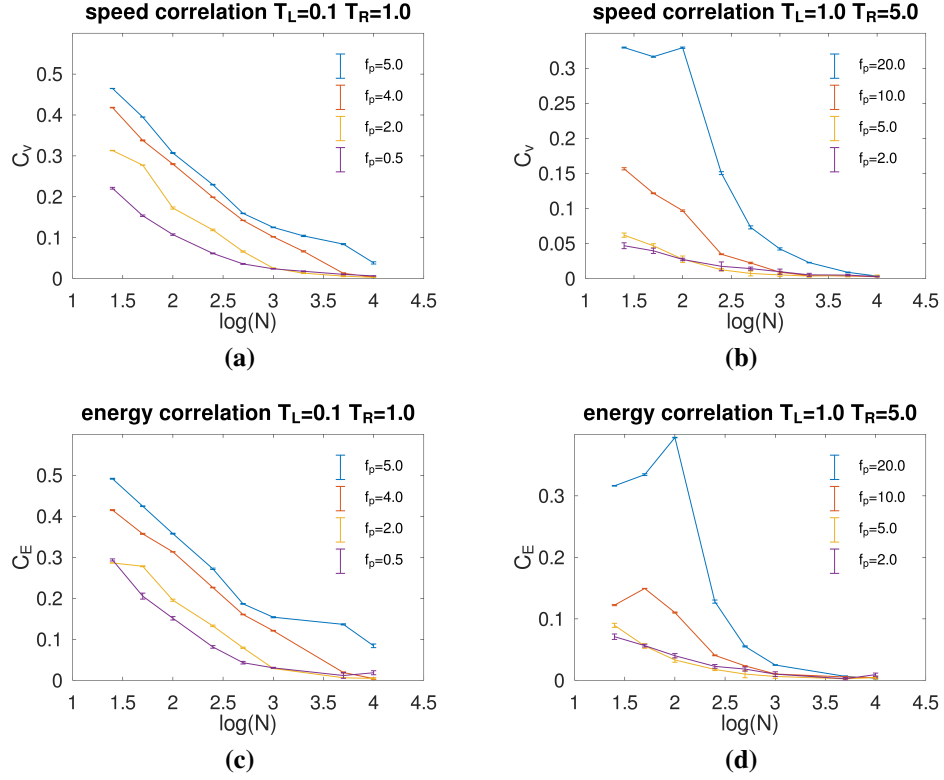


Figure 3.4: The speed correlation C_v and energy correlation C_E defined in Eq. (3.2.4) and (3.2.5). The others is the same with Fig. 3.3.

Interestingly, a simulation on a $N = 1000$ chain with $T_L = 0.1, T_R = 1.0$ reveals a non-zero length correlation, as shown by the upper-left point in Fig. 3.2. In principle, either increasing the number of oscillators N or decreasing the temperature differences ΔT can make this correlation diminish, because both ways reduce the temperature gradient $\frac{\Delta T}{N}$. However, Fig. 3.2 shows these two methods are not equivalent: the length correlation C_q drops rapidly with decreasing ΔT while keeping almost unchanged with increasing N . This phenomenon is not surprising: equilibrium states with zero C_q will be realised when we take $\Delta T = 0$ with finite N , but N large with nonzero ΔT still corresponds to a nonequilibrium state. Hence in the remainder of this paper, we will focus on the influence of N with constant ΔT . The blue line in Fig. 3.3a is an extension of the one in Fig. 3.2, which shows that C_q decays with N slowly, at low temperature $T_L = 0.1, T_R = 1.0$ and high constraining force as strong as $f_p = 5.0$, causing a non-zero correlation to persist up to $N = 10,000$. The decay can be enhanced either by reducing f_p (see the other lines in Fig. 3.3a) or increasing temperature (see Fig. 3.3b). A similar decay is also observed in

the speed correlation C_v and energy correlation C_E as shown in Fig. 3.4.

We assume that, as the length correlation C_q in Fig. 3.3, and the other correlations C_v and C_E in Fig. 3.4, decrease to zero, the corresponding non-equilibrium distribution converges to the factorised distribution in Eq. (3.1.1), and thus the single oscillator relations in Eq. (3.1.2) and Eq. (3.1.3) are valid.

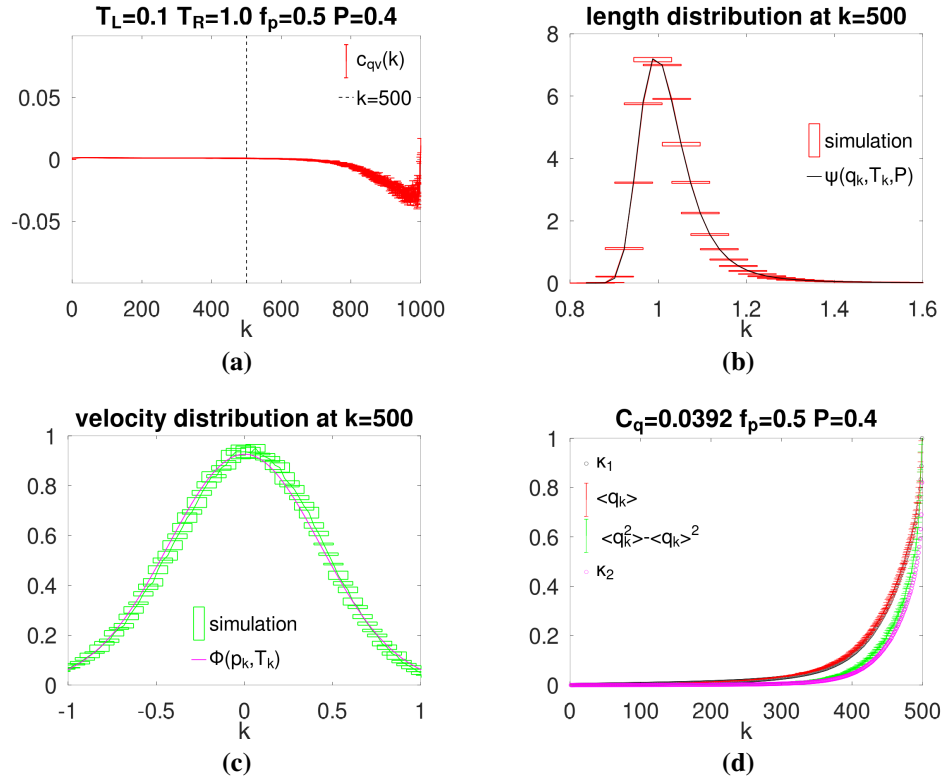


Figure 3.5: (a) The correlation between length and velocity of the same oscillator. (b-c) The length and velocity distribution of the middle oscillator. (d) The normalised length and fluctuation profile fitted by κ_1 and κ_2 .

The example of a chain with $N = 1000$ at low temperatures ($T_L = 0.1$, $T_R = 1.0$) and a weak constraining force ($f_p = 0.5$), validates this assumption. As shown in Fig. 3.3a, 3.4a and 3.4c, this chain exhibits weak correlations $C_q = 0.0242$, $C_v = 0.0239$, $C_E = 0.0307$, which indicates the motion of different oscillators are approximately independent. Fig. 3.5a further implies that the length and velocity of the same oscillator are almost independent. So that the nonequilibrium distribution should be a product of a series of single-particle distributions, which can be further factorised as the single-particle length distribution times single-particle velocity distribution. Then we examine the oscillator at $k = 500$

in Fig. 3.5a. The length distribution follows the potential term $\psi(q_k, T_k, P)$ of the factorised distribution in Eq. (3.1.1) and the velocity distributions align with the kinetic term $\phi(p_k, T_k)$ (see Fig. 3.5b and 3.5c). We thus conclude that the validity of the factorised distribution is sound and explains the accurate fit of Eq. (3.1.2) and Eq. (3.1.3) observed in Fig. 3.5d, where all data has been normalised to the range $[0, 1]$ by the following expressions:

$$\begin{aligned}
 \langle q_k \rangle &= \frac{\langle q_k \rangle - \langle q_1 \rangle}{\langle q_N \rangle - \langle q_1 \rangle} \\
 \langle q_k^2 \rangle - \langle q_k \rangle^2 &= \frac{(\langle q_k^2 \rangle - \langle q_k \rangle^2) - (\langle q_1^2 \rangle - \langle q_1 \rangle^2)}{(\langle q_N^2 \rangle - \langle q_N \rangle^2) - (\langle q_1^2 \rangle - \langle q_1 \rangle^2)} \\
 \kappa_1(T_k, P) &= \frac{\kappa_1(T_k, P) - \kappa_1(T_1, P)}{\kappa_1(T_N, P) - \kappa_1(T_1, P)} \\
 \kappa_2(T_k, P) &= \frac{\kappa_2(T_k, P) - \kappa_2(T_1, P)}{\kappa_2(T_N, P) - \kappa_2(T_1, P)}.
 \end{aligned} \tag{3.2.10}$$

Here κ_1 and κ_2 denote an ensemble average based on the non-equilibrium distribution in Eq. (3.1.1) and terms in angular brackets $\langle \rangle$ indicate the average value given by the simulation. Note that decreasing f_p also means decreasing the average force P across the chain, though these two quantities differ slightly in numerical values because of the non-zero net force exerted by Nosé-Hoover thermostats at different temperatures. This confirms that the deterministic thermostat is applying extra force on the system, as expected. Interestingly, the application of a Langevin thermostat will solve this problem and a short comparison between Langevin and Nosé Hoover thermostats have been added in Appendix B.3.

As we have seen in the preceding example, the validity of κ_1 and κ_2 follows the zero-correlation condition. From the data in Fig. 3.3 and Fig. 3.4, we find three components that weaken correlations and increase the range of validity of Eq. (3.1.2) and Eq. (3.1.3): increasing the boundary temperatures (T_L, T_R), reducing the constraining force f_p , and enlarging the number of oscillators N . These findings are systematically shown by Figs. 3.6 - 3.10. For conciseness, we restrict our detailed discussion to the length correlation

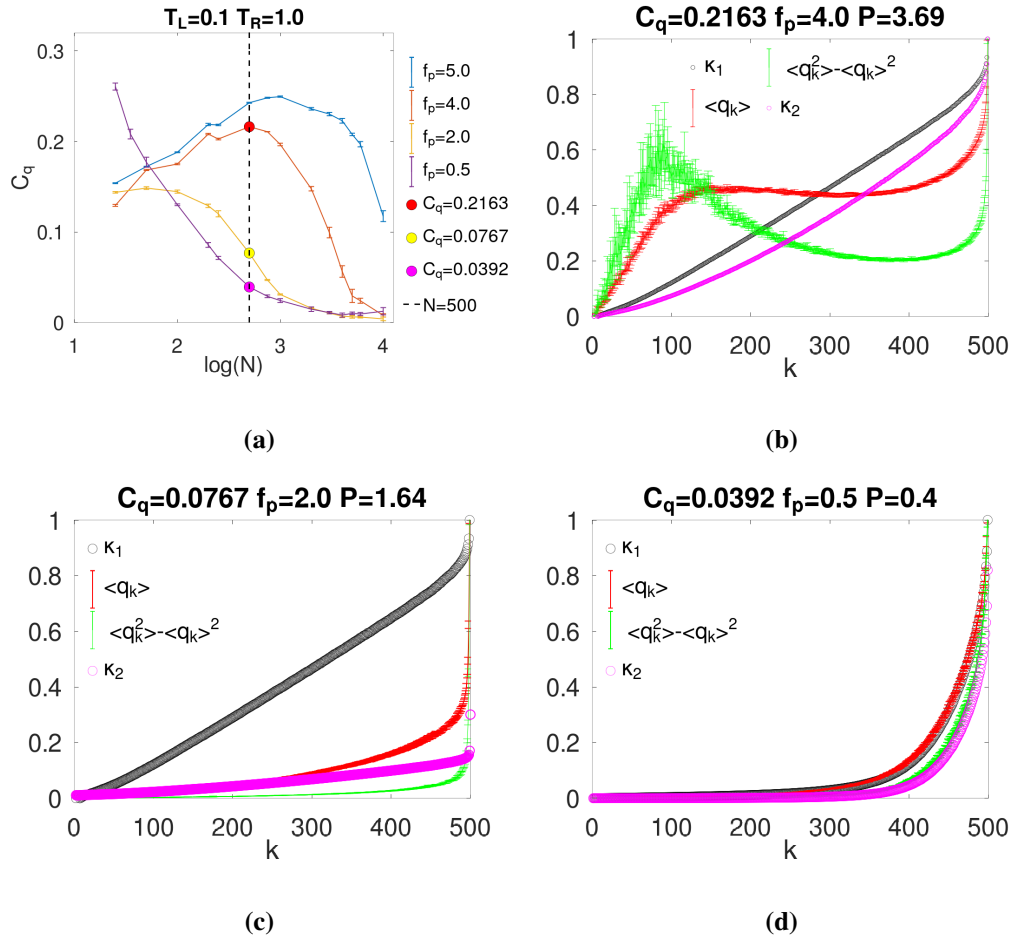


Figure 3.6: (a) Three state points at $T_L = 0.1, T_R = 1.0$ for different f_p . The validity of $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ is tested at each point (b-d). All data are obtained by averages over four different initial states and normalised to the range $[0, 1]$ by Eq. (3.2.10).

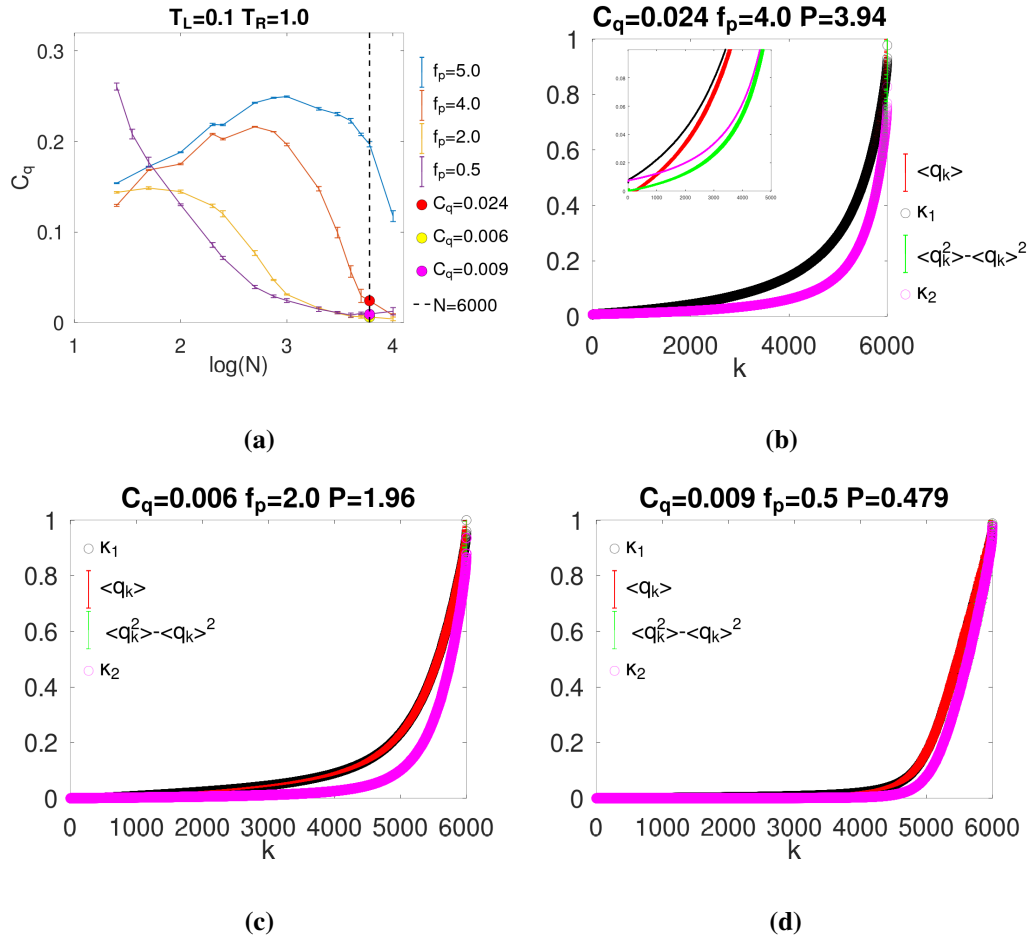


Figure 3.7: Same approach as per previous figure except that the chain is extended to $N = 6,000$. The inset of Fig. 3.7b is the enlarged view of the left end, where the agreement is still poor.

C_q , because this is the most relevant one and the trends of other correlations are similar.

Fig. 3.6 describes the length and fluctuation profiles for chains of $N = 500$ and small temperature differences at low temperatures $(T_L, T_R) = (0.1, 1.0)$. Fig. 3.6b shows that $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ are functionally incorrect for $f_p = 4.0$: both of them give monotonous curves, while the profiles given by simulations are clearly not. This large disagreement is reduced when $f_p = 2.0$ and a satisfactory agreement is attained at $f_p = 0.5$. Cumulants $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ become more and more aligned with simulations when f_p decreases from 5.0 to 0.5, with the correlation index dropping one order of magnitude from $C_q = 0.22$ to $C_q = 0.039$.

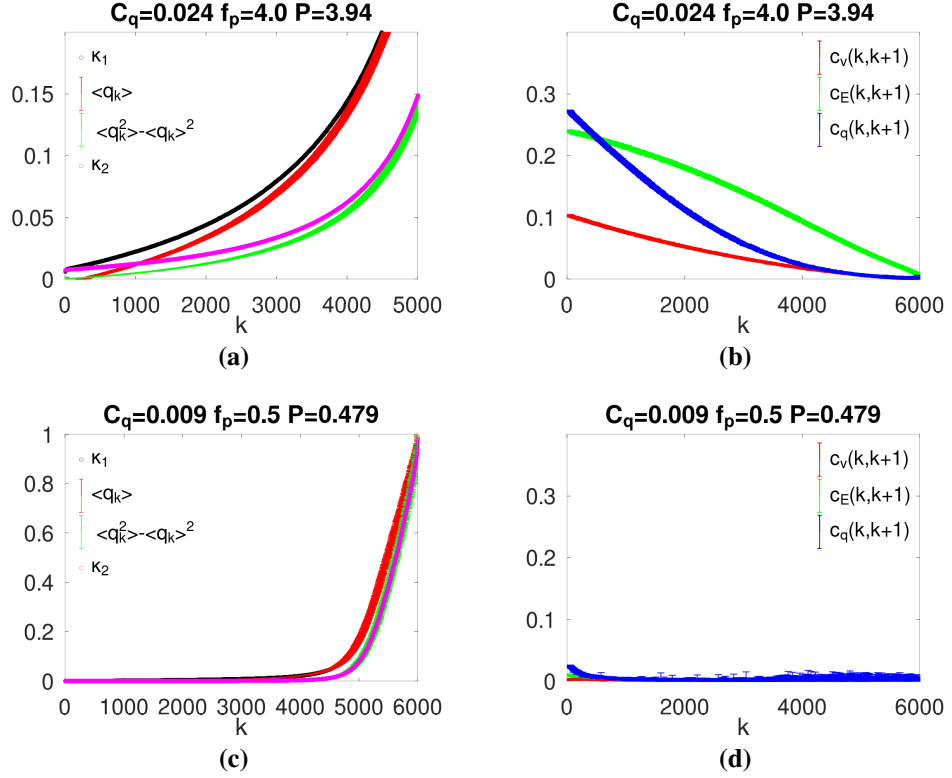


Figure 3.8: (a-b) The inset of Fig. 3.7b and the corresponding local correlations. (c-d) Fig. 3.7d and the corresponding local correlations.

Long chains of $N = 6,000$ in Fig. 3.7 show an increasingly improved agreement. The correlation under $f_p = 4.0$ has dropped to $C_q = 0.024$, κ_1 and κ_2 have an almost perfect agreement on the right end where the kinetic energy is high, but still deviate from the simulation on the low kinetic energy end (see the inset of the Fig. 3.7b). When the constraining force is further decreased to 2.0 and then to 0.5, C_q reduces significantly further.

Both κ_1 and κ_2 now agree with simulations even in the low kinetic energy end, as shown in Fig. 3.7c and Fig. 3.7d. The imperfect fitting in Fig. 3.7b could be attributed to the localised, strong correlations on the low kinetic energy end. Fig. 3.8b presents the corresponding local correlation profiles obtained for the k^{th} oscillator and its nearest neighbor by using Eqs. (3.2.6)-(3.2.8). The strong correlation at the left end corresponds to the failure of κ_1 and κ_2 in Fig. 3.8a. Conversely, when κ_1 and κ_2 perform globally well in Fig. 3.8c, the local correlation across the system is nearly negligible, as seen in Fig. 3.8d.

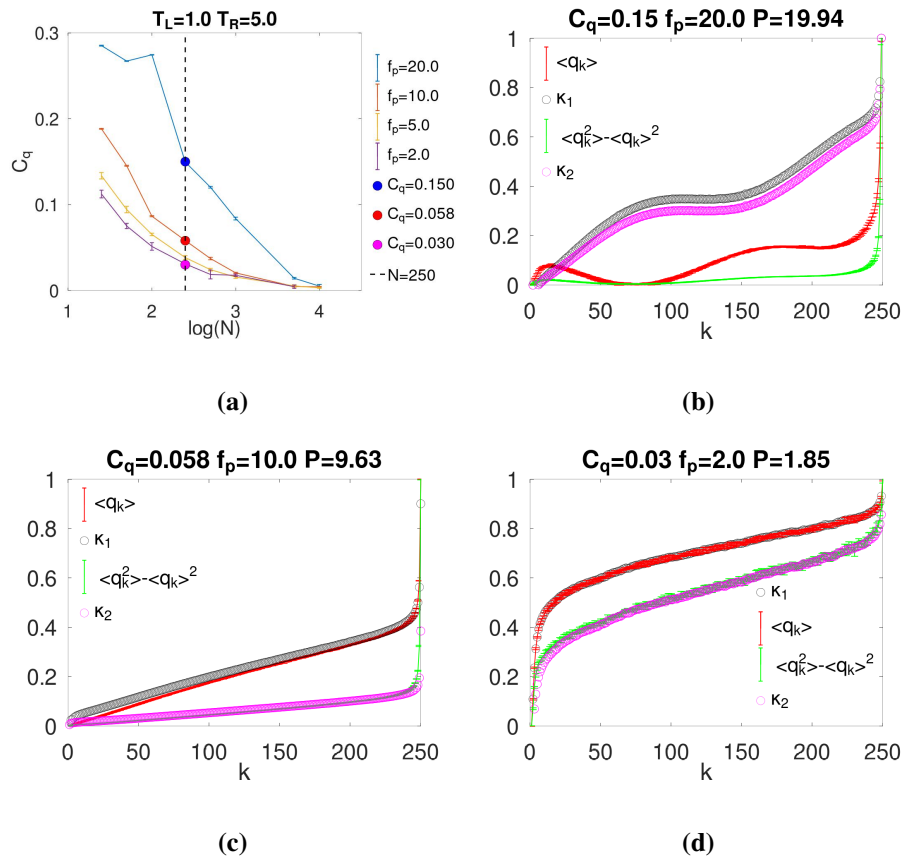


Figure 3.9: The same approach with Fig. 3.6 except the boundary temperature and number of oscillators.

So, Eq. (3.1.2) and Eq. (3.1.3) are valid when we weaken the constraining force f_p , as shown in Fig. 3.6, or increase the number of oscillators N , as shown by comparing Fig. 3.6 with Fig. 3.7. The same conclusion persists to higher boundary temperatures T_L, T_R and could be realised with smaller N and stronger f_p . Fig. 3.9d in fact shows that, under high temperature difference $(T_L, T_R) = (1.0, 5.0)$, short chains of $N = 250$ under a constraining force at $f_p = 2.0$ behave as expected except for small deviations on the low

kinetic energy end. For longer chains as $N = 5,000$, the constraining force could be as strong as $f_p = 10.0$ (see Fig. 3.10c) and the agreement persists. Under extremely strong constraint as $f_p = 20.0$, the short chain of $N = 250$ also shows a non-monotonous profile (see Fig. 3.9b), which disappears at $N = 5,000$, with κ_1 and κ_2 valid at the high kinetic energy end, as shown in Fig. 3.10b. As $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ become more and more indistinguishable from simulations, the correlation defined in Eq. (3.2.3) assumes lower and lower values.

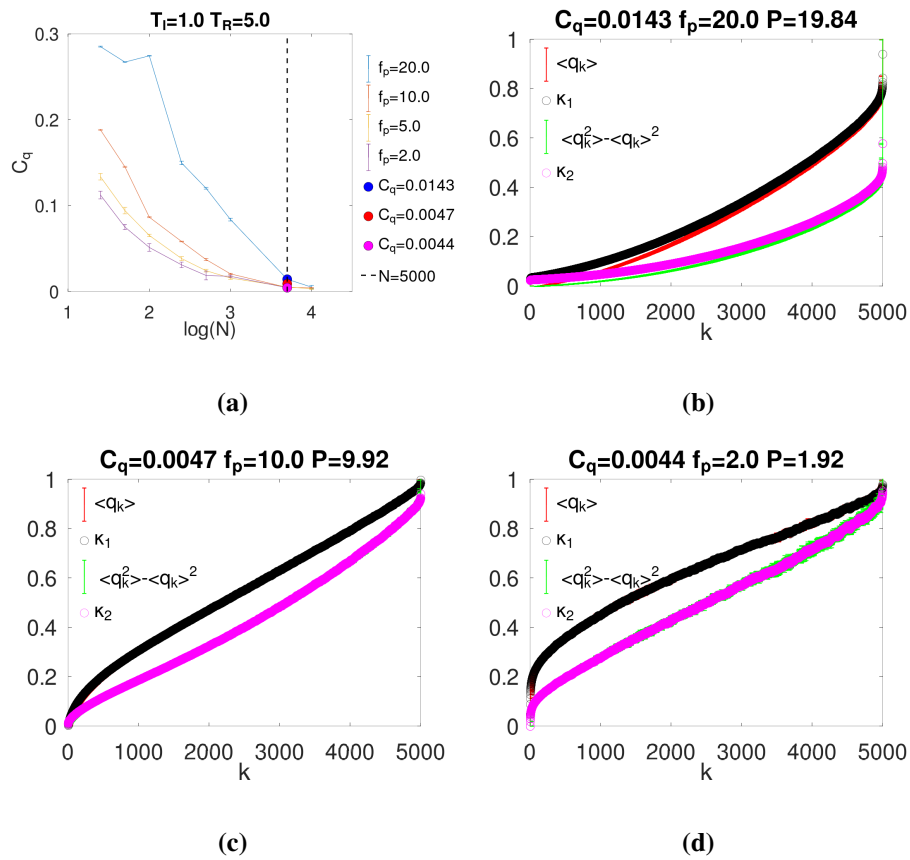


Figure 3.10: Same approach as per the previous figure except that the chain is extended to $N = 5,000$.

The discussion above demonstrates that $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ derived from the factorised distribution in Eq. (3.1.1) are valid for long chains under high temperature and weak constraining force. It is worth noting that compared to $\kappa_2(T_k, P)$, $\kappa_1(T_k, P)$ has a wider range of validity, independently of the factorised distribution in Eq. (3.1.1). For instance, Fig. 3.11a shows that $\kappa_1(T_k, P)$ is valid for chains as short as $N = 25$ under $f_p = 5.0$ and $(T_L, T_R) = (1.0, 10.0)$, while $\kappa_2(T_k, P)$ is still invalid. Fig. 3.11b to 3.11d

give the length and velocity distribution of three oscillators located on positions $k = 8$, $k = 12$ and $k = 16$ in the chain. In particular, note how the distributions from simulations differ significantly from those obtained from the factorised distribution Eq. (3.1.1). We attribute the broader validity of $\kappa_1(T_k, P)$ to the following assumption: as correlations vanish, the true distribution converges toward its factorised limit. This convergence is not synchronised across statistical cumulants. The mean (the first-order term in the generating function) converges faster than higher-order terms, such as the standard deviation. Consequently, some conclusions drawn under the factorisation assumption, particularly those about lower order terms, may persist even if that general assumption itself is violated.

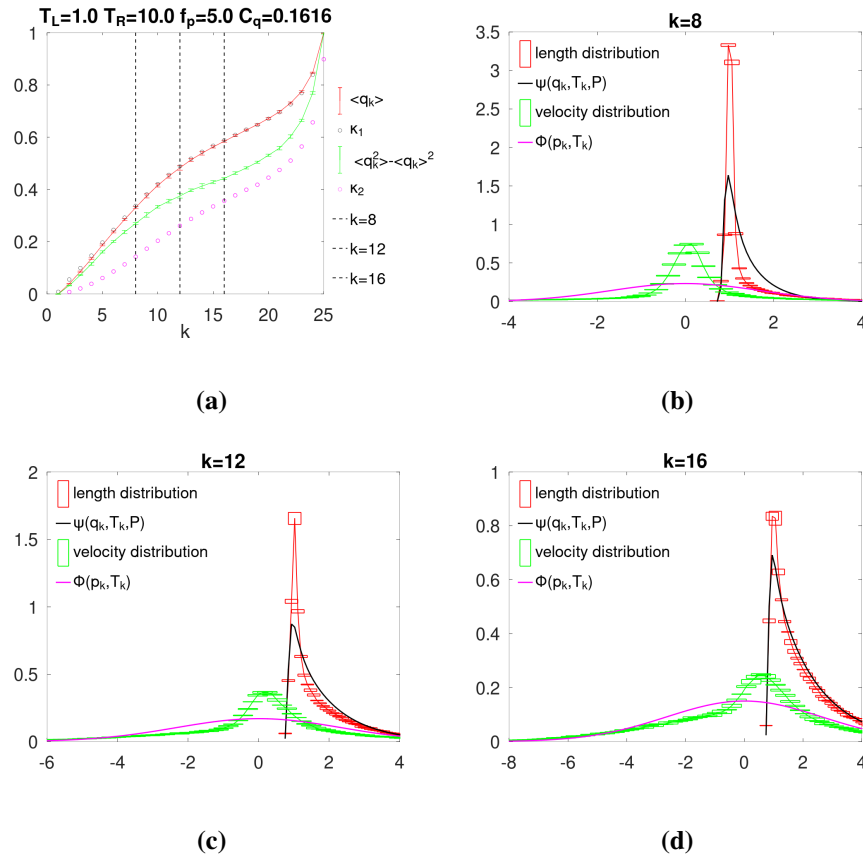


Figure 3.11: (a) The local length $\langle q_k \rangle$ and fluctuation $\langle q_k^2 \rangle - \langle q_k \rangle^2$ profile of a $N = 25$ chain under $T_L = 1.0$, $T_R = 10.0$ and $f_p = 5.0$, fitted by the first-order cumulant κ_1 in Eq. (3.1.2) and second-order cumulant κ_2 in Eq. (3.1.3). (b-d) Distribution of q_k i.e., the length of oscillator, and distribution of p_k i.e., the velocity for the three oscillators chosen in Fig. 3.11a, fitted by the factorised distribution in Eq. (3.1.1). Note the different symmetry among distributions.

3.3 Comparison with chains' phase diagrams

The previous Section shows that for sufficiently long chains with negligible correlations, $\langle q_k \rangle = \kappa_1(T_k, P)$ is a valid single-oscillator relation representing the single oscillator length as a function of single-oscillator kinetic energy T_k and average force P . We notice that it is identical to Eq. (2.2.1), the inverse density state equation shown in Section 2.2, as long as we interpret the single oscillator length as inverse density, kinetic energy as temperature and average force as pressure. Also in Section 2.2 we know that the $\rho^{-1}(T, P)$ state equation could be approximated by a microscopic van der Waals (mvdW) and Tonks (mTonks) equations, with Fig. 2.9 describing their range of validity.

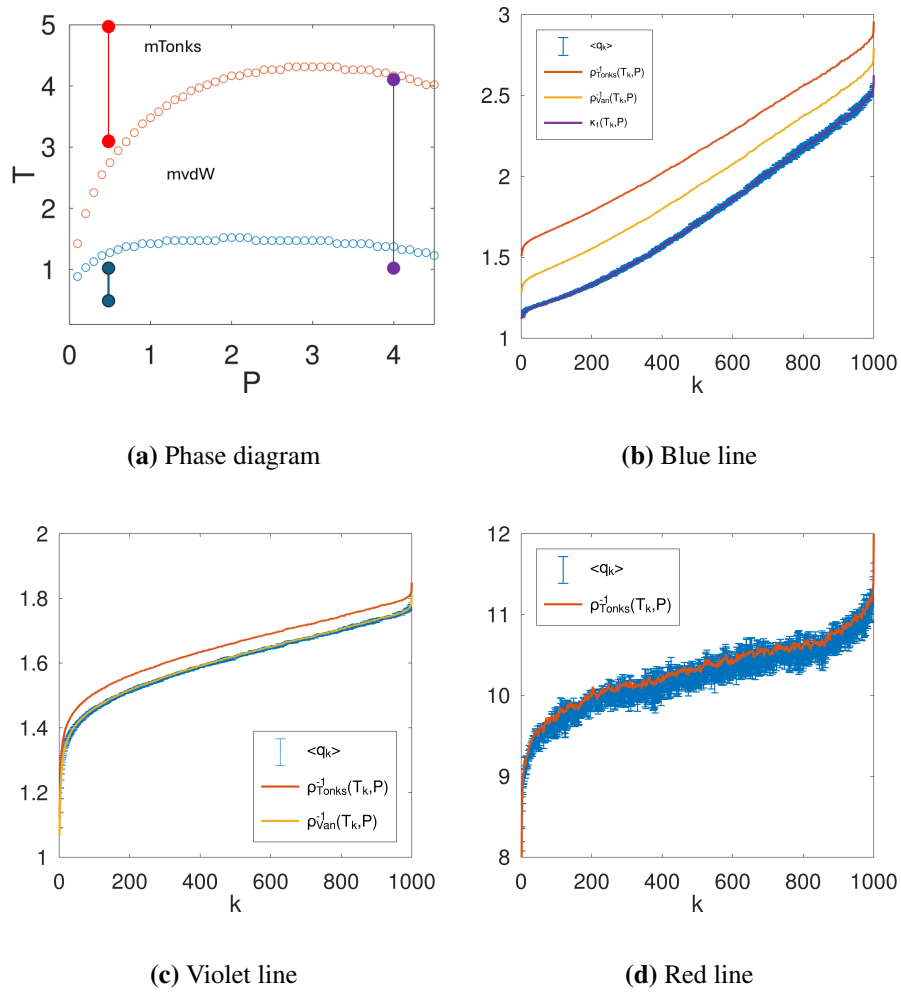


Figure 3.12: (a) Three segments at different (P, T_L) and (P, T_R) . The validity of microscopic van der Waals and Tonks equations is tested at each segment in Figures (b-d).

Fig. 2.9 is designed to describe Lennard-Jones chains at equilibrium, but considering the

validity of κ_1 for nonequilibrium Lennard-Jones chains with sufficiently large N , we can use it to assess the validity of the localised, microscopic equations (see Eq. (3.3.1)) for nonequilibrium Lennard-Jones chains,

$$\begin{aligned}\langle q_k \rangle &= \rho_{Van}^{-1}(T_k, P) = \frac{T_k}{(1+a)P} + b \\ \langle q_k \rangle &= \rho_{Tonks}^{-1}(T_k, P) = \frac{T_k}{P} + \Omega.\end{aligned}\tag{3.3.1}$$

In a non-equilibrium simulation, we keep the boundary temperatures T_L, T_R constant, and the steady states give a pressure profile homogeneous at P . So a vertical segment with two ends located at (P, T_L) and (P, T_R) on Fig. 2.9 displays which region is relevant and which equation can be used. Fig. 3.12 gives three examples: the blue points at $(P, T_L) = (0.48, 0.3)$ and $(P, T_R) = (0.48, 1.0)$ are outside both mTonks and mvdW regions. Both equations fail, as shown in Fig. 3.12b. The violet points at $(P, T_L) = (3.90, 1.0)$ and $(P, T_R) = (3.90, 4.0)$ lie within the mvdW region but outside the mTonks region, so that the mvdW works while the mTonks fails, as shown in Fig. 3.12c. Finally, the red points at $(P, T_L) = (0.44, 3.0)$ and $(P, T_R) = (0.44, 5.0)$ are well represented by both mTonks and mvdW equations and, as shown in Fig. 3.12d.

Note that the mvdW equation and mTonks equation we use here are also single-oscillator relations that give a linear relation between the single-oscillator length and single-oscillator kinetic energy. It is worthy of noting that [Giberti and Rondoni, 2011] have proposed a linear relation between those two quantities along non-equilibrium monodimensional chains. The two microscopic relations discussed here help to understand such linear relations based on first principles.

Properties of coupled chains

In the previous Chapters, we have computed the equilibrium state equation by statistical mechanics, approximated it in high temperatures and compared the computation to simulations. Then we have generalised the equilibrium expression to nonequilibrium and discussed the role of correlations. Up to now, all discussions are based on monodimensional Lennard-Jones chains with nearest-neighbor interactions. The framework we have created is applicable to any nearest-neighbor potentials and can be extended to more complicated systems. This Chapter is devoted to one of the simplest extensions: Lennard-Jones chains coupled with harmonic chains by hard rods. Section 4.1 describes this coupled chain model we employ and rewrites the formulae to accommodate the new system. Section 4.2 discusses the statistical mechanics approach and compares it with the equilibrium simulation, whereas Section 4.3 discusses the generalisation to nonequilibrium and the role of correlations.

4.1 Details of the model

The coupled chain model is sketched in Fig. 4.1, where the red line denotes a Lennard-Jones chain of $2N$ oscillators, the green line is a harmonic chain, and hard rods drawn in black bind them. Similarly to previous examples, this system can be divided into N cells

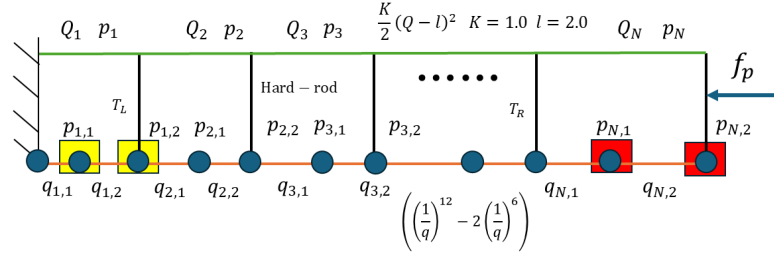


Figure 4.1: Sketch of the coupled chain model, considered in this Chapter. The leftward force f_p is applied at the right end, and the left end is fixed. Two thermostats regulate the temperature. We use $T_R \geq T_L$. The chain will attain equilibrium states for $T_R = T_L$ and will be in non-equilibrium steady states for $T_R > T_L$.

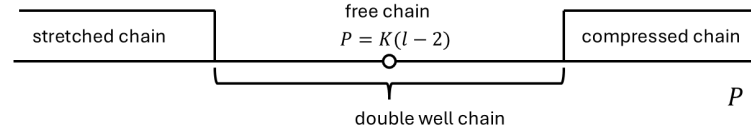
with the length of the k^{th} cell being the sum of two consecutive oscillators $Q_k = q_{k,1} + q_{k,2}$, and the corresponding momenta given by $p_k = p_{k,1} + p_{k,2}$. All cells contain two particles of unitary mass, as per previous examples for single chains. The left boundary of the first cell is fixed at position $x_0 = 0$, while the right boundary of the last cell is subjected to a constant constraining force f_p , the leftward direction of which is set as positive, as shown in Fig. 4.1. Again, all $q_{k,1}, q_{k,2}$ remain positive as a consequence of the repelling part of the Lennard-Jones potential, while the f_p could be either positive (leftward) or negative (rightward) due to the properties of harmonic chains.

In line with previous cases, we also apply two separate Nosé-Hoover (NH) thermostats at kinetic temperature T_L on the leftmost cell with momentum $p_{1,1}$ and $p_{1,2}$ and two at T_R on the rightmost cell with momentum $p_{N,1}$ and $p_{N,2}$. The relaxation times, as previously, are all set as unitary. Then the following $4N + 4$ equations of motion hold:

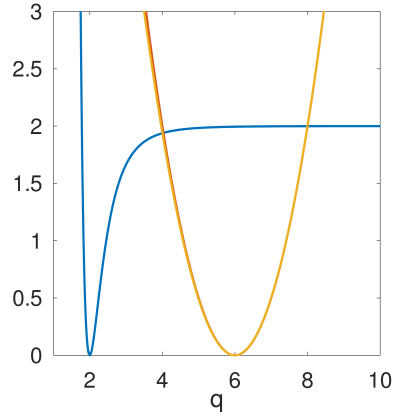
$$\begin{aligned} \frac{dq_{1,1}}{dt} &= p_{1,1} \\ \frac{dq_{k,1}}{dt} &= p_{k,1} - p_{k-1,2} \quad k = 2, \dots, N \end{aligned}$$

$$\begin{aligned}
\frac{dq_{k,2}}{dt} &= p_{k,2} - p_{k,1} \quad k = 1, \dots, N \\
\frac{dp_{k,1}}{dt} &= F^{(1)}(q_{k,1}) - F^{(1)}(q_{k,2}) \quad k = 2, \dots, N-1 \\
\frac{dp_{1,1}}{dt} &= F^{(1)}(q_{1,1}) - F^{(1)}(q_{1,2}) - \xi_{1,1}p_{1,1} \\
\frac{dp_{N,1}}{dt} &= F^{(1)}(q_{N,1}) - F^{(1)}(q_{N,2}) - \xi_{N,1}p_{N,1} \\
\frac{dp_{k,2}}{dt} &= F^{(1)}(q_{k,2}) - F^{(1)}(q_{k+1,1}) + F^{(2)}(Q_k) - F^{(2)}(Q_{k+1}) \quad k = 2, \dots, N-1 \\
\frac{dp_{1,2}}{dt} &= F^{(1)}(q_{1,2}) - F^{(1)}(q_{2,1}) + F^{(2)}(Q_1) - F^{(2)}(Q_2) - \xi_{1,2}p_{1,2} \\
\frac{dp_{N,2}}{dt} &= F^{(1)}(q_{N,2}) + F^{(2)}(Q_N) - f_p - \xi_{N,2}p_{N,2} \\
F^{(1)}(q_{i,j}) &= -\frac{dV_{LJ}(q_{i,j})}{dq_{i,j}} \quad i = 1, 2, \dots, N \quad j = 1, 2 \\
F^{(2)}(Q_k) &= -K(Q_k - l) \quad Q_k = q_{k,1} + q_{k,2} \quad k = 1, 2, \dots, N \\
\dot{\xi}_{1,j} &= \frac{p_{1,j}^2}{T_L} - 1 \quad j = 1, 2 \\
\dot{\xi}_{N,j} &= \frac{p_{N,j}^2}{T_R} - 1 \quad j = 1, 2
\end{aligned} \tag{4.1.1}$$

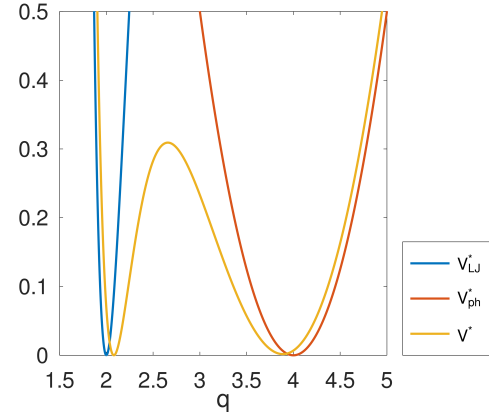
with the last two terms representing the equations for the constraints in the NH thermostats. As it is customary in this thesis, all variables are assumed to be in reduced units, with the Boltzmann constant k_B , the mass of every particle, as well as the relaxation times of the thermostats, set to unity. The parameters for the harmonic potential are set at $K = 1.0, l = 2.0$. The boundary temperature T_L, T_R will be set to equal or unequal values, depending on whether the system is studied at equilibrium or out of equilibrium. The constraining force f_p will be varied, and the way properties scale with the number of cells N will also be explored. During the simulations, we again numerically integrate Eqs. (4.1.1) with specific values of (T_L, T_R, f_p, N) via a fourth-order Runge-Kutta method with step size $\Delta t = 0.001$. Time averages are typically taken after equilibration, over the usual time interval $[1 \cdot 10^8, 4 \cdot 10^8]$ to evaluate various statistical quantities. In the equilibrium case where $T_L = T_R$, the system reaches a homogeneous state in which the statistical properties of each oscillator are identical, similar to the case of single chains. So, the average length of the chain per cell is simply given by the total length of the chain



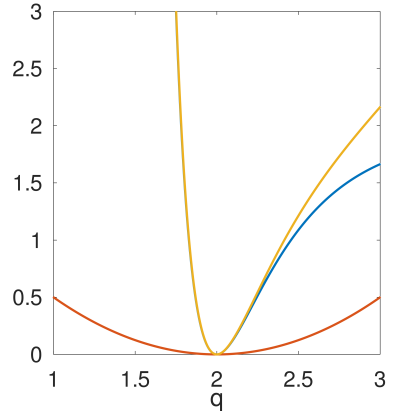
(a)



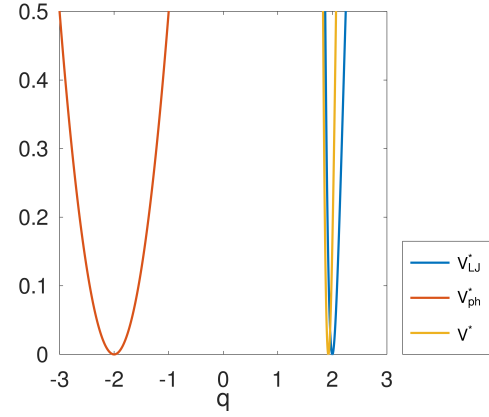
(b) $P = -4.0$
 $K = 1, l = 2$
 stretched



(c) $P = -2.0$
 $K = 1, l = 2$
 doublewell



(d) $P = 0.0$
 $K = 1, l = 2$
 free



(e) $P = 4.0$
 $K = 1, l = 2$
 compressed

Figure 4.2: Four types of V^* controlled by the value of pressure P when K and l are fixed. As the pressure increases, the parabola moves leftwards and becomes less relevant for the chain's dynamics. Note that the curves have been translated to make the minimum located at the same horizontal line.

divided by N :

$$\langle Q \rangle = \frac{\sum_{k=1}^N \langle Q_k \rangle}{N} = \frac{\sum_{k=1}^N \langle q_{k,1} \rangle + \langle q_{k,2} \rangle}{N}, \quad (4.1.2)$$

where the angular brackets $\langle \cdot \rangle$ indicate the average value given by the simulation. We also compute the length fluctuation per cell as the total fluctuation σ^2 divided by N :

$$\begin{aligned} \langle Q^2 \rangle - \langle Q \rangle^2 &= \frac{\sigma^2}{N} = \frac{\sum_{k=1}^N \sum_{m=1}^N \langle Q_k Q_m \rangle - \langle Q_k \rangle \langle Q_m \rangle}{N} \\ &= \frac{\sum_{k=1}^N \sum_{m=1}^N \sum_{j=1,2} \langle q_{k,j} q_{m,j} \rangle - \langle q_{k,j} \rangle \langle q_{m,j} \rangle}{N}, \end{aligned} \quad (4.1.3)$$

where we sum up also on $k = m$, as previously.

On the other hand, for non-equilibrium steady states where a heat flux is present due to $T_R \neq T_L$, we must compute the local properties specifically for each cell, including the average local length, the local length fluctuation, and the local cell temperature. These are all microscopic quantities and read:

$$\langle Q_k \rangle = \langle q_{k,1} \rangle + \langle q_{k,2} \rangle \quad (4.1.4)$$

$$\sigma_k^2 = \langle Q_k^2 \rangle - \langle Q_k \rangle^2 = \sum_{j=1,2} \sum_{i=1,2} \langle q_{k,i} q_{k,j} \rangle - \langle q_{k,i} \rangle \langle q_{k,j} \rangle. \quad (4.1.5)$$

The cell temperature is now the total kinetic energy:

$$T_k = \frac{\langle p_{k,1}^2 \rangle + \langle p_{k,2}^2 \rangle}{2}. \quad (4.1.6)$$

The mechanical pressure along the chain in these settings could be derived via the mo-

mentum conservation of a given cell:

$$\begin{aligned}
 \left\langle \frac{dp_k}{dt} \right\rangle &= \left\langle \frac{dp_{k,1}}{dt} \right\rangle + \left\langle \frac{dp_{k,2}}{dt} \right\rangle \\
 &= \left\langle F^{(1)}(q_{k,1}) - F^{(1)}(q_{k,2}) \right\rangle \\
 &\quad + \left\langle F^{(1)}(q_{k,2}) - F^{(1)}(q_{k+1,1}) + F^{(2)}(Q_k) - F^{(2)}(Q_{k+1}) \right\rangle \\
 &= \left\langle F^{(1)}(q_{k,1}) + F^{(2)}(Q_k) \right\rangle - \left\langle F^{(1)}(q_{k+1,1}) + F^{(2)}(Q_{k+1}) \right\rangle \\
 &= -(P_{k+1} - P_k) \\
 &= 0,
 \end{aligned}$$

from which we know that the momentum flux, i.e. the pressure, remains homogeneous at equilibrium and at steady states at non-equilibrium. This is given by:

$$\begin{aligned}
 P &= P_1 = P_2 = \dots = P_k = \dots = P_N \\
 P_k &= \left\langle F^{(1)}(q_{k,1}) + F^{(2)}(Q_k) \right\rangle.
 \end{aligned} \tag{4.1.7}$$

Correlation is another important focus as we have shown in the previous Chapter, and could also be represented by various variables. The length correlation C_Q is represented by the ratio between the total fluctuation in Eq. (4.1.3) and the sum of cell fluctuations in Eq. (4.1.5), written as:

$$C_Q = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sigma^2}{\sum_{k=1}^N \sigma_k^2} - 1}. \tag{4.1.8}$$

In the same way we can also define the velocity correlation

$$C_v = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sum_{k,m=1}^N \langle p_{k,1} + p_{k,2} \rangle \langle p_{m,1} + p_{m,2} \rangle}{\sum_{k=1}^N \langle p_{k,1} + p_{k,2} \rangle^2} - 1}. \tag{4.1.9}$$

and the energy correlation

$$C_E = \frac{1}{\sqrt{N-1}} \sqrt{\frac{\sum_{k,m=1}^N \langle H_k H_m \rangle}{\sum_{k=1}^N \langle H_k \rangle^2} - 1}. \tag{4.1.10}$$

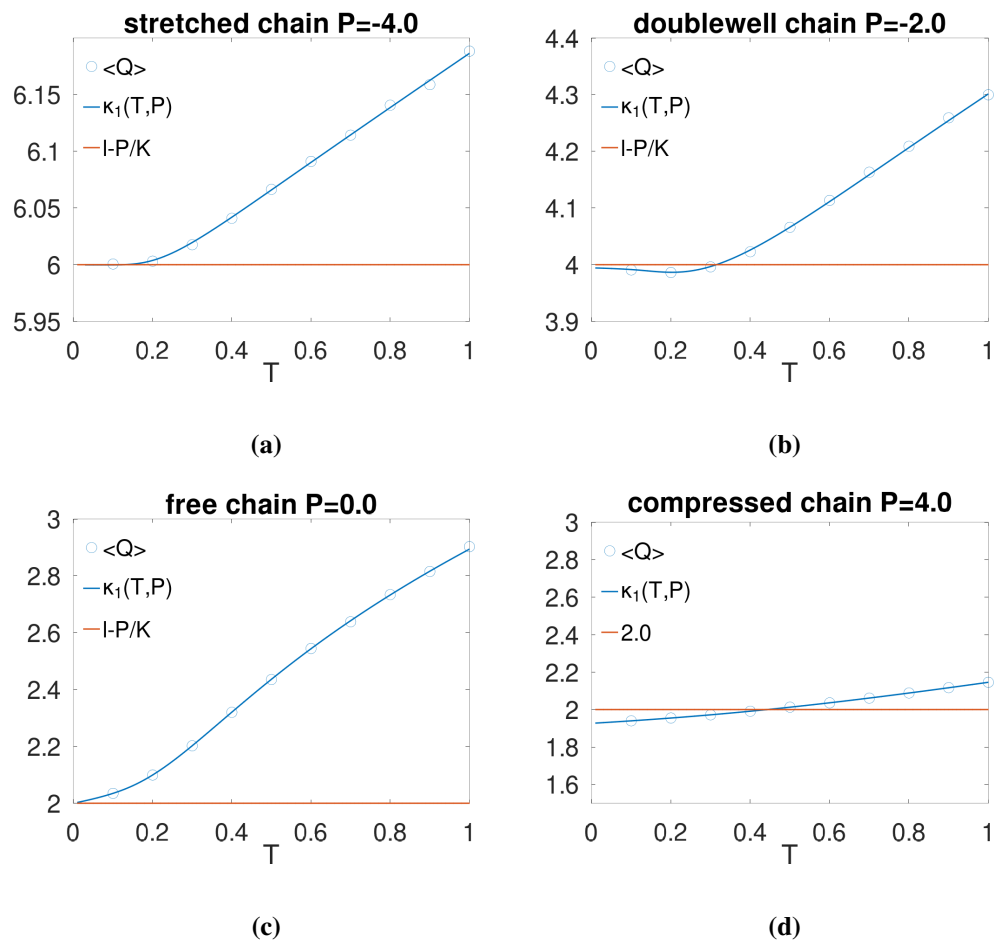


Figure 4.3: Average length per cell at equilibrium for (a) stretched chain, (b) double well chain, (c) free chain, (d) compressed chain.

with

$$H_k = \frac{p_{k,1}^2}{2} + \frac{p_{k,2}^2}{2} + V_{LJ}(q_{k,1}) + V_{LJ}(q_{k,2}) + \frac{K}{2}(q_{k,1} + q_{k,2} - l)^2. \quad (4.1.11)$$

Similarly to the monodimensional case, there are single-cell relations among the quantities in Eq. (4.1.4)-(4.1.6) and (4.1.7). As anticipated, we imagine that the non-equilibrium distribution of the coupled chain model can be approximated as a product of independent single-cell distributions, as previously: the length of each cell (e.g., the k^{th} cell) follows a distribution of the form $\exp(-\frac{H_k + PQ_k}{T_k})$, where H_k is the Hamiltonian of the cell, Q_k is the length, P is the time average force it experiences, as computed in (4.1.7). Again, that force is homogeneous along the chain, being interpreted as the single-cell pressure, and the T_k is the time average kinetic energy, computed by Eq. (4.1.6) and interpreted as the single-cell temperature. This follows the single-chain approach and in the next Section we will show how we obtain $\langle Q_k \rangle = \kappa_1(T_k, P)$, e.g., the first-order cumulant of the potential part of the single-cell distribution. This expresses the average length of the k^{th} cell, seen as the single-cell inverse density, as a function of the single-cell temperature T_k and the pressure P . We can then also express the single cell length fluctuation as the second-order cumulant, $\langle Q_k^2 \rangle - \langle Q_k \rangle^2 = \kappa_2(T_k, P)$, which is also a function of T_k and P .

4.2 The equilibrium case

We begin by considering the case of coupled chains at equilibrium, work out the factorised statistical mechanics expressions and compare them with simulation. We will follow exactly the same approach for single chains and generalise it to this case. At constant temperature $T_L = T_R = T$ and constant pressure P , the constant pressure ensemble distribution is appropriate for the system considered:

$$\rho(\Gamma; T, P) \propto \exp\left(-\frac{H(\Gamma) + PA(\Gamma)}{T}\right).$$

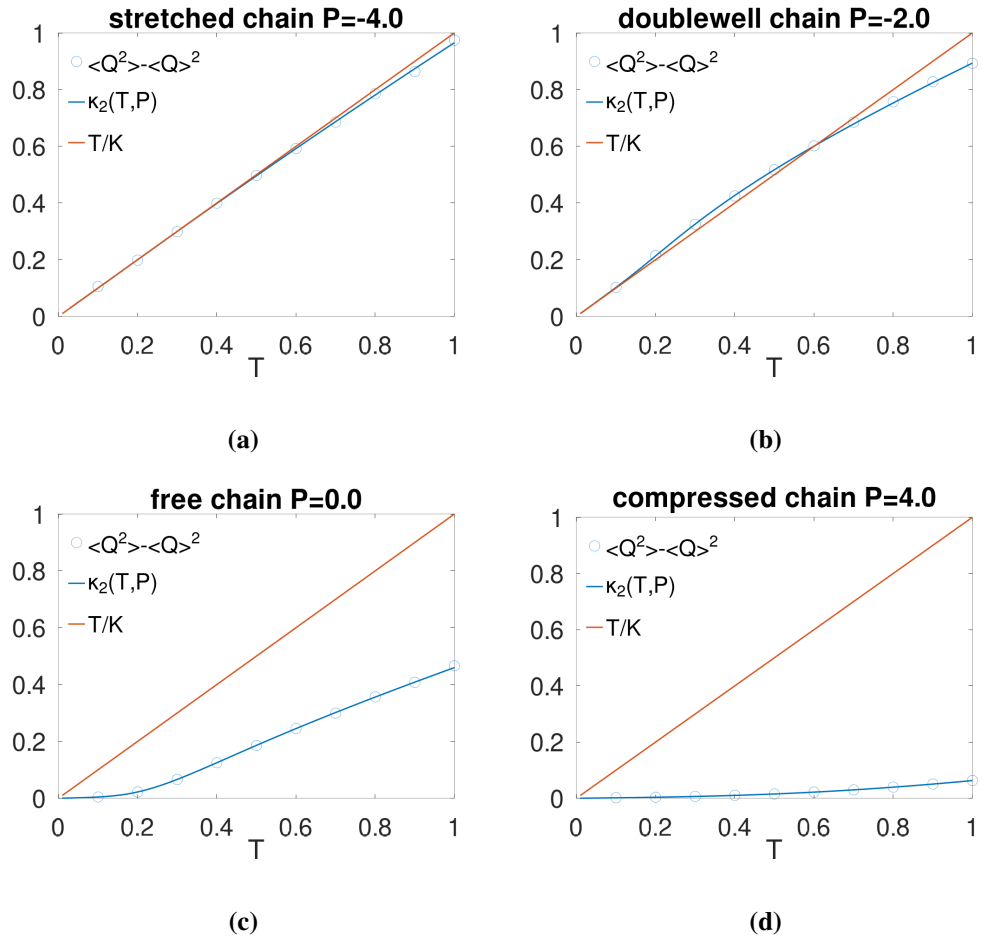


Figure 4.4: Length fluctuation per cell at equilibrium for the (a) stretched chain, (b) double well chain, (c) free chain, (d) compressed chain.

Again, here H is the Hamiltonian and A is the volume. Note that, also in this case, the Boltzmann constant has been set as $k_B = 1$. Both A and H are still functions of the phase vector Γ . The ensemble-averaged value of a given phase variable $Y(\Gamma)$ is

$$\bar{Y}(T, P) = \int \rho(\Gamma, T, P) Y(\Gamma) d\Gamma$$

and for chains shown in Fig. 4.1 with $T_L = T_R = T$, the homogeneous pressure P along the chain equals the constraining force applied at the right end, whereas the “volume” A represents the total chain length. Thus:

$$P = f_p \quad A = \sum_{k=1}^N q_{k,1} + q_{k,2}.$$

The Hamiltonian in reduced units is the sum of the cell Hamiltonians:

$$\begin{aligned} & H(p_{1,1}, q_{1,1}, p_{1,2}, q_{1,2}, \dots, p_{N,1}, q_{N,1}, p_{N,2}, q_{N,2}) \\ &= \sum_{k=1}^N H_k \\ &= \sum_{k=1}^N \frac{p_{k,1}^2}{2} + \frac{p_{k,2}^2}{2} + V_{LJ}(q_{k,1}) + V_{LJ}(q_{k,2}) + \frac{K}{2}(q_{k,1} + q_{k,2} - l)^2. \end{aligned}$$

We now have all the terms for the final distribution $\rho(\Gamma, T, A)$. It is possible to factorise the result into a product of identical distributions for each cell, where each distribution is decomposed further into a kinetic part ϕ times a potential part ψ . This means:

$$\begin{aligned} & \rho(p_{1,1}, q_{1,1}, \dots, p_{N,1}, q_{N,1}; T, P) \\ &= \prod_{j=1}^N \phi(p_{j,1}, p_{j,2}, T) \psi(q_{j,1}, q_{j,2}, Q_j, T, P) \\ &= \prod_{j=1}^N \frac{e^{-\frac{p_{j,1}^2 + p_{j,2}^2}{2T}}}{\int e^{-\frac{p_{j,1}^2 + p_{j,2}^2}{2T}} dp_{j,1} dp_{j,2}} \cdot \\ & \quad \cdot \frac{e^{-\frac{V_{LJ}(q_{j,1}) + V_{LJ}(q_{j,2}) + \frac{K}{2}(Q_j - l)^2 + PQ_j}}{T}}{\delta(q_{j,1} + q_{j,2} - Q_j)} \\ & \quad \cdot \frac{1}{\int e^{-\frac{V_{LJ}(q_{j,1}) + V_{LJ}(q_{j,2}) + \frac{K}{2}(Q_j - l)^2 + PQ_j}}{T}} \delta(q_{j,1} + q_{j,2} - Q_j) dq_{j,1} dq_{j,2} dQ_j. \end{aligned} \tag{4.2.1}$$

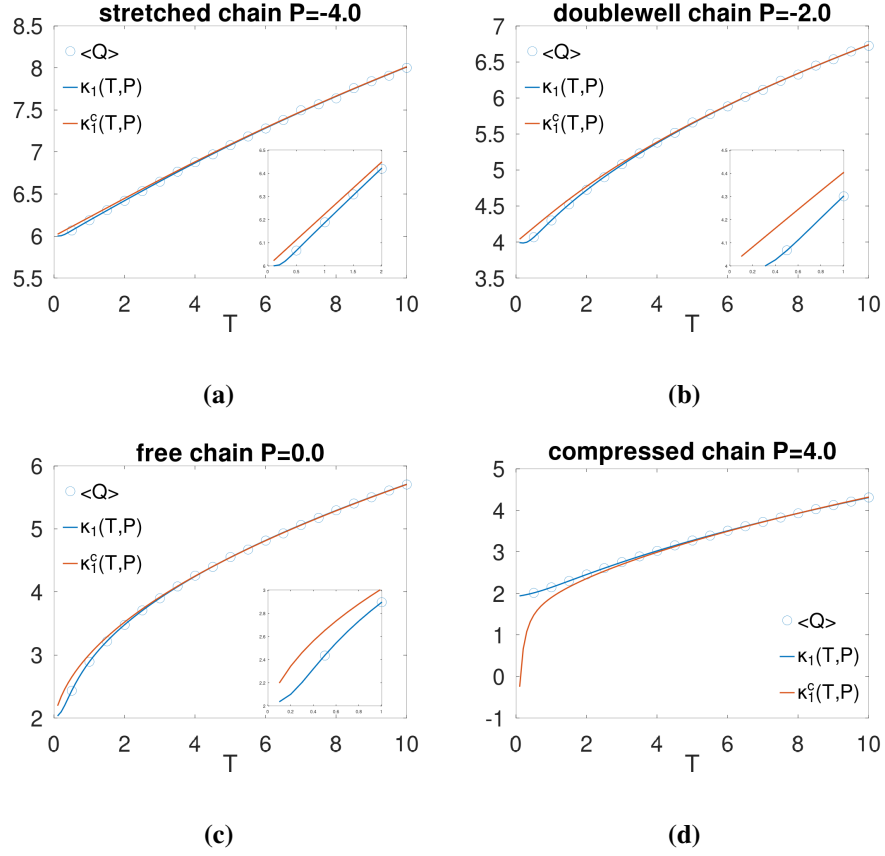


Figure 4.5: We use here the same approach as per Fig. 4.3 except that the temperature is higher. Note that the insets are the enlarged view of the left end, where the agreement of the critical line κ_1^c remains poor.

We can now expand the mean $\langle \dots \rangle$ in Eq. (4.1.2) by using the integral over the distribution in Eq. (4.2.1). After canceling the irrelevant kinetic term $\phi(p_{j,1}, p_{j,2}, T)$, the equivalent formula using $\rho(\Gamma, T, A)$ becomes:

$$\begin{aligned}
 \langle Q \rangle &= \frac{1}{N} \sum_{k=1}^N \prod_{j=1}^N \int Q_k \psi(q_{j,1}, q_{j,2}, Q_j, P, T) dq_{j,1} dq_{j,2} dQ_j \\
 &= \frac{1}{N} \sum_{k=1}^N \int Q_k \psi(q_{k,1}, q_{k,2}, Q_k, P, T) dq_{k,1} dq_{k,2} dQ_k \\
 &= \int Q \psi(q_1, q_2, Q, P, T) dq_1 dq_2 dQ,
 \end{aligned}$$

where the last equality stems from the fact that every term under the summation is identical. Now, note that the average length of a coupled chain per single cell at equilibrium for a given (T, P) is, similarly to the case of single chains previously discussed, the first-order

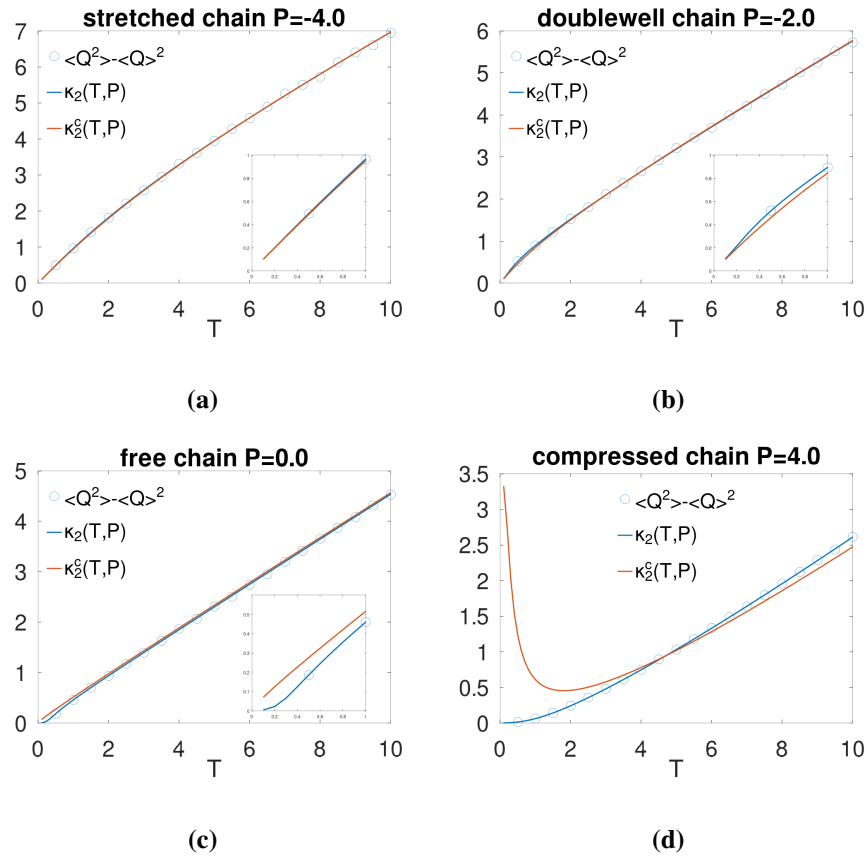


Figure 4.6: Same approach as per Fig. 4.4 except that the temperature is higher. The insets are the enlarged view of the left end, where the agreement is comparatively poor.

cumulant of the potential part $\psi(q_1, q_2, Q, P, T)$:

$$\langle Q \rangle = \kappa_1(T, P) = \frac{\Phi_1}{\Phi_0}, \quad (4.2.2)$$

where terms Φ_n are defined as:

$$\Phi_n(T, P) = \int dq_1 dq_2 dQ e^{-\frac{V_{LJ}(q_1) + V_{LJ}(q_2) + \frac{K}{2}(Q-l)^2 + PQ}{T}} \cdot Q^n \delta(q_1 + q_2 - Q), \quad \text{for } n = 0, 1, 2, \dots \quad (4.2.3)$$

Remember that Φ_0 is a part of the partition function, the n -th derivative of which defines Φ_n as follows:

$$\Phi_n(P, T) = (-T)^n \frac{\partial^n}{\partial P^n} \Phi_0(P, T). \quad (4.2.4)$$

In the same way, we can expand the mean $\langle \dots \rangle$ in Eq. (4.1.3) by using $\rho(\Gamma, T, A)$,

which leads us to the second-order cumulant, as follows:

$$\begin{aligned}
& \langle Q^2 \rangle - \langle Q \rangle^2 \\
&= \frac{1}{N} \sum_{k=1}^N \sum_{m=1}^N \langle Q_k Q_m \rangle - \langle Q_k \rangle \langle Q_m \rangle \\
&= \frac{1}{N} \sum_{k=1}^N \sum_{m=1}^N \prod_{j=1}^N \int Q_k Q_m \psi(q_{j,1}, q_{j,2}, Q_j, T, P) dq_{j,1} dq_{j,2} dQ_j \\
&\quad - \frac{1}{N} \sum_{k=1}^N \sum_{m=1}^N \prod_{s=1}^N \int Q_k \psi(q_{s,1}, q_{s,2}, Q_s, T, P) dq_{s,1} dq_{s,2} dQ_s \cdot \\
&\quad \prod_{i=1}^N \int Q_m \psi(q_{i,1}, q_{i,2}, Q_i, T, P) dq_{i,1} dq_{i,2} dQ_i
\end{aligned}$$

Reducing all terms irrelevant to Q_k and Q_m to 1, the remaining terms have $k = m$ and $k \neq m$:

$$\begin{aligned}
& \langle Q^2 \rangle - \langle Q \rangle^2 \\
&= \frac{1}{N} \sum_{k=1}^N \sum_{m \neq k}^N \int Q_k Q_m \psi(q_{k,1}, q_{k,2}, Q_k, T, P) \cdot \\
&\quad \cdot \psi(q_{m,1}, q_{m,2}, Q_m, T, P) dq_{m,1} dq_{m,2} dQ_m dq_{k,1} dq_{k,2} dQ_k - \\
&\quad - \int Q_k \psi(q_{k,1}, q_{k,2}, Q_k, T, P) dq_{k,1} dq_{k,2} dQ_k \cdot \\
&\quad \cdot \int Q_m \psi(q_{m,1}, q_{m,2}, Q_m, T, P) dq_{m,1} dq_{m,2} dQ_m \\
&\quad + \frac{1}{N} \sum_{k=1}^N \int Q_k^2 \psi(q_{k,1}, q_{k,2}, Q_k, T, P) dq_{k,1} dq_{k,2} dQ_k - \\
&\quad - \left(\int Q_k \psi(q_{k,1}, q_{k,2}, Q_k, T, P) dq_{k,1} dq_{k,2} dQ_k \right)^2 \\
&= \int Q^2 \psi(q_1, q_2, Q, T, P) dq_1 dq_2 dQ - \left(\int Q \psi(q_1, q_2, Q, T, P) dq_1 dq_2 dQ \right)^2.
\end{aligned}$$

The crossing terms with $k \neq m$ cancel each other. Then we are left with the summation of N identical terms divided by N . Finally, the fluctuation is expressed as the second-order cumulant as follows

$$\langle Q^2 \rangle - \langle Q \rangle^2 = \kappa_2(T, P) = \frac{\Phi_2}{\Phi_0} - \left(\frac{\Phi_1}{\Phi_0} \right)^2, \quad (4.2.5)$$

where Φ_n again satisfies Eq. (4.2.3). Integrating out the Dirac function in Eq. (4.2.3), we find that Φ_n are determined by the potential V^* defined on the (q_1, q_2) plane,

$$\begin{aligned}\Phi_n(P, T) &= \int Q^n e^{-\frac{V^*(Q, q, P)}{T}} dq dQ \\ &= \int_0^{+\infty} Q^n e^{-\frac{V_{ph}^*(Q, P)}{T}} \int_0^Q e^{-\frac{V_{LJ}^*(Q, q)}{T}} dq dQ\end{aligned}\quad (4.2.6)$$

with

$$V^*(q_1, q_2, P) = V_{LJ}^*(q_1, q_2) + V_{ph}^*(q_1, q_2; P) \quad V_{LJ}^*(q_1, q_2) = V_{LJ}(q_1) + V_{LJ}(q_2) \quad (4.2.7)$$

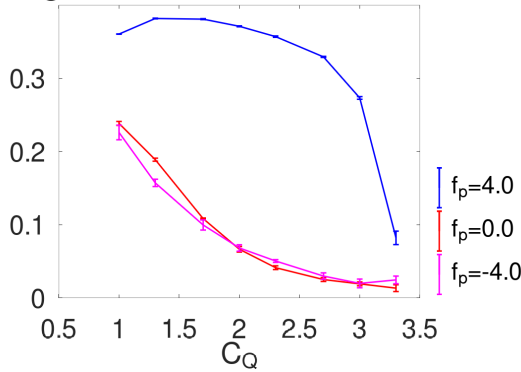
$$\begin{aligned}V_{ph}^*(q_1, q_2; P) &= \frac{K}{2}(q_1 + q_2 - l)^2 + P(q_1 + q_2) \\ &= \frac{K}{2}(q_1 + q_2 - l^*)^2 + V_{ph}^0\end{aligned}\quad (4.2.8)$$

$$l^* = l - \frac{P}{K} \quad V_{ph}^0 = \frac{K}{2}(l^2 - l^{*2}),$$

$$l^* = l - \frac{P}{K} \quad V_{ph}^0 = \frac{K}{2}(l^2 - l^{*2}),$$

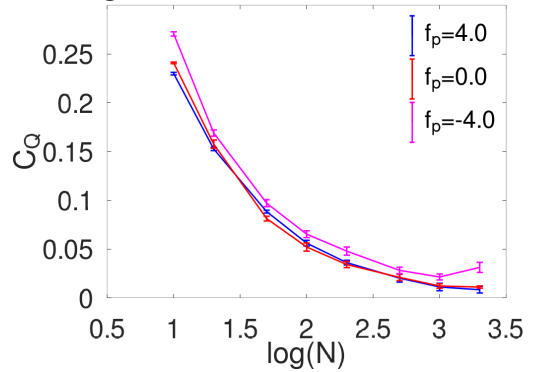
which contains a composite Lennard-Jones potential V_{LJ}^* and a regulated harmonic potential V_{ph}^* . The composite Lennard-Jones potential V_{LJ}^* is a potential with a well located at a

length correlation at $T_L=0.1$ $T_R=1.0$



(a)

length correlation at $T_L=1.0$ $T_R=10.0$



(b)

Figure 4.7: The correlation C_Q defined in Eq. (4.1.8) respect to the number of cells N , with fixed boundary temperature T_L, T_R and constraining force f_p . The error bars are obtained by averaging over four different initial states, each one over the time interval $[1 \cdot 10^8, 4 \cdot 10^8]$. For illustrative purposes, N is plotted on a logarithmic scale.

fixed point $(q_1, q_2) = (1, 1)$ with fixed depth -2 . The regulated harmonic potential V_{ph}^* has a moving minimum line at $q_1 + q_2 = l^* = l - \frac{P}{K}$ with the depth $V_{ph}^0 = \frac{K}{2}(l^2 - l^{*2})$, which will be determined by the value of pressure P when both K and l are fixed. The interplay between these two minima determines the geometry of the V^* surface. Fig. 4.2a gives four types of V^* surface characterised by the section profile cut at $q_1 = q_2 = q$, with varying P and fixed K, l . V_{ph}^* dominates for $P \ll K(l - 2)$ in Fig. 4.2b. We call it the “stretched chain” case. The term “stretched” here means the Lennard-Jones chain in Fig. 4.1 is being stretched to longer lengths than its mechanical equilibrium. On the other hand, V_{LJ}^* dominates for $P \gg K(l - 2)$, as shown in Fig. 4.2e, which we call the “compressed chain” because the coupled length is shorter than that of the uncoupled one. Specifically, the two wells merge when $P = K(l - 2)$ (see Fig. 4.2d) and, at that point, the Lennard-Jones chain is neither stretched nor compressed: we call it the “free chain” scenario. These three types are what we will focus in the following content. The fourth type, i.e. the “double well chain” shown in Fig. 4.2c, is simply a continuous transition among them. In this scenario, V_{LJ}^* and V_{ph}^* contribute a separated potential well. The chain behaves similarly to the compressed chain when the V_{LJ}^* is deeper, resembles the stretched chain when the V_{ph}^* dominates, and approximates the free chain when the two wells are closely matched.

For all the four types of chains, Eq. (4.2.2) and Eq. (4.2.5) relate the average length and its fluctuations at equilibrium with temperature and pressure via $\kappa_1(T, P)$ and $\kappa_2(T, P)$. The same values can also be obtained from direct numeric simulations by integrating Eq. (4.1.1) under $T_L = T_R = T$, $f_p = P$ and calculating the average length and fluctuation via Eqs. (4.1.2) and (4.1.3). We will now evaluate the validity and the agreement between the predictions by Eqs. (4.2.2), (4.2.5) and the simulation results by Eqs. (4.1.2) and (4.1.3), as we have done for the single chain case.

Fig. 4.3 shows a perfect validity of Eq. (4.2.2), where the circles denoted by $\langle \dots \rangle$ represent the simulation results by Eqs. (4.1.2) and the $\kappa_1(T, P)$ are the predictions by statistical mechanics. Note also that there is universality in the behaviour at the zero temperature

limit. The average cell length converges to $l - \frac{P}{K}$ (see Fig. 4.3a to 4.3c) except for the compressed chain state (see Fig. 4.3d), which converges to a constant $\langle Q \rangle \approx 2.0$. This is because, as previously remarked, as $T \rightarrow 0$, thermodynamic equilibrium approaches mechanical equilibrium. The mechanical equilibrium length for compressed chain is fixed at around $\langle Q \rangle = 2.0$ because of the hard-core repulsive nature of the composite LJ potential V_{LJ}^* , while for other chains, this value is determined by the regulated harmonic potential V_{ph}^* , giving $\langle Q \rangle = l^* = l - \frac{P}{K}$. Fig. 4.3a and 4.3b also show that the stretched and double well chains give rise to a plateau at the low-temperature limit, indicating that the contribution of V_{LJ}^* is negligible in this region. If we neglect the $e^{-\frac{V_{LJ}^*}{T}}$ term in Eq. (4.2.6), we can use the properties of Gaussian integrals:

$$\begin{aligned}
\Phi_n &\propto \int_{-\infty}^{+\infty} Q^n e^{-\frac{V_{ph}^*}{T}} dQ \\
&= e^{-\frac{V_{ph}^0}{T}} \int_{-\infty}^{+\infty} Q^n e^{-\frac{K(Q-l^*)^2}{2T}} dQ \\
&= e^{-\frac{V_{ph}^0}{T}} \int_{-\infty}^{+\infty} (X + l^*)^n e^{-\frac{KX^2}{2T}} dX \\
&= e^{-\frac{V_{ph}^0}{T}} \sum_{k=0}^n \binom{n}{k} (l^*)^k \int_{-\infty}^{+\infty} X^{n-k} e^{-\frac{KX^2}{2T}} dX \\
&= \sqrt{2\pi} e^{-\frac{V_{ph}^0}{T}} \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \binom{n}{n-2m} (l^*)^{n-2m} \left(\frac{K}{T} \right)^{-\frac{2m+1}{2}} (2m-1)!!,
\end{aligned}$$

where we use the substitution $Q = X + l^*$ in the third equality and the $\lfloor \frac{n}{2} \rfloor$ in the last equality is the floor function that takes the greatest integer less than or equal to $\frac{n}{2}$. The term $(2m-1)!!$ is a double factorial defined as:

$$(2m-1)!! = \begin{cases} \prod_{k=1}^m (2k-1) & m = 1, 2, \dots \\ 1 & m = 0 \end{cases}$$

Applying $n = 0, 1, 2$ into the definitions above, we have:

$$\begin{aligned}\Phi_0 &= \sqrt{\frac{2\pi T}{K}} e^{-\frac{v_{ph}^0}{T}} \\ \Phi_1 &= \Phi_0 l^* \\ \Phi_2 &= \Phi_0 \left((l^*)^2 + \frac{T}{K} \right).\end{aligned}\tag{4.2.9}$$

Using the expressions in Eq. (4.2.2), we have an average length with no dependence on

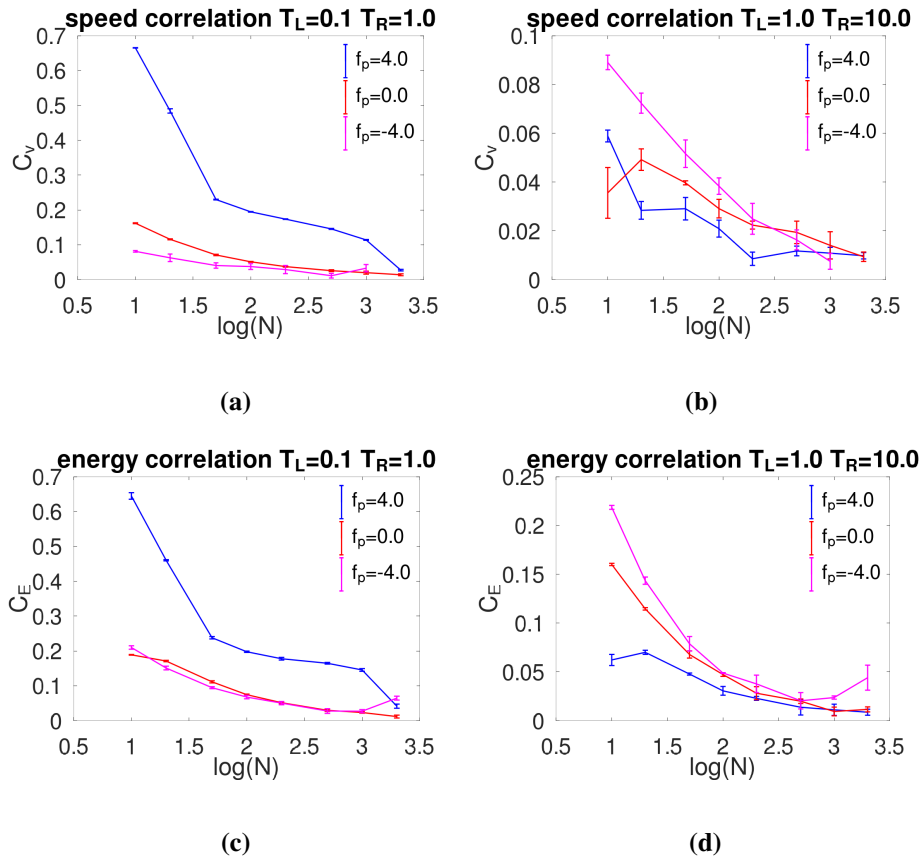


Figure 4.8: The speed correlation C_v and energy correlation C_E defined in Eq. (4.1.9) and Eq. (4.1.10). The others are the same as the previous figure.

temperature:

$$\lim_{T \rightarrow 0} \langle Q \rangle = \lim_{T \rightarrow 0} \kappa_1(T, P) = l^* = l - \frac{P}{K}.\tag{4.2.10}$$

This is the ordinate of the constant in Fig. 4.3a and 4.3b. We can also use Eqs. (4.2.9) to approximate the fluctuation at low temperature limit, which gives a linear increasing

fluctuation with temperature:

$$\lim_{T \rightarrow 0} \langle Q^2 \rangle - \langle Q \rangle^2 = \lim_{T \rightarrow 0} \kappa_2(T, P) = \frac{T}{K}. \quad (4.2.11)$$

This behaviour is verified in the stretched and double well chains, as shown in Fig. 4.4a and 4.4b. The free and compressed case, as shown in Fig. 4.4c and 4.4d, also has a linearly increasing fluctuation in the low temperature region but with smaller slope. The linearity is due to the quadratic approximation. In low temperature limit, the fluctuation is focused in a small region around the minimum point $[\mu_1 \quad \mu_2]^T$, which could be well approximated by the following quadratic form:

$$V^* \approx \frac{1}{2} K_1 x_1^2 + \frac{1}{2} K_2 x_2^2,$$

with x_1, x_2 relating to Q, q through a normalised eigenvector matrix:

$$\begin{bmatrix} Q - \mu_1 \\ q - \mu_2 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \quad a_{11}^2 + a_{21}^2 = a_{12}^2 + a_{22}^2 = 1,$$

and the eigenvalues K_1, K_2 much larger than K :

$$K_1 > K_2 > 2K,$$

because the potential well of free and compressed chain must be much “steeper” than the harmonic potential due to the contribution of Lennard-Jones potential. Applying the equations above into Eq. (4.2.5), we find κ_2 is approximated by a two-dimensional Gaussian

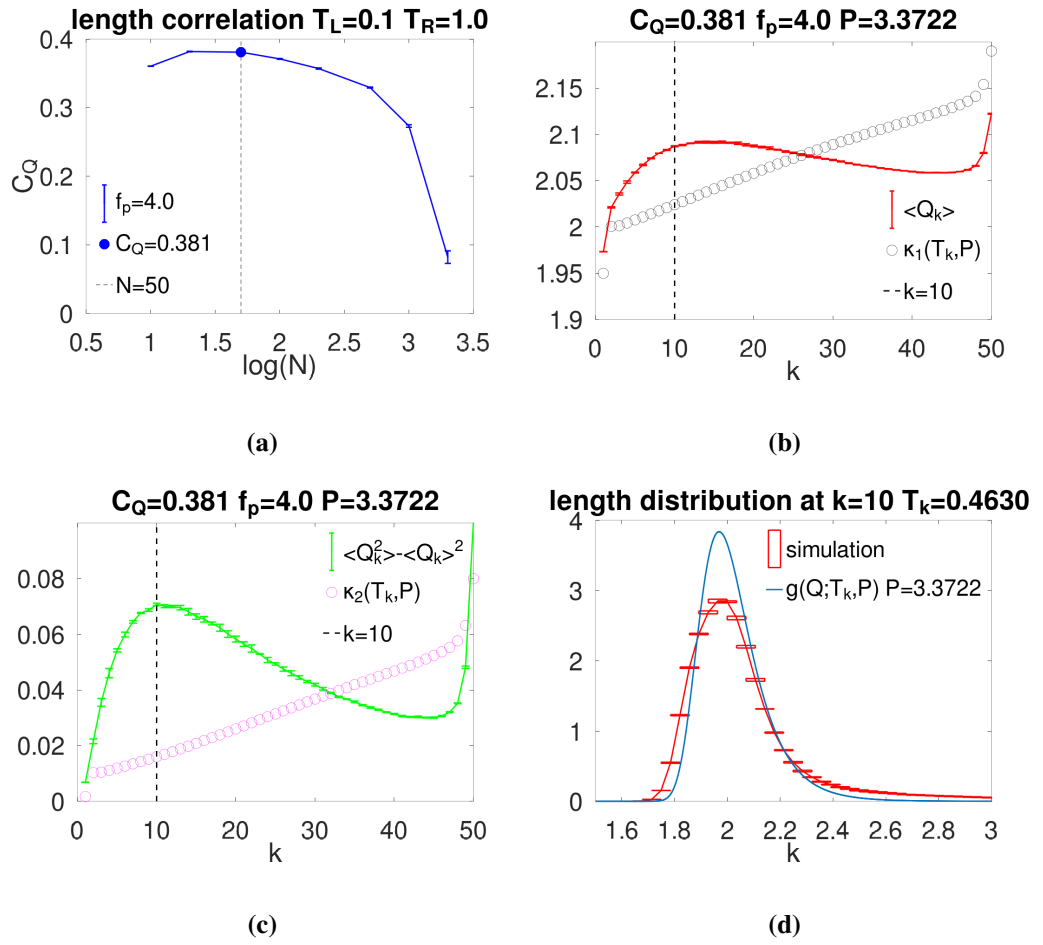


Figure 4.9: (a) The state point with $N = 50$, $f_p = 4.0$ and $T_L = 0.1$, $T_R = 1.0$ (b-c) Test of κ_1 and κ_2 by simulation. (d) The length distribution of the cell at $k = 10$

integral:

$$\begin{aligned}
 \kappa_2 &= \langle (Q - \mu_1)^2 \rangle \\
 &= \frac{\int (a_{11}x_1 + a_{12}x_2)^2 \exp[-\frac{K_1x_1^2}{2T}] \exp[-\frac{K_2x_2^2}{2T}] dx_1 dx_2}{\int \exp[-\frac{K_1x_1^2}{2T}] \exp[-\frac{K_2x_2^2}{2T}] dx_1 dx_2} \\
 &= a_{11}^2 \frac{T}{K_1} + a_{12}^2 \frac{T}{K_2} \\
 &< \frac{T}{K_1} + \frac{T}{K_2} < \frac{T}{K'},
 \end{aligned}$$

which explains the slopes lower than unity in Fig. 4.4b-4.4d. It is worth noting that the linear region of the free chain is quite narrow for the corresponding potential well is highly unsymmetric, as shown in Fig. 4.2d, so the symmetric quadratic approximation fails rapidly.

Again, the κ_2 term in Eq. (4.2.5) shows a wide range of validity and, in all four panels of Fig. 4.4, it fits with the simulation results denoted by $\langle Q^2 \rangle - \langle Q \rangle^2$. The $\kappa_2(T, P)$ profiles also confirm a zero fluctuation at the theoretical value $T = 0.0$ for all four types of chains, which fits with the fact that the mechanical equilibrium at $T = 0.0$ gives rise to no fluctuation.

Let us now turn to the high temperature limit. Fig. 4.5 show that $\kappa_1(T, P)$ profiles are valid in high temperature for all types of chains, and they converge to a critical curve κ_1^c at the high temperature limit. The expression of the curve depicted in the panels can be derived as follows.

According to Eq. (4.2.2), κ_1^c is the ratio between the high temperature limit of Φ_1 and Φ_0 :

$$\kappa_1^c = \lim_{T \rightarrow +\infty} \kappa_1 = \lim_{T \rightarrow +\infty} \Phi_1 / \lim_{T \rightarrow +\infty} \Phi_0. \quad (4.2.12)$$

In this limit, as we discussed before, the Lennard-Jones potential is indistinguishable from the hard-core potential and the term $e^{-\frac{V_{LJ}^*}{T}}$ in Eq. (4.2.6) can be approximated by the

product of two “altered” unit step functions:

$$e^{-\frac{V_{LI}^*}{T}} \approx \epsilon(q_1 - \Omega)\epsilon(q_2 - \Omega),$$

where the unit step function $\epsilon(x)$ is defined as:

$$\epsilon(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0. \end{cases} \quad (4.2.13)$$

Then the Φ_0 in Eq. (4.2.6) can be explicitly evaluated:

$$\lim_{T \rightarrow +\infty} \Phi_0 = e^{-\frac{V_{ph}^0}{T}} \int dq_1 dq_2 dQ \epsilon(q_1 - \Omega) \epsilon(q_2 - \Omega) e^{-\frac{K(Q-l^*)^2}{2T}} \delta(q_1 + q_2 - Q)$$

where we have used the definition of V_{ph}^* in Eq. (4.2.8). Then we integrate out q_1 and q_2 to reduce the three-dimensional integral to one-dimension:

$$\lim_{T \rightarrow +\infty} \Phi_0 = e^{-\frac{V_{ph}^0}{T}} \int_{2\Omega}^{+\infty} (Q - 2\Omega) e^{-\frac{K(Q-l^*)^2}{2T}} dQ.$$

Applying the transform $X = \sqrt{\frac{K}{2T}}(Q - l^*)$ and using $\gamma = \sqrt{\frac{K}{2T}}(2\Omega - l^*)$ to denote the updated lower bound, we get:

$$\lim_{T \rightarrow +\infty} \Phi_0 = e^{-\frac{V_{ph}^0}{T}} \int_{\gamma=\sqrt{\frac{K}{2T}}(2\Omega-l^*)}^{+\infty} \left(X \sqrt{\frac{2T}{K}} + l^* - 2\Omega \right) e^{-X^2} \sqrt{\frac{2T}{K}} dX.$$

Finally, the equation is separated into two terms

$$\lim_{T \rightarrow +\infty} \Phi_0 = e^{-\frac{V_{ph}^0}{T}} \left(\frac{2T}{K} \int_{\gamma}^{+\infty} X e^{-X^2} dX + \frac{2T}{K} (-\gamma) \int_{\gamma}^{+\infty} e^{-X^2} dX \right)$$

In the end, we get

$$\lim_{T \rightarrow +\infty} \Phi_0 = e^{-\frac{V_{ph}^0}{T}} \frac{2T}{K} (g_1 - \gamma g_0), \quad (4.2.14)$$

in which g_1 has an analytic form:

$$g_1 = \frac{e^{-\gamma^2}}{2},$$

and g_0 is proportional to the complementary error function $\text{erfc}(\gamma)$:

$$g_0 = \int_{\gamma}^{+\infty} e^{-X^2} dX = \frac{\sqrt{\pi}}{2} \text{erfc}(\gamma).$$

By using Eq. (4.2.4), we immediately obtain Φ_1 by differentiating Φ_0 :

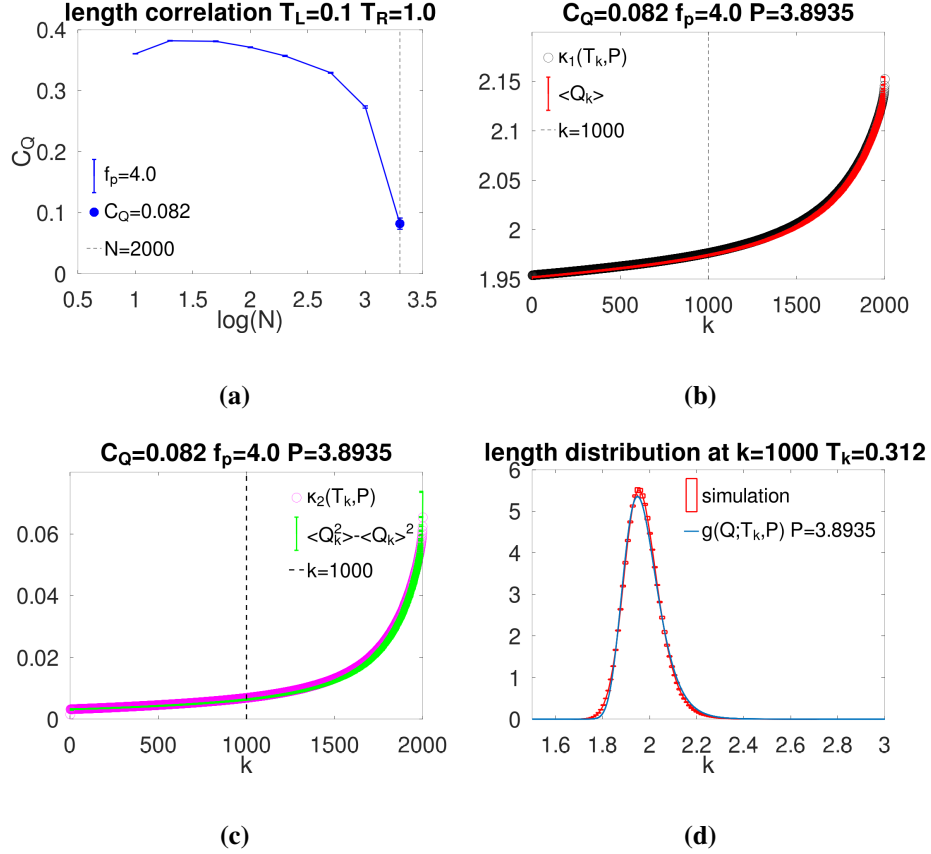


Figure 4.10: (a) The state point with $N = 2000$, $f_p = 4.0$ and $T_L = 0.1$, $T_R = 1.0$ (b-c) Test of κ_1 and κ_2 by simulation. (d) The length distribution of the cell at $k = 1000$.

$$\begin{aligned}
 \lim_{T \rightarrow +\infty} \Phi_1 &= -T \frac{\partial}{\partial P} \lim_{T \rightarrow +\infty} \Phi_0 \\
 &\propto \left(-T \frac{\partial}{\partial P} e^{-\frac{v_{ph}^0}{T}} \right) \frac{2T}{K} (g_1 - \gamma g_0) + e^{-\frac{v_{ph}^0}{T}} \frac{2T}{K} \left(-T \frac{\partial}{\partial P} (g_1 - \gamma g_0) \right) \\
 &= l^* \lim_{T \rightarrow +\infty} \Phi_0 + e^{-\frac{v_{ph}^0}{T}} \frac{2T}{K} \sqrt{\frac{T}{2K}} g_0 \\
 &= l^* \lim_{T \rightarrow +\infty} \Phi_0 + A.
 \end{aligned}
 \tag{4.2.15}$$

Here are the relevant differential expressions involved in the computation:

$$\begin{aligned}
 -T \frac{\partial}{\partial P} e^{-\frac{v_{ph}^0}{T}} &= l^* e^{-\frac{v_{ph}^0}{T}} & -T \frac{\partial}{\partial P} \gamma &= -\sqrt{\frac{T}{2K}} & -T \frac{\partial}{\partial P} g_0 &= \sqrt{\frac{2T}{K}} g_1 \\
 -T \frac{\partial}{\partial P} g_1 &= \gamma \sqrt{\frac{2T}{K}} g_1 \\
 -T \frac{\partial}{\partial P} l^* &= \frac{T}{K} & -T \frac{\partial}{\partial P} A &= l^* A + B & B &= e^{-\frac{v_{ph}^0}{T}} \frac{2T}{K} \frac{T}{K} g_1.
 \end{aligned}
 \tag{4.2.16}$$

Substituting Eq. (4.2.14) and (4.2.15) into Eq. (4.2.12) gives the expression of the critical curve in the high temperature limit. The results and the expressions involved are given by:

$$\begin{aligned}
 \kappa_1^c &= l^* + \sqrt{\frac{T}{2K}} \frac{g_0}{g_1 - \gamma g_0} \\
 l^* &= l - \frac{P}{K} \\
 \gamma &= \sqrt{\frac{K}{2T}} (2\Omega - l^*).
 \end{aligned}
 \tag{4.2.17}$$

In extreme high temperature with $\gamma \rightarrow 0$, we have:

$$\begin{aligned}
 \lim_{\gamma \rightarrow 0} g_0 &= \int_0^{+\infty} e^{-X^2} dX = \frac{\sqrt{\pi}}{2} \\
 \lim_{\gamma \rightarrow 0} g_1 &= \frac{1}{2},
 \end{aligned}$$

then there is a square root scaling on temperature and an independent linear scaling on pressure:

$$\lim_{\gamma \rightarrow 0} \kappa_1^c = l^* + \sqrt{\frac{\pi}{2K}} \sqrt{T} = l - \frac{P}{K} + \sqrt{\frac{\pi}{2K}} \sqrt{T}.
 \tag{4.2.18}$$

By contrast, the average length for a monodimensional chain with harmonic potential only is proportional to P with no dependence on T and the Lennard-Jones chain is proportional to $\frac{T}{P}$ in the high temperature limit (see Fig. 2.11b). Their combination lies in between, proportional to the linear combination of $\sqrt{T}$ and P . This can also be derived using a physical argument. The average force along a harmonic spring is proportional to

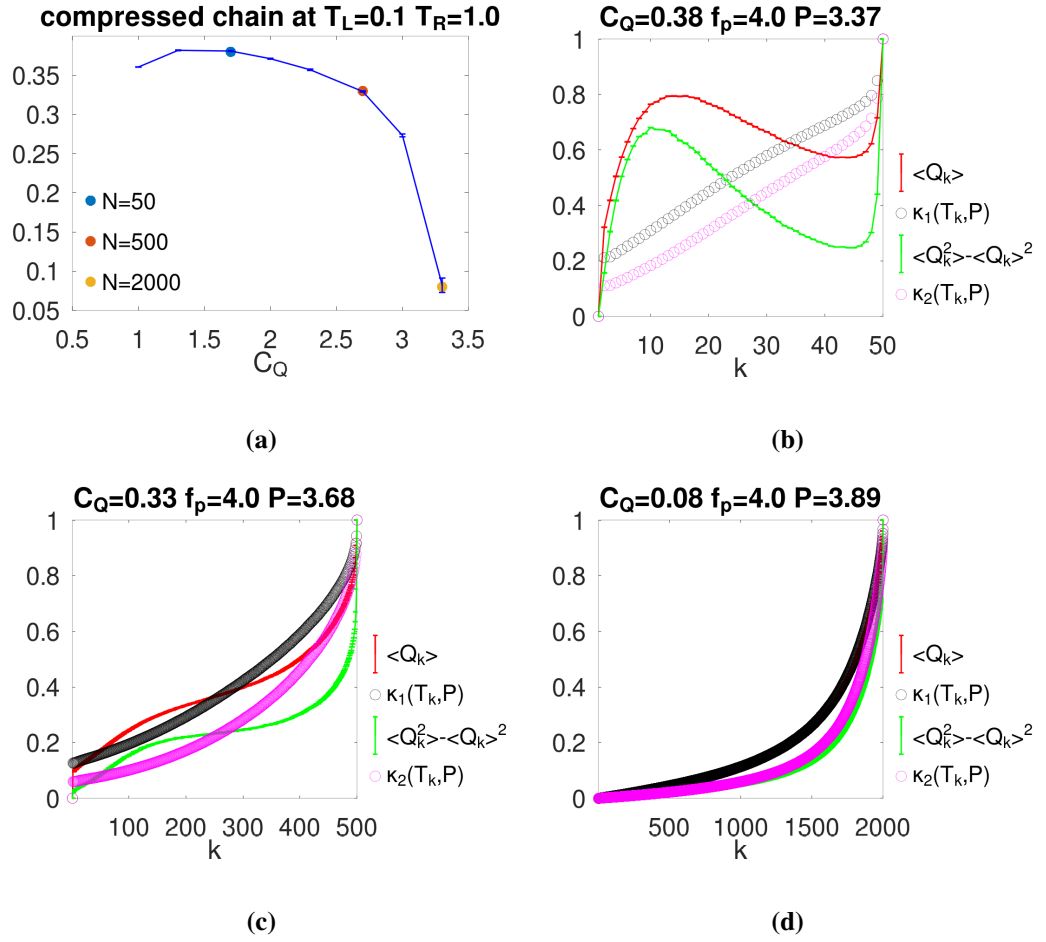


Figure 4.11: (a) Three state points at $T_L = 0.1, T_R = 1.0, f_p = 4.0$. The validity of $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ is tested at each point in (b-d).

its average length $\langle Q \rangle$

$$P_h = -K (\langle Q \rangle - l),$$

and the average force of a hardcore oscillator is as the Tonks equation

$$P_{Tonks} = \frac{T}{\langle Q \rangle - b}.$$

Their summation equals the total pressure:

$$P = P_h + P_{Tonks} = -K (\langle Q \rangle - l) + \frac{T}{\langle Q \rangle - b},$$

the solution of which for $\langle Q \rangle$ gives a similar scaling to Eq. (4.2.18).

We can now compute the high temperature limit for Φ_2 by differentiating Eq. (4.2.15):

$$\begin{aligned} \lim_{T \rightarrow +\infty} \Phi_2 &= -T \frac{\partial}{\partial P} \lim_{T \rightarrow +\infty} \Phi_1 \\ &\propto \left(-T \frac{\partial}{\partial P} l^* \right) \lim_{T \rightarrow +\infty} \Phi_0 + l^* \left(-T \frac{\partial}{\partial P} \lim_{T \rightarrow +\infty} \Phi_0 \right) + -T \frac{\partial}{\partial P} A \quad (4.2.19) \\ &= \left(\frac{T}{K} + (l^*)^2 \right) \lim_{T \rightarrow +\infty} \Phi_0 + 2Al^* + B. \end{aligned}$$

We have used Eq. (4.2.15) and Eq. (4.2.16) to derive the last equality. Combining Eq. (4.2.14), (4.2.15) and (4.2.19) in Eq. (4.2.5) gives the high temperature limit of κ_2 :

$$\begin{aligned} \lim_{T \rightarrow +\infty} \kappa_2 &= \kappa_2^c \\ &= \lim_{T \rightarrow +\infty} \frac{\Phi_2 \Phi_0 - \Phi_1 \Phi_1}{\Phi_0 \Phi_0} \quad (4.2.20) \\ &= \frac{T}{K} \left(1 + \frac{g_1}{g_1 - \gamma g_0} - \frac{1}{2} \left(\frac{g_0}{g_1 - \gamma g_0} \right)^2 \right). \end{aligned}$$

At the extreme high temperature limit with $\gamma \rightarrow 0$, the term κ_2^c is proportional to $\frac{T}{K}$, identically to the harmonic chain but with a slightly different slope. Note that for Lennard-Jones chains, the high temperature limit is proportional to $\left(\frac{T}{P}\right)^2$, as shown in Fig. 2.13b. Fig. 4.6a shows that the κ_2^c works almost everywhere for the stretched chain under $P =$

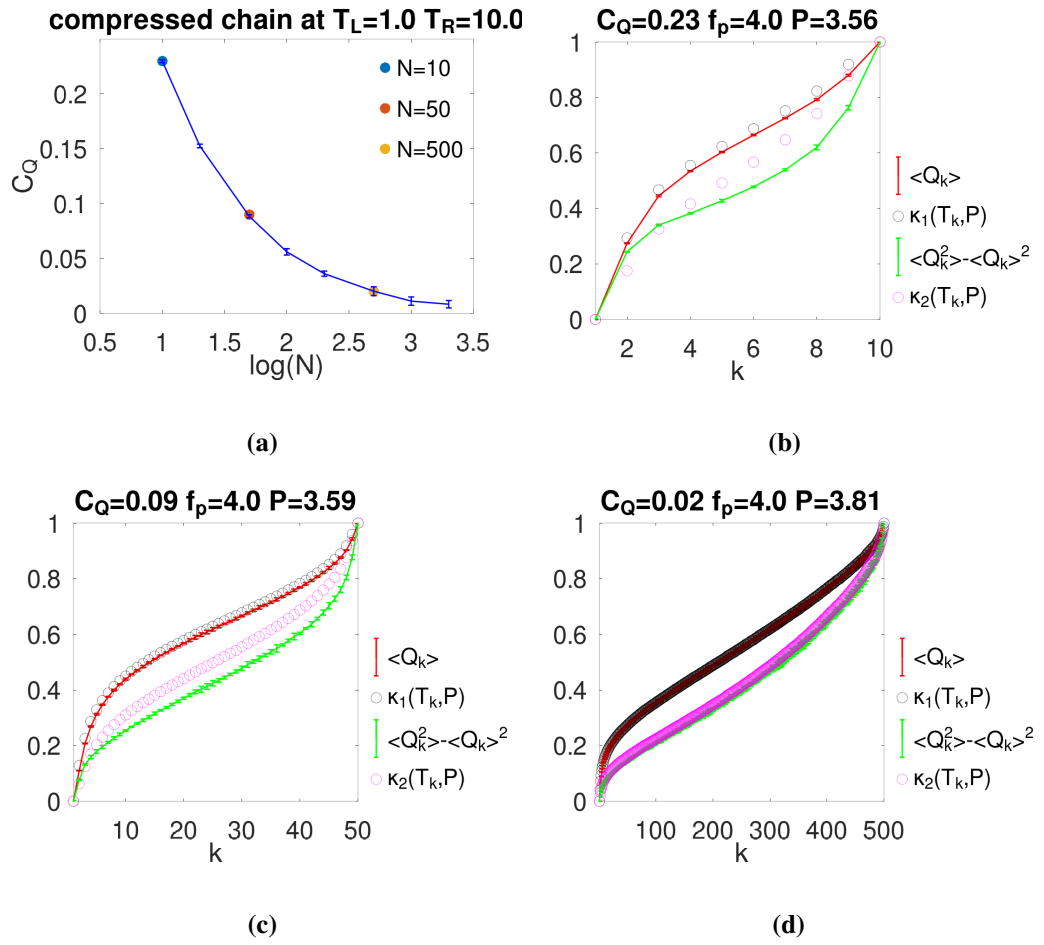


Figure 4.12: Same approach as per the previous figure except that the boundary temperature increases to $T_L = 1.0$, $T_R = 10.0$.

–4.0. As we increase the pressure to $P = -2.0$ and $P = 0.0$, the range of validity shrinks slightly (see the insets of Fig. 4.6b and 4.6c). When we compress the chain at $P = 4.0$, κ_2^c captures the linear dependence at high temperature but fails to numerically fit with simulation, as shown in Fig. 4.6d. Instead, the integral expression $\kappa_2(T, P)$ perfectly fits with simulation everywhere.

Equilibrium thus provides results that show agreement across simulations, statistical mechanics calculations and phenomenological approximations for all four types of chains.

4.3 The non-equilibrium case

In non-equilibrium steady states with $T_L \neq T_R$, as we have discussed before for the single chain cases, we assume that each cell arrives at some sort of stationary state with its kinetic energy as an approximation to the local temperature and the average force along the cell as the local pressure. Thus, we can hypothesise the following non-equilibrium distribution:

$$\begin{aligned} & \rho(p_{1,1}, q_{1,1}, p_{1,2}, q_{1,2}, \dots, p_{N,1}, q_{N,1}, p_{N,2}, q_{N,2}; T_1, T_2, \dots, T_N, P) \\ &= \prod_{k=1}^N f(p_{k,1}, p_{k,2}, T_k, q_{k,1}, q_{k,2}, Q_k, T_k, P) \end{aligned} \quad (4.3.1)$$

This expression is the product of the single-cell distributions characterised by the average kinetic energy T_j defined in Eq. (4.1.6) and the homogeneous average force P defined in Eq. (4.1.7).

According to this, the motions of distinct cells are statistically independent:

$$\begin{aligned} \delta_{km} &= \langle Q_k Q_m \rangle - \langle Q_k \rangle \langle Q_m \rangle \\ \delta_{km} &= \langle (p_{k,1} + p_{k,2})(p_{m,1} + p_{m,2}) \rangle - \langle (p_{k,1} + p_{k,2}) \rangle \langle (p_{m,1} + p_{m,2}) \rangle \\ \delta_{km} &= \langle H_k H_m \rangle - \langle H_k \rangle \langle H_m \rangle \end{aligned} \quad (4.3.2)$$

and thus the various correlations, the length correlations C_Q in Eq. (4.1.8), speed cor-

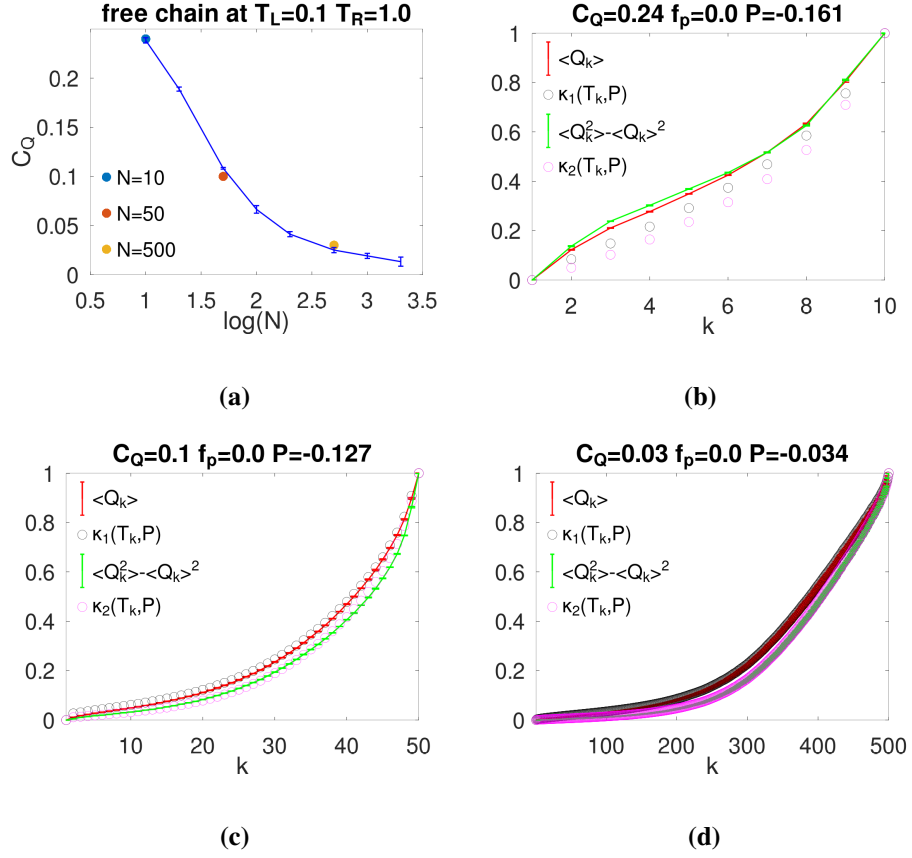


Figure 4.13: Same approach as per Fig. 4.11 except that the constraining force is set to $f_p = 0.0$.

relations C_v in Eq. (4.1.9) and energy correlations C_E in Eq. (4.1.10) all vanish to 0. However, simulations for coupled chains with fixed constraining force f_p and fixed unequal boundary temperature $T_L \neq T_R$ reveal a non-zero length correlation C_Q , as shown by Fig. 4.7a. The length correlation rapidly diminishes with the number of cells increasing for the free chain with $f_p = 0.0$ and stretched chain with $f_p = -4.0$, but the decay is slow for compressed chains with $f_p = 4.0$ at low temperature with small differences (i.e. $T_L = 0.1, T_R = 1.0$) and can be enhanced by increasing temperature (see Fig. 4.7b). A similar decay is also observed in the speed correlation C_v and energy correlation C_E as shown in Fig. 4.8. We assume that, as the various correlations in Fig. 4.7 and Fig. 4.8 decrease to zero, the corresponding non-equilibrium distribution is well approximated by the product of single-cell distribution as shown in Eq. (4.3.1). We further assume that the nonequilibrium single-cell distribution $f(p_{k,1}, p_{k,2}, q_{k,1}, q_{k,2}, Q_k; T_k, P)$ share the

same low-dimensional projection with the equilibrium one in Eq. (4.2.1):

$$\begin{aligned} & \int f(p_{k,1}, p_{k,2}, q_{k,1}, q_{k,2}, Q_k; T_k, P) dp_{k,1} dp_{k,2} dq_{k,1} dq_{k,2} \\ = & g(Q_k; T_k, P) = \frac{\exp\left[-\frac{V_{ph}^*(Q_k; P)}{T_k}\right] \int_0^{Q_k} \exp\left[-\frac{V_{LJ}^*(q, Q_k)}{T_k}\right] dq}{\int_0^{+\infty} \exp\left[-\frac{V_{ph}^*(Q_k; P)}{T_k}\right] \int_0^{Q_k} \exp\left[-\frac{V_{LJ}^*(q, Q_k)}{T_k}\right] dq dQ_k}, \end{aligned} \quad (4.3.3)$$

where the definition of V_{ph}^* and V_{LJ}^* could be found in Eq. (4.2.8) and Eq. (4.2.7) by using the transform $Q_k = q_1 + q_2$ and $q = q_1$. According to this, we have the expressions for the average length per single cell:

$$\langle Q_k \rangle = \kappa_1(T_k, P) = \frac{\Phi_1(T_k, P)}{\Phi_0(T_k, P)}, \quad (4.3.4)$$

and for the length fluctuation per single cell as

$$\langle Q_k^2 \rangle - \langle Q_k \rangle^2 = \kappa_2(T_k, P) = \frac{\Phi_2(T_k, P)}{\Phi_0(T_k, P)} - \left(\frac{\Phi_1(T_k, P)}{\Phi_0(T_k, P)} \right)^2. \quad (4.3.5)$$

These assumptions are verified by the example of a chain at low temperatures ($T_L = 0.1, T_R = 1.0$) compressed by $f_p = 4.0$, as shown in Fig. 4.9 and 4.10. For conciseness, we restrict our detailed discussion to the length correlation C_Q because this is the most relevant one and the trends of other correlations are similar. Fig. 4.9a presents the strong length correlation for chains of $N = 50$. Accordingly, both $\kappa_1(T_k, P)$ in Eq. (4.3.4) and $\kappa_2(T_k, P)$ in Eq. (4.3.5) are functionally incorrect as they give monotonous curves, while the profiles given by simulations are clearly not (see Fig. 4.9b and 4.9c). Then we examine the cell at $k = 10$: Fig. 4.9d shows that the distribution of Q_k drawn from simulation deviates from the projection term $g(Q; T_k, P)$ in Eq. (4.3.3). On the other hand, if we extend the chain to $N = 2000$, as shown in Fig. 4.10, the length correlation reduces to $C_Q = 0.082$. Both κ_1 and κ_2 agree with simulation. The length distribution in the middle cell at $k = 1000$ also fits with the projection $g(Q; T_k, P)$ in Eq. (4.3.3). Note also that there is a slight numeric difference between the constraining force f_p and average force P because of the non-zero net force exerted by NH thermostats at different

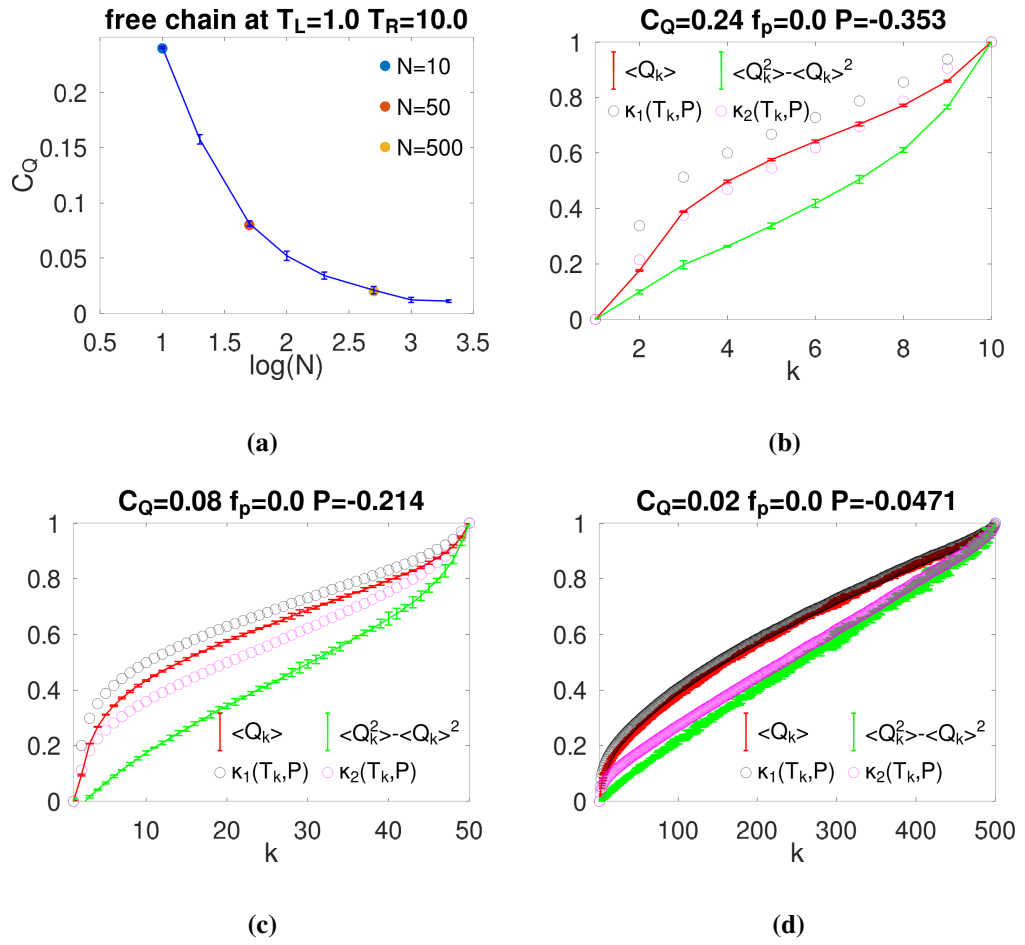


Figure 4.14: Same approach as per the previous figure except that the boundary temperature increases to $T_L = 1.0$, $T_R = 10.0$.

temperatures. This confirms that the deterministic thermostat are applying extra force on the system, as expected.

Note that the κ_1 and κ_2 here are based on two-dimensional integral defined in Eq. (4.2.3), not the one-dimensional integrals we have used in monodimensional LJ chains. But similarly to the monodimensional case, they improve their validity as the length correlation defined in Eq. (4.1.8) vanishes to $C_Q = 0.0$, which has been verified to occur for all three types of chains at either low or high temperature. These findings are systematically shown in Fig. 4.11 to 4.16. Note that all data in those figures has been normalised to the range $[0, 1]$ by the following expressions, in line with the same formulism we use for single chains:

$$\begin{aligned}\langle Q_k \rangle &= \frac{\langle Q_k \rangle - \langle Q_1 \rangle}{\langle Q_N \rangle - \langle Q_1 \rangle} \\ \langle Q_k^2 \rangle - \langle Q_k \rangle^2 &= \frac{(\langle Q_k^2 \rangle - \langle Q_k \rangle^2) - (\langle Q_1^2 \rangle - \langle Q_1 \rangle^2)}{(\langle Q_N^2 \rangle - \langle Q_N \rangle^2) - (\langle Q_1^2 \rangle - \langle Q_1 \rangle^2)} \\ \kappa_1(T_k, P) &= \frac{\kappa_1(T_k, P) - \kappa_1(T_1, P)}{\kappa_1(T_N, P) - \kappa_1(T_1, P)} \\ \kappa_2(T_k, P) &= \frac{\kappa_2(T_k, P) - \kappa_2(T_1, P)}{\kappa_2(T_N, P) - \kappa_2(T_1, P)}.\end{aligned}\tag{4.3.6}$$

Note that, in some cases, we choose to disregard the first or last few cells to avoid the influence of contact resistance on the chains.

Fig. 4.11 describes the length and fluctuation profiles for compressed chains under $f_p = 4.0$ and small temperature differences at low temperatures $(T_L, T_R) = (0.1, 1.0)$. Fig. 4.11b shows that $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ are functionally incorrect for $N = 50$: both of them give monotonous curves, while the profiles given by simulations differ. This is analogous to the findings for single chains. This large disagreement is reduced when $N = 500$ and a satisfactory agreement is attained at $N = 2,000$. Cumulants $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ become more and more aligned with simulations when N increases from 50 to 2,000, with the correlation index dropping again one order of magnitude from $C = 0.38$ to $C = 0.08$.

Higher temperature at $T_L = 1.0, T_R = 10.0$ in Fig. 4.12 shows an increasingly improved

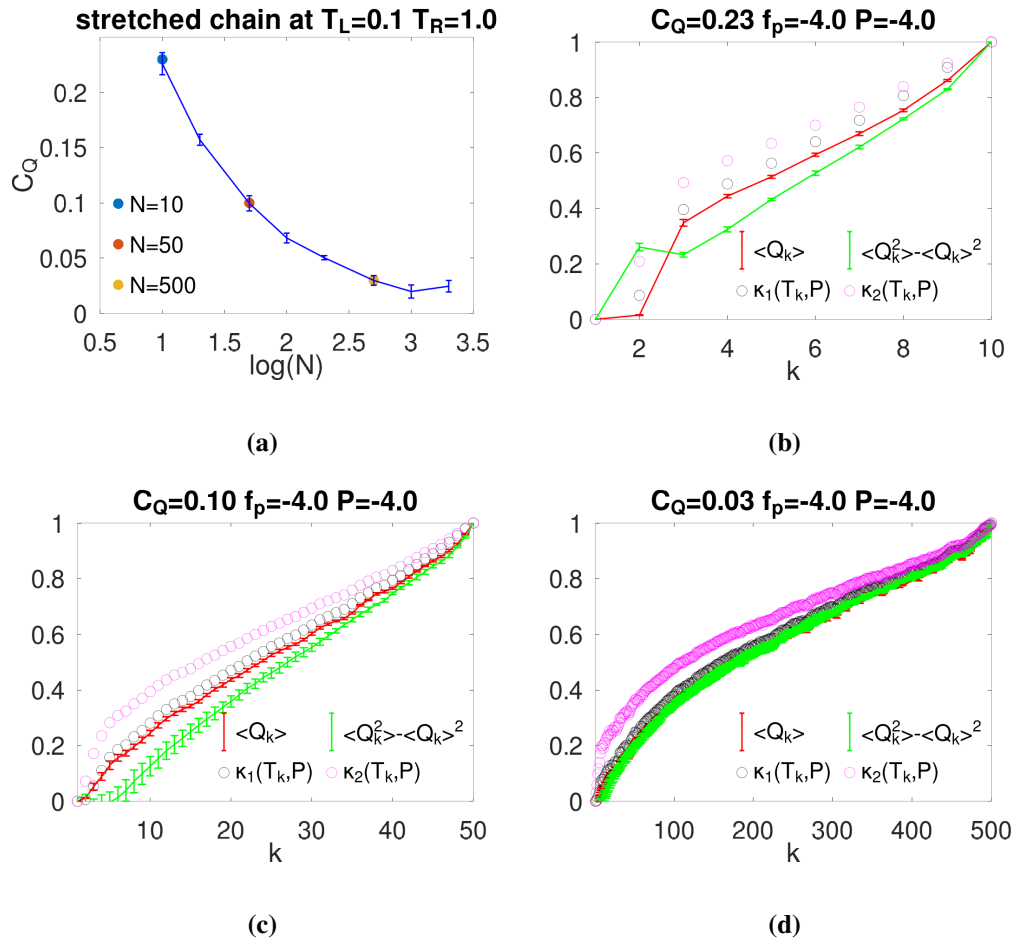


Figure 4.15: (a) Three state points at $T_L = 0.1, T_R = 1.0, f_p = -4.0$ for different N . The validity of $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ is tested at each point in (b-d).

agreement. The correlation under $N = 50$ has dropped to $C = 0.09$, κ_1 works very well while κ_2 deviates from the simulation, which again indicates that in some cases the validity of κ_1 may not depend on the validity of the nonequilibrium distribution in Eq. (4.3.1). When N further increases to 2,000, κ_2 agrees with simulation, as shown in Fig. 4.12d.

So, Eq. (4.3.4) and Eq. (4.3.5) are valid when we increase the number of cells N , as shown in both Fig. 4.11 and Fig. 4.12. This conclusion is drawn from compressed chains, but also holds for other cases. Plots show coupled free chains in Fig. 4.13 and Fig. 4.14, and stretched chains in Fig. 4.15 and Fig. 4.16. On the other hand, the validity of Eq. (4.3.4) and Eq. (4.3.5) depends on temperature for compressed chains: $N = 500$ makes Eq. (4.3.4) and Eq. (4.3.5) valid for $T_L = 1.0$ and $T_R = 10.0$ (see Fig. 4.12d) but for lower temperature it requires $N = 2,000$ (see Fig. 4.11c and 4.11d). For other chains, the temperature dependence is remarkably not as influential: $N = 500$ is sufficient for the validity of Eq. (4.3.4) and Eq. (4.3.5), regardless of the boundary temperatures. This is true for free chains in Fig. 4.13d and Fig. 4.14d, and stretched chains in Fig. 4.15d and Fig. 4.16d.

The discussion above demonstrates that $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ derived from the factorised distribution in Eq. (4.3.1) are valid for chains with a large number of repeated units N (in the context of the coupled chain model, this is the number of cells) and a compressed chain at low temperature requires a larger N . This conclusion aligns well with the insights drawn from monodimensional chains but it seems that $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$ are more reliable and converge in a quicker way to the expected results in coupled chains than in single chains. For instance, values of κ_1 and κ_2 are not completely aligned with the simulation data in single Lennard-Jones chains of $N = 6,000$ at $T_L = 0.1$, $T_R = 1.0$ and $f_p = 4.0$ (see Fig. 3.7b). Under the same condition, the coupled chain with $N = 2000$ has instead attained a perfect agreement (see Fig. 4.11d). This characteristics of coupled chain models also lie in the correlation of other quantities such as speed and energy. A thorough comparison between coupled and single models is an interesting extension of

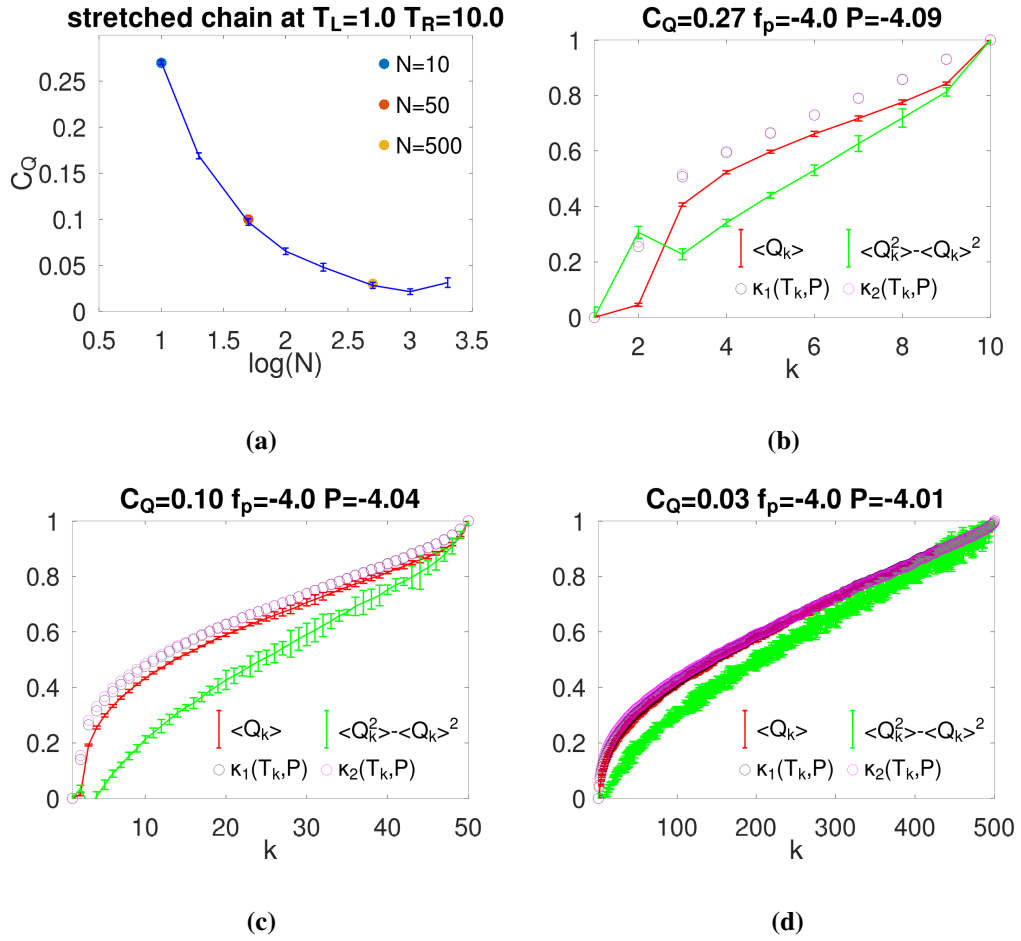


Figure 4.16: Same approach as per the previous figure except that the temperature on boundary is increased to $T_L = 1.0$, $T_R = 10.0$.

this work, which is currently still in progress. At this stage, one possible explanation for this behaviour is that harmonic links allow for better thermalisation when chains are paired together. It would be interesting to also extend these ideas to anharmonic links and combinations of different types of coupling terms. In any case, it is still an important finding that coupled chain models described in this Section can be well-described by ensemble distributions in appropriate regimes.

Conclusions and final remarks

A number of original results have been presented in this thesis, in the context of monodimensional Lennard-Jones chains of oscillators. Firstly, a detailed analysis of equilibrium properties for Lennard-Jones chains subject to fixed-length and fixed-force boundaries has been provided. Using statistical mechanics methods, chain length and fluctuations have been expressed as $\kappa_1(T, P)$ and $\kappa_2(T, P)$, the first and second order cumulants of the potential part of the Gibbs distribution. Investigations through comparison between numerical integration of $\kappa_1(T, P)$ and $\kappa_2(T, P)$ with molecular dynamics simulations have been detailed. The equivalence between fixed-length and fixed-force boundaries has thus been confirmed. Secondly, the use of linear approximation and analytical considerations have guided us to approximate the behaviour of $\kappa_1(T, P)$. As temperature increases, $\kappa_1(T, P)$ is first reduced to microscopic versions of the van der Waals equation and then of the Tonks equation. Their range of validity depends on boundary conditions and the number of oscillators, and a thorough discussion has been completed through numerical computation and comparison. Furthermore, we apply the equilibrium expressions $\kappa_1(T, P)$ and $\kappa_2(T, P)$ to non-equilibrium states and investigate the validity of the single-oscillator relations $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$, with their microscopic basis, i.e. the factorisation condition. Comparison between numerical integration and simulation has found that those single-oscillator expressions are valid provided that various correlations vanish and the

factorised distributions become appropriate approximations. Three aspects regulate and control the validity of $\kappa_1(T_k, P)$ and $\kappa_2(T_k, P)$: a high boundary temperature T_L, T_R , a weak constraining force f_p and large number of oscillators N in the chain. Notably, in high-temperature regimes, $\kappa_1(T_k, P)$ is valid even when the factorised distribution does not properly capture the oscillators' dynamics.

In the final Chapter, we extend our analysis to a coupled chain model of Lennard-Jones (LJ) oscillators bound with harmonic chains. Both $\kappa_1(T, P)$, $\kappa_2(T, P)$, even if they assume a more complicated form, remained in agreement with the simulation. They all converge to some analytic form at the extreme temperature limit and show a different scaling behaviour from the monodimensional case. In nonequilibrium states, the same expressions remain valid provided that the various correlations such as length correlation C_q , speed correlation C_v and energy correlation C_E is sufficiently small, which aligns with the conclusion for monodimensional chains.

Several questions are left for the future. This thesis focuses on Lennard-Jones chains, the typical dissociable chain model. But the formalism constructed in this thesis, especially the arguments in Chapter 1, is quite general. For example, the inverse density formula Eq. (1.2.9) does not refer to any specific type of interactions. We can easily apply it to any other monodimensional chain with different interactions. We can generalise our discussion to indissociable chains such as FPUT chains and possibly give a general argument for the linear relation proposed in [Giberti and Rondoni, 2011]. In the last Chapter, we consider four types of chains, among which the behaviour of the double-well chain is worthy of further investigation. The double-well potential can give birth to a phase transition, but in our work we have not seen any thermodynamically unstable behaviours. We can, for example, use the linear expansion methods referred in Section 2.2.1 to derive a microscopic van der Waals equation in the coupled chain model. This can help us explore the problem of phase transition in low-dimensional systems in detail and explore the applications of the general theorem made by L. Van Hove [Chowdhury and Stauffer, 2000]: a one-dimensional model with short-range inter-particle interactions cannot exhibit a phase

transition at any non-zero temperature.

Among the many other possibilities for further studies, we would like to conclude the thesis by suggesting two more topics. The first one is about the nonequilibrium distribution. The nonequilibrium distribution proposed in Section 1.2.2 is incomplete. It is dependent on a given average kinetic energy and average force profiles, but fails to give rise to these profiles from first principles. A complete nonequilibrium distribution contains information about time correlation and nonlinear response theory addresses this problem successfully in nonequilibrium liquids [Evans and Morriss, 2008]. Considering that low-dimensional systems often show little difference between liquid and solid regimes, it might be instructive to apply nonlinear response theory and give some insights on anomalous phenomena for transport in low-dimensional systems. The methods and results proposed in this thesis are useful to investigate how anomalous properties of mono-dimensional systems depend on their constituents, on external forces and heat exchange.

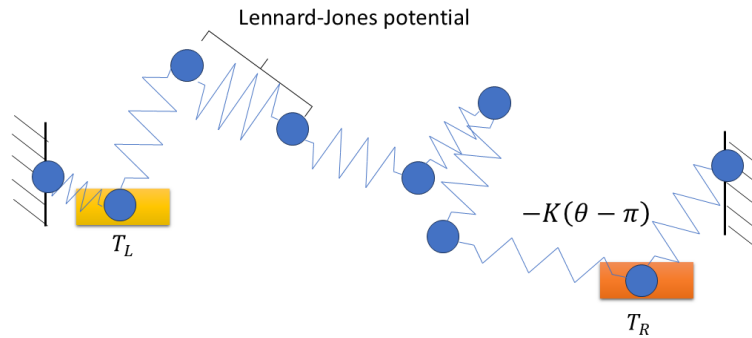


Figure 5.1: Sketch of the Lennard-Jones string.

The second topic is about the so-called Lennard-Jones string, shown in Fig. 5.1. It is a line of two-dimensional oscillators, and each oscillator repels its nearest neighbors via a harmonic angle potential. The two-dimensional vibration is expected to be weakened when the angle potential is sufficiently strong, so the string model is assumed to converge to the monodimensional Lennard-Jones chain discussed in this thesis. We can compute and simulate both the single oscillator relation and energy transport to clarify a long-standing problem: in which conditions is a strong constraining potential acting as a hard con-

straint? This approach on the Lennard-Jones string can be extended to polymer science, as polymers are often modeled as particles connected into a string.

References

- K. E. Atkinson, W. Han, and D. Stewart. *Numerical solution of ordinary differential equations*. Wiley, Hoboken, New Jersey, 2009.
- G. P. Berman and F. M. Izrailev. The Fermi-Pasta-Ulam problem: Fifty years of progress. *Chaos*, 15(1):015104–015104–18, 2005.
- J. Bricmont. *Making sense of statistical mechanics*. Springer International Publishing, Cham, 2022.
- H. B. Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, London, 1991.
- X. Cao and D. He. Interfacial thermal conduction and negative temperature jump in one-dimensional lattices. *Phys. Rev. E*, 92(3):032135, 2015.
- J. Casas-Vázquez and D. Jou. Temperature in non-equilibrium states: a review of open problems and current proposals. *Rep. Prog. Phys.*, 66(11):1937, 2003.
- M. Cencini, F. Cecconi, and A. Vulpiani. *Chaos: from simple models to complex systems*. World Scientific, Hackensack, N.J, 2010.
- S. Chen, Y. Zhang, J. Wang, and H. Zhao. Key role of asymmetric interactions in low-dimensional heat transport. *J. Stat. Mech.: Theor. Exp.*, 2016(3):033205, 2016.
- D. Chowdhury and D. Stauffer. *Principles of equilibrium statistical mechanics*. Wiley VCH, London, 2000.
- R. Courant and D. Hilbert. *Methods of mathematical physics*. Interscience Publishers, New York, 1962.
- M. Criado-Sancho, D. Jou, and J. Casas-Vázquez. Nonequilibrium kinetic temperatures in flowing gases. *Phys. Lett. A*, 350(5-6):339–341, 2006.
- A. Dhar. Heat transport in low-dimensional systems. *Adv. Phys.*, 57(5):457–537, 2008.
- M. Encinar, E. Guzmán, M. G. Prolongo, R. G. Rubio, C. Sandoval, F. González-Nilo, L. Gargallo, and D. Radić. Dielectric and dynamic-mechanical study of the mobility of poly(t-butylacrylate) chains in diblock copolymers: Polystyrene-b-poly(t-butylacrylate). *Polymer*, 49(26):5650–5658, 2008.

- H. Eslami, L. Mohammadzadeh, and N. Mehdipour. Anisotropic heat transport in nanoconfined polyamide-6,6 oligomers: Atomistic reverse nonequilibrium molecular dynamics simulation. *J. Chem. Phys.*, 136(10):104901–104901–8, 2012.
- D. J. Evans and G. P. Morriss. *Statistical mechanics of nonequilibrium liquids*. 2nd ed. Cambridge University Press, Cambridge, 2008.
- D. J. Evans, E. G. D. Cohen, and G. P. Morriss. Probability of second law violations in shearing steady states. *Phys. Rev. Lett.*, 71(15):2401–2404, 1993.
- M. Falcioni, L. Palatella, S. Pigolotti, L. Rondoni, and A. Vulpiani. Initial growth of Boltzmann entropy and chaos in a large assembly of weakly interacting systems. *Physica A*, 385(1):170–184, 2007.
- A. Fillipov, B. Hu, B. Li, and A. Zeltser. Energy transport between two attractors connected by a Fermi-Pasta-Ulam chain. *J. Phys. A*, 31(38):7719–7728, 1998.
- J. Ford. The Fermi-Pasta-Ulam problem: Paradox turns discovery. *Phys. Rep.*, 213(5):271–310, 1992.
- C. P. Fucetola, J. T. Wang, O. A. Bolonduro, C. M. Lieber, and B. P. Timko. Single-crystal silicon nanotubes, hollow nanocones, and branched nanotube networks. *ACS Nano*, 18(4):3775–3782, 2024.
- P. Ghosh, J. Lu, H. Luo, W. Wang, Z. Xu, M. Qiu, and Q. Li. Constructing metal arch nanobridges utilizing a photothermal-induced nanobonding technique. *Adv. Electron. Mater.*, 5(7), 2019.
- C. Giberti and L. Rondoni. Anomalies and absence of local equilibrium, and universality, in one-dimensional particles systems. *Phys. Rev. E*, 83(4):041115, 2011.
- C. Giberti, L. Rondoni, and C. Vernia. $O(N)$ fluctuations and lattice distortions in 1-dimensional systems. *Front. Phys.*, 7:180, 2019a.
- C. Giberti, L. Rondoni, and C. Vernia. Temperature and correlations in 1-dimensional systems. *Eur. Phys. J. Spec. Top.*, 228:129–142, 2019b.
- J. Hartbaum, P. Jakobs, H. Leiste, and M. Kohl. Development of magnetic nanoactuator systems. *Microelectron. Eng.*, 88(8):2263–2266, 2011.
- S. Iida, K. Negoro, and K. Yamada. Second moments of work and heat for a single-particle stochastic heat engine in a breathing harmonic potential. *PTEP*, 2022(4), 2022.
- S. Iijima. Helical microtubules of graphitic carbon. *Nature*, 354(6348):56–58, 1991.
- S. Iijima and T. Ichihashi. Single-shell carbon nanotubes of 1-nm diameter. *Nature*, 363(6430):603–605, 1993.
- D. Jou and L. Restuccia. Caloric and entropic temperatures in non-equilibrium steady states. *Physica A*, 460:246–253, 2016.
- M. Kardar. *Statistical physics of particles*. Cambridge University Press, Cambridge, 2007.

- D. Kondepudi and I. Prigogine. *Modern thermodynamics: from heat engines to dissipative structures*. Wiley, Hoboken, 2014.
- N. Kostoglou, C. Tampaxis, G. Charalambopoulou, G. Constantinides, V. Ryzhkov, C. Doumanidis, B. Matovic, C. Mitterer, and C. Rebholz. Boron nitride nanotubes versus carbon nanotubes: A thermal stability and oxidation behavior study. *Nanomaterials*, 10(12), 2020.
- L. D. Landau and E. M. Lifshitz. *Landau and Lifshitz Course of Theoretical Physics, Statistical Physics, Volume 5*. Elsevier, Amsterdam, 1980.
- G. R. Lee-Dadswell, N. Barrett, and M. Power. Cluster sizes in a classical Lennard-Jones chain. *Phys. Rev. E*, 96:032144, 2017.
- F. Legoll, M. Luskin, and R. Moeckel. Non-ergodicity of Nosé–Hoover dynamics. *Nonlinearity*, 22(7):1673–1694, 2009.
- S. Lepri, P. Sandri, and A. Politi. The one-dimensional Lennard-Jones system: collective fluctuations and breakdown of hydrodynamics. *Eur. Phys. J. B*, 47(4):549–555, 2005.
- S. Lepri, C. Mejía-Monasterio, and A. Politi. Nonequilibrium dynamics of a stochastic model of anomalous heat transport. *J. Phys. A: Math. Theor.*, 43(6):065002, 2010.
- S. J. Marrink, A. H. de Vries, and A. E. Mark. Coarse grained model for semiquantitative lipid simulations. *J. Phys. Chem. B*, 108(2):750–760, 2004.
- C. Mejía-Monasterio, A. Politi, and L. Rondoni. Heat flux in one-dimensional systems. *Phys. Rev. E*, 100(3):032139, 2019.
- G. P. Morriss and C. P. Dettmann. Thermostats: analysis and application. *Chaos*, 8(2): 321–336, 1998.
- G. P. Morriss and L. Rondoni. Definition of temperature in equilibrium and nonequilibrium systems. *Phys. Rev. E*, 59(1):R5, 1999.
- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
- A. Puglisi, A. Sarracino, and A. Vulpiani. Temperature in and out of equilibrium: A review of concepts, tools and attempts. *Phys. Rep.*, 709:1–60, 2017.
- A. Rahman. Correlations in the motion of atoms in liquid argon. *Phys. Rev.*, 136(2A): A405–A411, 1964.
- L. Rondoni and S. Pigolotti. On γ - and μ -space descriptions: Gibbs and Boltzmann entropies of symplectic coupled maps. *Phys. Scr.*, 86(5):058513, 2012.
- J. Ruben Gomez-Solano. Work extraction and performance of colloidal heat engines in viscoelastic baths. *Front. Phys.*, 9, 2021.
- H. H. Rugh. Dynamical approach to temperature. *Phys. Rev. Lett.*, 78(5):772, 1997.

- A. V. Savin and Y. A. Kosevich. Thermal conductivity of molecular chains with asymmetric potentials of pair interactions. *Phys. Rev. E*, 89(3):032102, 2014.
- J. Sheng, C. Yang, and H. Wu. Realization of a coupled-mode heat engine with cavity-mediated nanoresonators. *Sci. Adv.*, 7(50), 2021.
- H. Spohn. *Large Scale Dynamics of Interacting Particles*. Texts and Monographs in Physics. Springer Berlin, 1991.
- R. Sun, L. Rondoni, and F. Frascoli. On a microscopic equation of state for lennard-jones chains. *Commun. Nonlinear Sci. Numer. Simul.*, pages 108843–, 2025.
- B. D. Todd and P. J. Daivis. *Nonequilibrium molecular dynamics: theory, algorithms and applications*. Cambridge University Press, Cambridge, 2017.
- T. Wainweight and B. J. Alder. Molecular dynamics computations for the hard sphere system. *J. Chem. Phys.*, 9(S1):116–132, 1958.
- R. W. Welland, M. Shin, D. Allen, and J. B. Ketterson. Fracture in one dimension. *Phys. Rev. B*, 46(1):503–506, 1992.
- Y. Zhong, Y. Zhang, J. Wang, and H. Zhao. Normal heat conduction in one-dimensional momentum conserving lattices with asymmetric interactions. *Phys. Rev. E*, 85(6):060102, 2012.

Thermodynamics and statistical mechanics

A.1 Energy minimum principle

According to the basic differential Eq. (1.1.2), the entropy maximum principle is written as:

$$\left(\frac{\partial S}{\partial L}\right)_U = \frac{P(L, U)}{T(L, U)} = 0 \quad (\text{A.1.1})$$

$$\left(\frac{\partial^2 S}{\partial L^2}\right)_U = \left(\frac{\partial P}{\partial L}\right)_U < 0 \quad (\text{A.1.2})$$

and the positive temperature postulation is

$$\left(\frac{\partial S}{\partial U}\right)_L = \frac{1}{T(L, U)} > 0, \quad (\text{A.1.3})$$

where the basic differential Eq. (1.1.2) has been cited. Rearranging Eq. (1.1.2) to make S, L as the variables, we have:

$$dU = T(L, S)dS - P(L, S)dL, \quad (\text{A.1.4})$$

then the energy minimum principle we aim to prove is written as:

$$\left(\frac{\partial U}{\partial L}\right)_S = -P(L, S) = 0, \quad (\text{A.1.5})$$

$$\left(\frac{\partial^2 U}{\partial L^2}\right)_S = -\left(\frac{\partial P}{\partial L}\right)_S > 0. \quad (\text{A.1.6})$$

From Eq. (A.1.1) and Eq. (A.1.3), we have known that

$$P(L, U) = 0. \quad (\text{A.1.7})$$

To prove the $P(L, S) = 0$ in Eq. (A.1.5), we only need to use a variable substitution:

$$\begin{aligned} dU &= T(L, S)dS - P(L, S)dL \\ &= T(L, S) \left(\frac{1}{T(L, U)}dU + \frac{P(L, U)}{T(L, U)}dL \right) - P(L, S)dL. \end{aligned}$$

Collecting dU on the left-hand side, we have:

$$\left(1 - \frac{T(L, S)}{T(L, U)}\right) dU = \left(P(L, U) \frac{T(L, S)}{T(L, U)} - P(L, S)\right) dL.$$

Both dU and dL are independent: to make the equality work, we must make the coefficients zero:

$$\begin{aligned} 1 - \frac{T(L, S)}{T(L, U)} &= 0, \\ P(L, U) \frac{T(L, S)}{T(L, U)} - P(L, S) &= 0. \end{aligned}$$

Combining these two equations above, we obtain Eq. (A.1.5) by using Eq. (A.1.7).

To prove Eq. (A.1.6), we first expand Eq. (A.1.2):

$$\begin{aligned}
 \left(\frac{\partial \frac{P}{T}}{\partial L} \right)_U &= \frac{T(L, U) \left(\frac{\partial P}{\partial L} \right)_U - P(L, U) \left(\frac{\partial T}{\partial L} \right)_U}{T(L, U)^2} \\
 &= \frac{1}{T(L, U)} \left(\frac{\partial P}{\partial L} \right)_U \\
 &\propto \left(\frac{\partial P}{\partial L} \right)_U < 0,
 \end{aligned} \tag{A.1.8}$$

where the second line uses Eq. (A.1.7) and the third line uses Eq. (A.1.3). To prove the $-\left(\frac{\partial P}{\partial L} \right)_S > 0$ in Eq. (A.1.6), we need to write P as function of S and L :

$$\begin{aligned}
 dP &= \left(\frac{\partial P}{\partial L} \right)_U dL + \left(\frac{\partial P}{\partial U} \right)_L dU \\
 &= \left(\left(\frac{\partial P}{\partial L} \right)_U + \left(\frac{\partial P}{\partial U} \right)_L \left(\frac{\partial U}{\partial L} \right)_S \right) dL + \left(\frac{\partial P}{\partial U} \right)_L \left(\frac{\partial U}{\partial S} \right)_L dS \\
 &= \left(\frac{\partial P}{\partial L} \right)_U dL + \left(\frac{\partial P}{\partial U} \right)_L \left(\frac{\partial U}{\partial S} \right)_L dS \\
 &= \left(\frac{\partial P}{\partial L} \right)_S dL + \left(\frac{\partial P}{\partial S} \right)_L dS
 \end{aligned}$$

Here the third line is produced by using Eq (A.1.5). Comparing it with the fourth line and using Eq. (A.1.8), we finish the proof.

A.2 Stability condition

We aim at proving the condition that makes the following quadratic form positive on the (L, T) plane:

$$\delta^2 U = \begin{pmatrix} \delta S & \delta L \end{pmatrix} \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial L \partial S} \\ \frac{\partial^2 U}{\partial S \partial L} & \frac{\partial^2 U}{\partial L^2} \end{pmatrix} \begin{pmatrix} \delta S \\ \delta L \end{pmatrix} > 0. \tag{A.2.1}$$

Using the equality

$$\begin{aligned}
 dU &= \left(\frac{\partial U}{\partial S} \right)_L dS + \left(\frac{\partial U}{\partial L} \right)_S dL \\
 &= TdS - PdL,
 \end{aligned}$$

Eq. (A.2.1) is transformed into

$$\delta^2 U = \begin{pmatrix} \delta S & \delta L \end{pmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix} > 0. \quad (\text{A.2.2})$$

Expanding the δP and δS above on the (L, T) plane as follows:

$$\begin{aligned} \delta P &= \left(\frac{\partial P}{\partial T} \right)_L \delta T + \left(\frac{\partial P}{\partial L} \right)_T \delta L \\ \delta S &= \left(\frac{\partial S}{\partial T} \right)_L \delta T + \left(\frac{\partial S}{\partial L} \right)_T \delta L \\ &= \frac{C_L}{T} \delta T + \left(\frac{\partial P}{\partial T} \right)_L \delta L, \end{aligned}$$

where the last line uses the definition of C_L and the Maxwell relation. Eq. (A.2.2) finally becomes

$$\delta^2 U = \frac{C_L}{T} \delta T^2 - \left(\frac{\partial P}{\partial L} \right)_T \delta L^2 > 0.$$

The sufficient and necessary condition to make the equation above positive is thus the stability condition:

$$C_L > 0 \quad \left(\frac{\partial P}{\partial L} \right)_T < 0.$$

A.3 Three types of ensemble distribution

Entropy as a thermodynamic potential is a function of volume and internal energy. There are three different ways to define entropy in Γ space and the maximisation of each corresponds to a different distribution.

The first definition is based on the intersection of equal-length and equal-Hamiltonian (iso-energetic) surface,

$$\begin{aligned} S(L, U) &= - \int f(\Gamma) \ln f(\Gamma) \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma \\ &\quad - (\lambda_1 - 1) \left(\int f(\Gamma) \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - 1 \right) \end{aligned} \quad (\text{A.3.1})$$

where the Lagrangian term $\lambda_1 - 1$ is relevant to the normalisation condition. The maximisation of the equation above gives the microcanonical distribution:

$$f_{micr}(\Gamma) = e^{-\lambda_1}.$$

The value of λ_1 is determined by the normalisation condition, which is the logarithm of the volume of phase space, i.e. the entropy:

$$\lambda_1(L, U) = S(L, U) = \ln \int \delta(\mathbf{H}(\Gamma) - U) \delta(\mathbf{L}(\Gamma) - L) d\Gamma.$$

The temperature and pressure are defined by the total differential of entropy:

$$dS = \frac{dU + PdL}{T}.$$

The Dirac function $\delta(\mathbf{H}(\Gamma) - U)$ imposes that every microscopic state involved in Eq. (A.3.1) has exactly the same Hamiltonian U . If we “soften” this condition and only constrain the average Hamiltonian, we get the second definition:

$$\begin{aligned} S(L, U) &= - \int f(\Gamma) \ln f(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma \\ &\quad - (\lambda_1 - 1) \left(\int f(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - 1 \right) - \lambda_2 \left(\int f(\Gamma) \mathbf{H}(\Gamma) \delta(\mathbf{L}(\Gamma) - L) d\Gamma - U \right). \end{aligned} \quad (\text{A.3.2})$$

The maximization gives a canonical-like distribution. The remaining problem is to clarify the meaning of λ_1 and λ_2 .

$$f(\Gamma) = e^{-\lambda_1} e^{-\lambda_2 \mathbf{H}(\Gamma)}.$$

The value of λ_1 is determined by the normalisation condition:

$$\lambda_1(\lambda_2, L) = \ln \int_{L(\Gamma)=L} e^{-\lambda_2 \mathbf{H}(\Gamma)} d\Gamma,$$

the differential of which corresponds to internal energy and pressure:

$$\begin{aligned} P(\lambda_2, L) &= \frac{1}{\lambda_2} \frac{\partial \lambda_1}{\partial L} \\ &= \frac{\int_{L(\Gamma)=L} -\frac{\partial \mathbf{H}(\Gamma)}{\partial L(\Gamma)} e^{-\lambda_2 \mathbf{H}(\Gamma)} d\Gamma}{\int_{L(\Gamma)=L} e^{-\lambda_2 \mathbf{H}(\Gamma)} d\Gamma}, \end{aligned}$$

$$-\frac{\partial \lambda_1}{\partial \lambda_2} = \int_{L(\Gamma)=L} f(\Gamma) \mathbf{H}(\Gamma) d\Gamma = \frac{\int_{L(\Gamma)=L} \mathbf{H}(\Gamma) e^{-\lambda_2 \mathbf{H}(\Gamma)} d\Gamma}{\int_{L(\Gamma)=L} e^{-\lambda_2 \mathbf{H}(\Gamma)} d\Gamma} = U. \quad (\text{A.3.3})$$

We combine the two equations into the following thermodynamic relation

$$dS = \frac{dU + PdL}{T}, \quad (\text{A.3.4})$$

then we obtain

$$dS = \frac{1}{T} \left(d \left(-\frac{\partial \lambda_1}{\partial \lambda_2} \right) + \frac{1}{\lambda_2} \frac{\partial \lambda_1}{\partial L} dL \right),$$

the second term of which could be rewritten as

$$\frac{1}{\lambda_2} \frac{\partial \lambda_1}{\partial L} dL = \frac{1}{\lambda_2} \left(d\lambda_1 - \frac{\partial \lambda_1}{\partial \lambda_2} d\lambda_2 \right) = \frac{1}{\lambda_2} \left(d\lambda_1 - \left(d\lambda_2 \frac{\partial \lambda_1}{\partial \lambda_2} - \lambda_2 d \frac{\partial \lambda_1}{\partial \lambda_2} \right) \right).$$

Combining the two equations above, we rewrite the total differential as

$$dS = \frac{1}{T} \frac{1}{\lambda_2} d \left(\lambda_1 - \lambda_2 \frac{\partial \lambda_1}{\partial \lambda_2} \right). \quad (\text{A.3.5})$$

To make the right-hand side of Eq. (A.3.5) a total differential, the only choice of λ_2 is the inverse temperature

$$\lambda_2 = \frac{1}{T}. \quad (\text{A.3.6})$$

Using the Eq. (A.3.6) with Eq. (A.3.5) and considering Eq. (A.3.3), we get the following equation, indicating that λ_1 is the ratio of free energy and temperature, i.e. the Legendre transform of the entropy:

$$dS = d\left(\lambda_1 + \frac{U}{T}\right)$$

$$\lambda_1 = \frac{TS - U}{T} = -\frac{F}{T}.$$

The resultant canonical distribution is:

$$f_{cano}(\Gamma) = e^{\frac{F}{T}} e^{-\frac{\mathbf{H}(\Gamma)}{T}}.$$

The third and final definition of entropy replaces the last Dirac function in Eq. (A.3.2) with a third Lagrangian term.

$$S(L, U)$$

$$= - \int f(\Gamma) \ln f(\Gamma) d\Gamma -$$

$$(\lambda_1 - 1) \left(\int f(\Gamma) d\Gamma - 1 \right) - \lambda_2 \left(\int f(\Gamma) \mathbf{H}(\Gamma) d\Gamma - U \right) - \lambda_3 \left(\int f(\Gamma) \mathbf{L}(\Gamma) d\Gamma - L \right).$$

Its maximum gives

$$e^{-\lambda_1} e^{-\lambda_2 \mathbf{H}(\Gamma)} e^{-\lambda_3 \mathbf{L}(\Gamma)}.$$

The values of λ_1, λ_2 and λ_3 are given by the corresponding Lagrangian terms, summarised as follows:

$$\lambda_1(\lambda_2, \lambda_3) = \ln \int e^{-\lambda_2 \mathbf{H}} e^{-\lambda_3 \mathbf{L}} d\Gamma$$

$$-\frac{\partial \lambda_1}{\partial \lambda_2} = U \tag{A.3.7}$$

$$-\frac{\partial \lambda_1}{\partial \lambda_3} = L. \tag{A.3.8}$$

Applying Eq. (A.3.7) and Eq. (A.3.8) into the total differential Eq. (A.3.4), we have

$$dS = \frac{1}{T} \left[-d\frac{\partial\lambda_1}{\partial\lambda_2} - Pd\frac{\partial\lambda_1}{\partial\lambda_3} \right].$$

The first term above can be rewritten by using the formula $ydx = d(xy) - xdy$:

$$d\frac{\partial\lambda_1}{\partial\lambda_2} = \frac{1}{\lambda_2} \lambda_2 d\frac{\partial\lambda_1}{\partial\lambda_2} = \frac{1}{\lambda_2} \left(d\lambda_2 \frac{\partial\lambda_1}{\partial\lambda_2} - \frac{\partial\lambda_1}{\partial\lambda_2} d\lambda_2 \right).$$

And then using $d\lambda_1 = \frac{\partial\lambda_1}{\partial\lambda_2}d\lambda_2 + \frac{\partial\lambda_1}{\partial\lambda_3}d\lambda_3$, the equation above is transformed as:

$$d\frac{\partial\lambda_1}{\partial\lambda_2} = \frac{1}{\lambda_2} \left(d\lambda_2 \frac{\partial\lambda_1}{\partial\lambda_2} - d\lambda_1 + \frac{\partial\lambda_1}{\partial\lambda_3} d\lambda_3 \right).$$

And using $ydx = d(xy) - xdy$ again, we have

$$d\frac{\partial\lambda_1}{\partial\lambda_2} = \frac{1}{\lambda_2} \left(d\lambda_2 \frac{\partial\lambda_1}{\partial\lambda_2} - d\lambda_1 + d\frac{\partial\lambda_1}{\partial\lambda_3} \lambda_3 - \lambda_3 d\frac{\partial\lambda_1}{\partial\lambda_3} \right).$$

Combining those equations together, we finally get

$$dS = \frac{1}{T} \frac{1}{\lambda_2} \left(d\lambda_1 - d\lambda_2 \frac{\partial\lambda_1}{\partial\lambda_2} - d\lambda_3 \frac{\partial\lambda_1}{\partial\lambda_3} \right) + \left(\frac{1}{T} \frac{\lambda_3}{\lambda_2} - \frac{P}{T} \right) d\frac{\partial\lambda_1}{\partial\lambda_3}. \quad (\text{A.3.9})$$

To make the right-hand side a total differential, the only choice of λ_2 and λ_3 are

$$\lambda_2 = \frac{1}{T}$$

$$\lambda_3 = \frac{P}{T}.$$

Applying these terms back to Eq. (A.3.9) we find that λ_1 is the ratio between the Gibbs function and temperature, the other Legendre transform of entropy:

$$dS = d \left(\lambda_1 + \frac{U}{T} + \frac{PL}{T} \right)$$

$$\lambda_1 = \frac{TS - U - PL}{T} = -\frac{G}{T}.$$

The resultant Gibbs distribution becomes:

$$f_{Gibbs}(\Gamma) = e^{\frac{G}{T}} e^{-\frac{H(\Gamma) + PL(\Gamma)}{T}}.$$

In summary, the microcanonical distribution maximises entropy on the interface of equal-Hamiltonian and equal-length surfaces, the canonical distribution is the one that maximises entropy on the equal-length surface, whereas the Gibbs distribution is the one that maximises entropy in the whole phase space. Temperature corresponds to the multiplier for the average Hamiltonian constraint and pressure corresponds to the multiplier for the average length constraint. The Lagrangian multiplier for the normalisation condition is entropy and its Legendre transform. There is a profound connection between the method of Lagrangian multiplier and Legendre transform, with further details to be found in the classic [Courant and Hilbert, 1962].

A.4 Approximate equivalence between canonical and Gibbs distribution for linear chains

We aim at proving the following limit:

$$\begin{aligned} & \lim_{N \rightarrow +\infty} \lim_{L \rightarrow +\infty} \frac{-T \frac{\partial}{\partial L} \int \prod_{k=1}^N e^{-\frac{V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) dq_k}{\int \prod_{k=1}^N e^{-\frac{V(q_k)}{T}} \delta(\sum_{k=1}^N q_k - L) dq_k} \\ &= \frac{\int -\frac{\partial V(q)}{\partial q} e^{-\frac{V(q) + Pq}{T}} dq}{\int e^{-\frac{V(q) + Pq}{T}} dq}, \end{aligned} \quad (\text{A.4.1})$$

with the subsidiary condition that the ratio between L and N is constant:

$$\frac{L}{N} = \rho^{-1}. \quad (\text{A.4.2})$$

First, we replace the Dirac equation on the left-hand side of Eq. (A.4.1) with $\delta(x) = e^{ikx}$:

$$\begin{aligned}
& \lim_{N \rightarrow +\infty} \lim_{L \rightarrow +\infty} \frac{T \frac{\partial}{\partial L} \int \prod_{k=1}^N e^{-\frac{V(q_k)}{T}} e^{ik(\sum_{k=1}^N q_k - L)} dq_k d\mathbf{k}}{\int \prod_{k=1}^N e^{-\frac{V(q_k)}{T}} e^{ik(\sum_{k=1}^N q_k - L)} dq_k d\mathbf{k}} \\
&= \lim_{N \rightarrow +\infty} \lim_{L \rightarrow +\infty} \frac{T \frac{\partial}{\partial L} \int f(\mathbf{k}, L, N, T)^N d\mathbf{k}}{\int f(\mathbf{k}, L, N, T)^N d\mathbf{k}} \\
&\propto \frac{T \frac{\partial}{\partial L} f(\mathbf{k}_{\max}, L, N, T)^N}{f(\mathbf{k}_{\max}, L, N, T)^N} \\
&= -i\mathbf{k}_{\max} T.
\end{aligned} \tag{A.4.3}$$

Here the $f(\mathbf{k}, L, N, T)$ is defined as:

$$\begin{aligned}
f(\mathbf{k}, L, N, T) &= \int e^{-\frac{V(q)}{T} + i\mathbf{k}q - i\mathbf{k}\frac{L}{N}} dq \\
&= \int e^{-\frac{V(q)}{T} + i\mathbf{k}q - i\mathbf{k}\rho^{-1}} dq,
\end{aligned}$$

which remains invariant as N and L increase synchronously with the ratio being constant. That's why in the third line of Eq. (A.4.3) we make the integral proportional to the stationary value of $f(\mathbf{k}, L, N, T)$ taken at $\mathbf{k}_{\max}$, whose coordinate is determined by

$$\left(\frac{\partial f}{\partial \mathbf{k}} \right)_{\mathbf{k}=\mathbf{k}_{\max}} = \int (q - \rho^{-1}) e^{-\frac{V(q)}{T} + i\mathbf{k}_{\max}q - i\mathbf{k}_{\max}\rho^{-1}} dq = 0.$$

This can be written into an equivalent form:

$$\begin{aligned}
\rho^{-1} &= \frac{\int q e^{-\frac{V(q)}{T} + i\mathbf{k}_{\max}q - i\mathbf{k}_{\max}\rho^{-1}} dq}{\int e^{-\frac{V(q)}{T} + i\mathbf{k}_{\max}q - i\mathbf{k}_{\max}\rho^{-1}} dq} \\
&= \frac{\int q e^{-\frac{V(q)}{T} + i\mathbf{k}_{\max}q} dq}{\int e^{-\frac{V(q)}{T} + i\mathbf{k}_{\max}q} dq}.
\end{aligned} \tag{A.4.4}$$

Now, solve the $ik_{\max}$ term above through integration by part on the denominator:

$$\begin{aligned}
 \rho^{-1} &= \frac{\int q e^{-\frac{V(q)}{T} + ik_{\max}q} dq}{\frac{1}{ik_{\max}} \int e^{-\frac{V(q)}{T}} d e^{ik_{\max}q}} \\
 &= \frac{\int q e^{-\frac{V(q)}{T} + ik_{\max}q} dq}{\frac{1}{ik_{\max}T} \int \frac{\partial V(q)}{\partial q} e^{-\frac{V(q)}{T} + ik_{\max}q} dq} \\
 &= \frac{\rho^{-1}}{\frac{1}{ik_{\max}T} \frac{\int \frac{\partial V(q)}{\partial q} e^{-\frac{V(q)}{T} + ik_{\max}q} dq}{\int e^{-\frac{V(q)}{T} + ik_{\max}q} dq}}.
 \end{aligned}$$

The third equality above has used Eq. (A.4.4) by dividing $\int e^{-\frac{V(q)}{T} + ik_{\max}q} dq$ on both numerator and denominator. Now we have the following result:

$$ik_{\max}T = \frac{\int \frac{\partial V(q)}{\partial q} e^{-\frac{V(q)}{T} + ik_{\max}q} dq}{\int e^{-\frac{V(q)}{T} + ik_{\max}q} dq}$$

which, combined with Eq. (A.4.3), proves the equality in Eq. (A.4.1) as long as we take $ik_{\max} = -\frac{P}{T}$.

Properties of monodimensional chains

B.1 Eulerian form of thermodynamic fluxes

The Eulerian form of thermodynamic fluxes could be derived following the derivation in [Todd and Daivis, 2017] adapted to our system. First, we have a balance equation of energy and momentum:

$$\frac{\partial \rho e}{\partial t} = -\frac{\partial}{\partial x} J_q - \frac{\partial}{\partial x} (\rho e v + P v) \quad (\text{B.1.1})$$

$$\frac{\partial \rho v}{\partial t} = -\frac{\partial}{\partial x} P - \frac{\partial}{\partial x} \rho v v + \rho F^e. \quad (\text{B.1.2})$$

The first partial differential on the right side of the equations is due to the thermodynamic flux and the second is because of convective flow, e.g. the variation of average position. For chains of oscillators, no matter if single or coupled, the average position of each oscillator is fixed in steady states. The convection term could be reduced to zero and we can apply a spatial Fourier transform on both sides of Eq. (B.1.1) and Eq. (B.1.2) to cancel

the partial differential on space. We have:

$$\tilde{J}_q = \frac{1}{ik} \frac{\partial}{\partial t} \tilde{\rho} e \quad (\text{B.1.3})$$

$$\tilde{P} = \frac{1}{ik} \frac{\partial}{\partial t} \tilde{\rho} \tilde{v}. \quad (\text{B.1.4})$$

For oscillator systems, the distribution of momentum and energy is a summation of δ functions:

$$\rho e(x, t) = \sum_i^N e_i(t) \delta(x - x_i)$$

$$\rho v(x, t) = \sum_i^N m_i v_i(t) \delta(x - x_i)$$

and their Fourier modes are given by:

$$\tilde{\rho} e(k, t) = \sum_i^N e_i(t) e^{ikx_i(t)} \quad (\text{B.1.5})$$

$$\tilde{\rho} \tilde{v}(k, t) = \sum_i^N m_i v_i(t) e^{ikx_i(t)}. \quad (\text{B.1.6})$$

Combining Eq. (B.1.5) and Eq. (B.1.6) with Eq. (B.1.3) and Eq. (B.1.4), expanding the partial differential and gathering the terms, we obtain:

$$\tilde{J}_q(k, t) = \frac{1}{ik} \sum_i^N \dot{e}_i(t) e^{ikx_i} + \sum_{i=1}^N e_i v_i e^{ikx_i}$$

$$\tilde{P}(k, t) = \frac{1}{ik} \sum_i^N m_i \dot{v}_i(t) e^{ikx_i} + \sum_{i=1}^N m_i v_i v_i e^{ikx_i},$$

then applying an inverse transformation, by using the Fourier formula, we have:

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{e^{ikx}}{ik} dk = \text{sgn}(x_i - x).$$

This gives us the formula of heat flux and pressure in real space:

$$J_q(x, t) = \frac{1}{2} \sum_i^N \dot{e}_i \text{sgn}(x_i - x) + \sum_{i=1}^N e_i v_i \delta(x_i - x)$$

$$P(x, t) = \frac{1}{2} \sum_i^N m_i \dot{v}_i \text{sgn}(x_i - x) + \sum_{i=1}^N m_i v_i v_i \delta(x_i - x)$$

By Newton's law, the $\dot{v}_i$ could be expanded as the net force. For chains with first nearest interactions, it could be written as:

$$\begin{aligned} P(x, t) &= \frac{1}{2} \sum_i^N \left[-\frac{\partial V(x_i - x_{i-1})}{\partial x_i} + \frac{\partial V(x_{i+1} - x_i)}{\partial x_i} \right] \text{sgn}(x_i - x) + \sum_{i=1}^N m_i v_i v_i \delta(x_i - x) \\ &= \frac{1}{2} \sum_{i=1}^N (F_{i-1,i} - F_{i,i+1}) \text{sgn}(x_i - x) + \sum_{i=1}^N m_i v_i v_i \delta(x_i - x) \\ &= P^V + P^K \end{aligned}$$

The first summation over sgn functions above is interpreted as the “potential” part of pressure, because it is the momentum flux caused by the force, i.e. the negative potential differential between each pair of neighboring particle. In that expression, the $F_{i-1,i}$ and $F_{i,i+1}$ denote the force from the $(i-1)^{th}$ particle to the i^{th} particle and from the i^{th} to the $(i+1)^{th}$ particle. Since the potential we choose depends on $|x_{i+1} - x_i|$ only, there is $F_{i+1,i} = -F_{i,i+1}$.

On the other hand, the second summation over δ functions is denoted as the “kinetic” part of pressure, because it is the momentum flux taken by the moving particles.

By shifting indices, the potential part of pressure may be rewritten as:

$$\begin{aligned} 2P^V(x, t) &= \sum_{i=1}^N (F_{i-1,i} - F_{i,i+1}) \text{sgn}(x_i - x) \\ &= \sum_{i=1}^N F_{i-1,i} \text{sgn}(x_i - x) - \sum_{j=2}^{N+1} F_{j-1,j} \text{sgn}(x_{j-1} - x) \\ &= F_{0,1} \text{sgn}(x_0 - x) + \sum_{k=2}^N F_{k-1,k} [\text{sgn}(x_k - x) - \text{sgn}(x_{k-1} - x)] - \\ &\quad - F_{N,N+1} \text{sgn}(x_N - x). \end{aligned}$$

Under fixed boundary conditions, for any position inside the chain, i.e. $x = \theta \in (x_1, x_N)$, the first sgn takes the value -1 and the last takes 1 . For the middle summation, all terms will be canceled except when x_k and x_{k-1} are on different sides of $x = \theta$. In this case we definitely have $\text{sgn}(x_k - x) = 1$ and $\text{sgn}(x_{k-1} - x) = -1$ because for Lennard-Jones chains the order of particles will be kept as $x_1 < x_2 < \dots < x_N$. In the end, the P^V can be expressed as

$$P^V(x = \theta, t) = \frac{1}{2}(F_{0,1} - F_{N,N+1}) + F_{k-1,k} \quad x_{k-1} < \theta < x_k.$$

As for the kinetic pressure, the δ functions can be converted using the fact that they are proportional to the derivative of the sgn function. This makes the expression easier to compute:

$$\begin{aligned} P^K(x = \theta, t) &= \sum_{i=1}^N m_i v_i \delta(x_i - \theta) = \frac{1}{2} \sum_{i=1}^N m_i v_i \frac{d}{dt} (\text{sgn}[x_i - \theta]) \\ &= \frac{1}{\Delta} \sum m_i v_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \quad t - \Delta/2 < t_{i,j} < t + \Delta/2. \end{aligned} \quad (\text{B.1.7})$$

The meaning of the last equality is made clearer by the definition of derivative

$$\frac{1}{2} \frac{d}{dt} \text{sgn}[x_i - \theta] = \lim_{\Delta \rightarrow 0} \frac{1}{2} \frac{\text{sgn}[x_i(t + \Delta/2) - \theta] - \text{sgn}[x_i(t - \Delta/2) - \theta]}{\Delta}.$$

The expression above equals $1/\Delta$ when $x_i(t - \Delta/2) < \theta < x_i(t + \Delta/2)$, i.e. the i^{th} particle crosses the threshold in $(t - \Delta/2, t + \Delta/2)$ with positive velocity, and it turns to $-1/\Delta$, when $x_i(t - \Delta/2) > \theta > x_i(t + \Delta/2)$, i.e. the i^{th} particle crosses the threshold in $(t - \Delta/2, t + \Delta/2)$ with negative velocity. Hence, the term $t_{i,j}$ in Eq. (B.1.7) is the time when the i^{th} particle crosses the threshold $x = \theta$ for the j^{th} time.

Finally, the Eulerian formula for pressure could be written as:

$$\begin{aligned}
 P(x = \theta, t) &= P^V(x = \theta, t) + P^K(x = \theta, t) \\
 &= \frac{1}{2}(F_{0,1} - F_{N,N+1}) + F_{k-1,k} + \frac{1}{\Delta} \sum m_i v_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \quad (\text{B.1.8}) \\
 x_{k-1}(t) &< \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2.
 \end{aligned}$$

Similarly, the Eulerian formula for the heat flux becomes:

$$\begin{aligned}
 J(x = \theta, t) &= J^V(x = \theta, t) + J^K(x = \theta, t) \\
 &= \frac{1}{2}(J_{0,1} - J_{N,N+1}) + J_{k-1,k} + \frac{1}{\Delta} \sum e_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \quad (\text{B.1.9}) \\
 x_{k-1}(t) &< \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2,
 \end{aligned}$$

where the $J_{k-1,k}$ is the energy flux due to the force $F_{k-1,k}$:

$$J_{k-1,k} = \frac{1}{2}(v_{k-1} + v_k)F_{k-1,k}.$$

Both Eq. (B.1.8) and Eq. (B.1.9) denote the “instantaneous” pressure and heat flux. For steady states, we need to run an average over long time (ideally speaking, if the system is ergodic, the time average will be equivalent to ensemble average, in the limit when time goes to infinity), and the average on the boundary term will be canceled, since at steady state the average momentum and energy of the whole system must be constant. So the final expression will be:

$$\begin{aligned}
 \langle P(x = \theta, t) \rangle &= \langle P^V(x = \theta, t) \rangle + \langle P^K(x = \theta, t) \rangle \\
 &= \langle F_{k-1,k} \rangle + \left\langle \frac{1}{\Delta} \sum m_i v_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \right\rangle \\
 x_{k-1}(t) &< \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2 \\
 \\
 \langle J(x = \theta, t) \rangle &= \langle J^V(x = \theta, t) \rangle + \langle J^K(x = \theta, t) \rangle \\
 &= \langle J_{k-1,k} \rangle + \left\langle \frac{1}{\Delta} \sum e_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \right\rangle \\
 x_{k-1}(t) &< \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2.
 \end{aligned}$$

The other point worthy of noting is that both expressions above are for chains with nearest neighbor interactions only. If there is a longer range of interactions, for example, second nearest neighbor interactions, the previous expressions should be modified as:

$$\begin{aligned}
\langle P(x = \theta, t) \rangle &= \langle P^V(x = \theta, t) \rangle + \langle P^K(x = \theta, t) \rangle \\
&= \langle F_{k-1,k}^{(1)} \rangle + \langle F_{k-1,k+1}^{(2)} \rangle + \langle F_{k-1,k+1}^{(2)} \rangle \\
&\quad + \left\langle \frac{1}{\Delta} \sum m_i v_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \right\rangle \\
&\quad x_{k-1}(t) < \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2
\end{aligned}$$

$$\begin{aligned}
\langle J(x = \theta, t) \rangle &= \langle J^V(x = \theta, t) \rangle + \langle J^K(x = \theta, t) \rangle \\
&= \langle J_{k-1,k}^1 \rangle + \langle J_{k-2,k}^2 \rangle + \langle J_{k-1,k+1}^2 \rangle + \left\langle \frac{1}{\Delta} \sum e_i(t_{i,j}) \text{sgn}[v_i(t_{i,j})] \right\rangle \\
&\quad x_{k-1}(t) < \theta < x_k(t) \quad t - \Delta/2 < t_{i,j} < t + \Delta/2,
\end{aligned}$$

where the $F^{(1)}$ and $F^{(2)}$ mean the force between the nearest neighbor and second nearest neighbour respectively and J^1 and J^2 are heat fluxes caused by them.

B.2 Fitting by microscopic van der Waals equation in standard form

The microscopic van der Waals equation in standard form [Sun et al., 2025] can also be used to fit the pressure P measured by simulating Lennard-Jones chains at equilibrium under thermostats at temperature T and fixed-length condition of $L = \frac{N+1}{\rho}$. Remember that though we use the terms “pressure” and “temperature” that are meant to describe macroscopic properties, all these considerations here are not macroscopic but on single particles only. To make the fitting easier, here we use P/ρ as the independent variable:

$$\frac{P}{\rho} = \frac{T}{1 - \rho b} - a\rho.$$

Similar to the microscopic van der Waals equation in linear form, the standard form is not adequate to describe the behaviour of equilibrium chains at low temperature (see Fig. B.1a), as the ratio between pressure and density does not seem to change sensibly with density. It also becomes a good model of the chain's behaviour as temperature increases, as can be seen from Fig. B.1b to Fig. B.1d. It is a very good predictor for temperature as high as $T = 0.5$, as shown in Fig. B.2a. Also at high temperatures, as per the linear form, it converges to the Tonks equation with $a = 0$ as illustrated from Fig. B.2b to Fig. B.2d. Again, all these considerations are microscopic only.

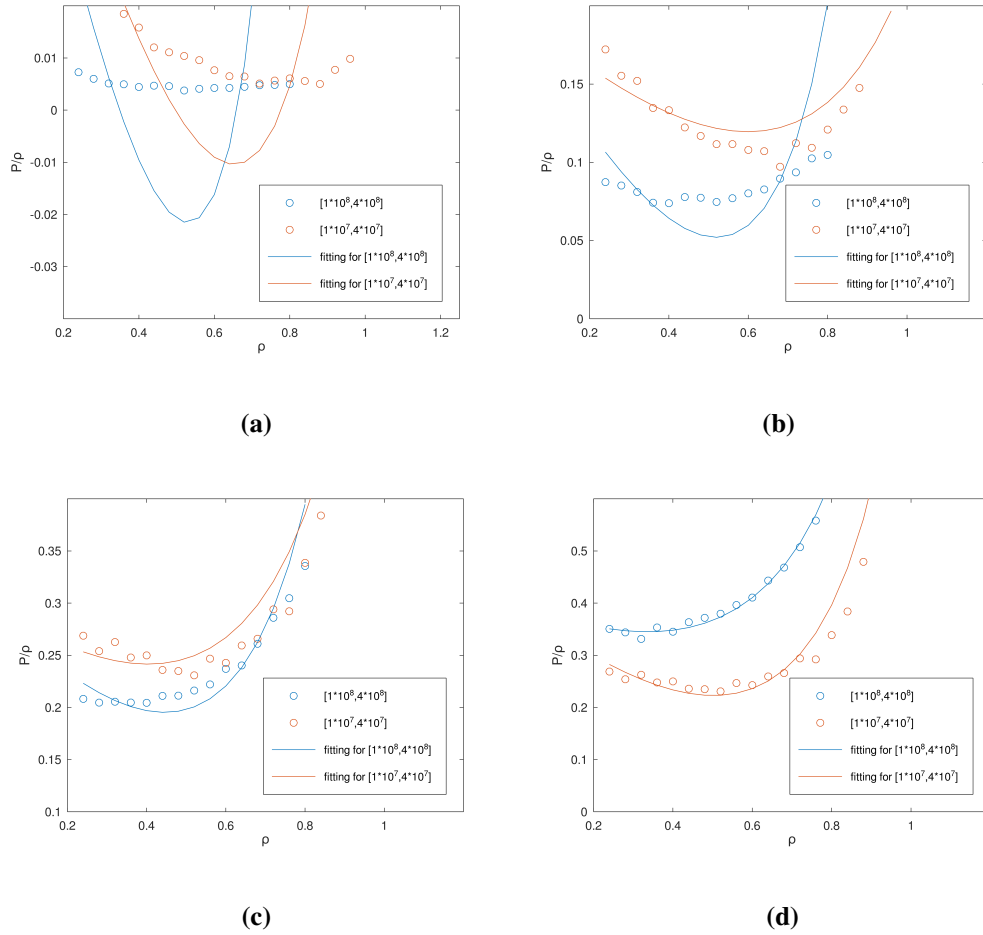


Figure B.1: An example of four profiles for P/ρ versus ρ from simulation, at increasing but low temperatures. (a) At $T_L = T_R = 0.1$ the microscopic van der Waals equation in standard form fails everywhere due to the low temperature regime, but as the temperature is risen to (b) $T_L = T_R = 0.2$, (c) $T_L = T_R = 0.3$ and (d) $T_L = T_R = 0.4$ the agreement gradually improves and becomes almost complete, except for very high densities.

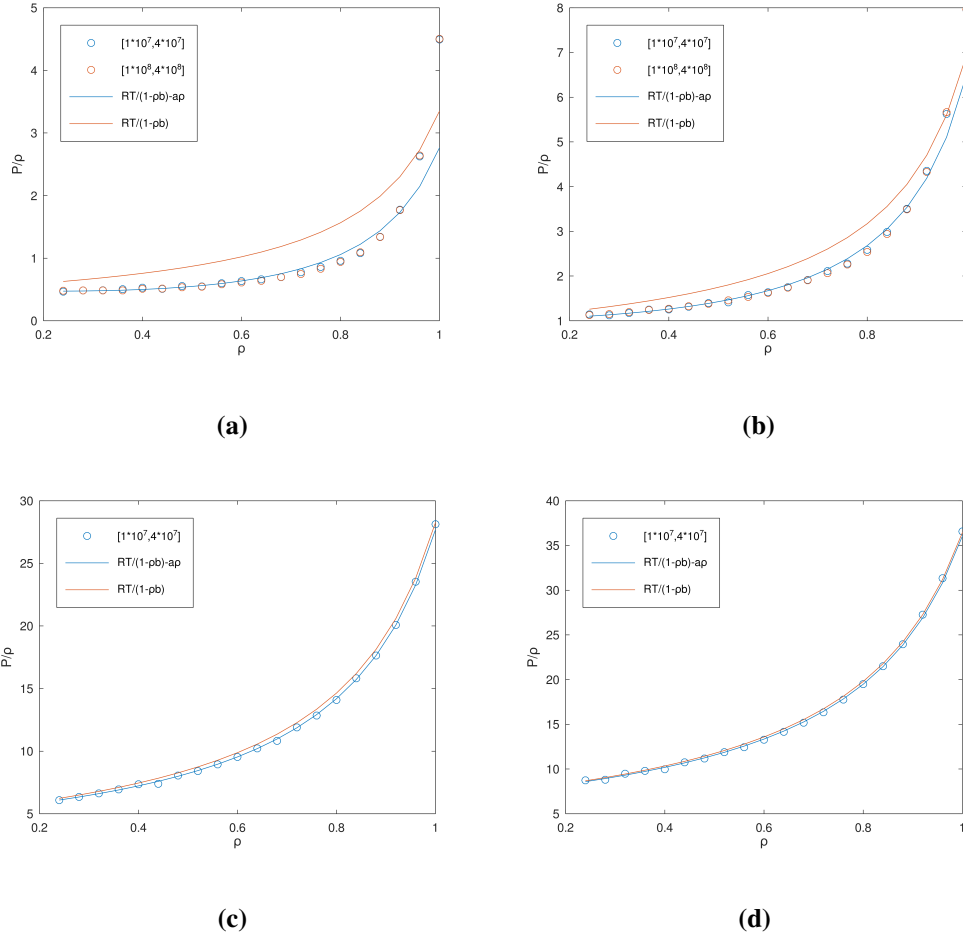


Figure B.2: Example of four profiles for P/ρ versus ρ from simulation, at moderate to high temperatures. (a) At $T_L = T_R = 0.5$, the microscopic van der Waals equation in standard form works quite well for almost every density considered, except for high ones. The accuracy increases for higher temperatures such as (b) $T_L = T_R = 1.0$, and the data are perfectly fit for higher temperatures (c) $T_L = T_R = 5.0$ and (d) $T_L = T_R = 7.0$. The microscopic Tonks equation increases its accuracy as temperature increases and is generally an overestimation of the actual data for average temperatures, as shown in panels (a) and (b). Everything is meant to be applied to single particles, microscopic regimes only.

B.3 Langevin and Nosé Hoover thermostats

The choice of thermostats influences the numerical values of correlation. For instance, as shown in Fig. B.3a and B.3b, Langevin thermostats yield weaker correlation than Nosé Hoover (NH) thermostats at low temperatures $T_L = 0.1$, $T_R = 1.0$ and strong constraining force $f_p = 5.0$. Note that there is $f_p = P$ by using Langevin thermostats since the random force exerted by the Langevin thermostat follows a Gaussian distribution with zero mean value.

Despite those differences, the qualitative conclusions of this work remain unchanged. Following the reduced correlations, the range of validity for Eq. (3.1.2), (3.1.3) expands in the Langevin case. Comparing Fig. B.3c and Fig. B.3d, we find that κ_1 and κ_2 fit simulations using Langevin thermostats but deviate from those using NH thermostats under otherwise identical conditions.

Furthermore, the factorised distribution in Eq. (3.1.1) is also proved to be a sufficient but unnecessary condition for the validity of κ_1 , as illustrated in Fig. B.4. Note that this figure is similar to Fig. 3.11 in the main text, but is made by simulations using Langevin thermostats with the Verlet integrator, whereas Fig. 3.11 is based on Nosé-Hoover thermostats with a Runge-Kutta integrator. This consistency across distinct numerical methodologies confirms that our conclusions reflect intrinsic properties of monodimensional Lennard-Jones chains.

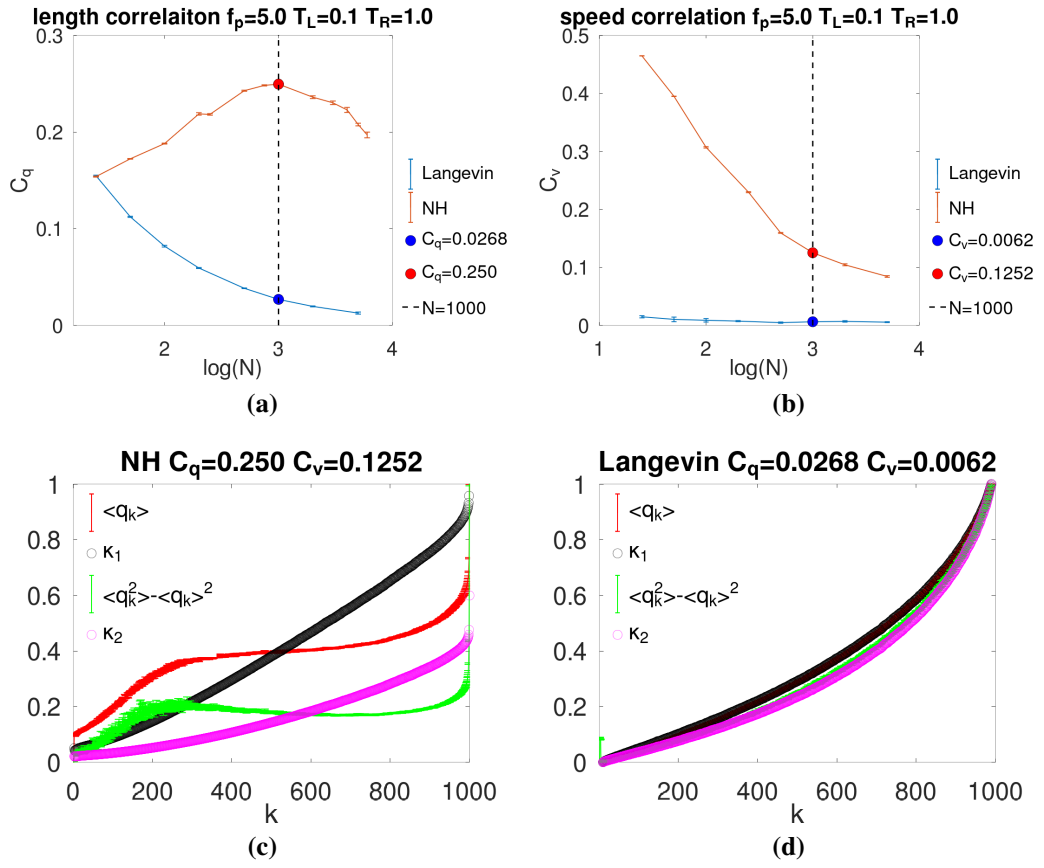


Figure B.3: (a) The length correlation C_q by using Langevin and Nosé Hoover thermostats. (b) The speed correlation. (c) Test of κ_1 and κ_2 using Nosé Hoover thermostats. (d) The same test using Langevin thermostats.

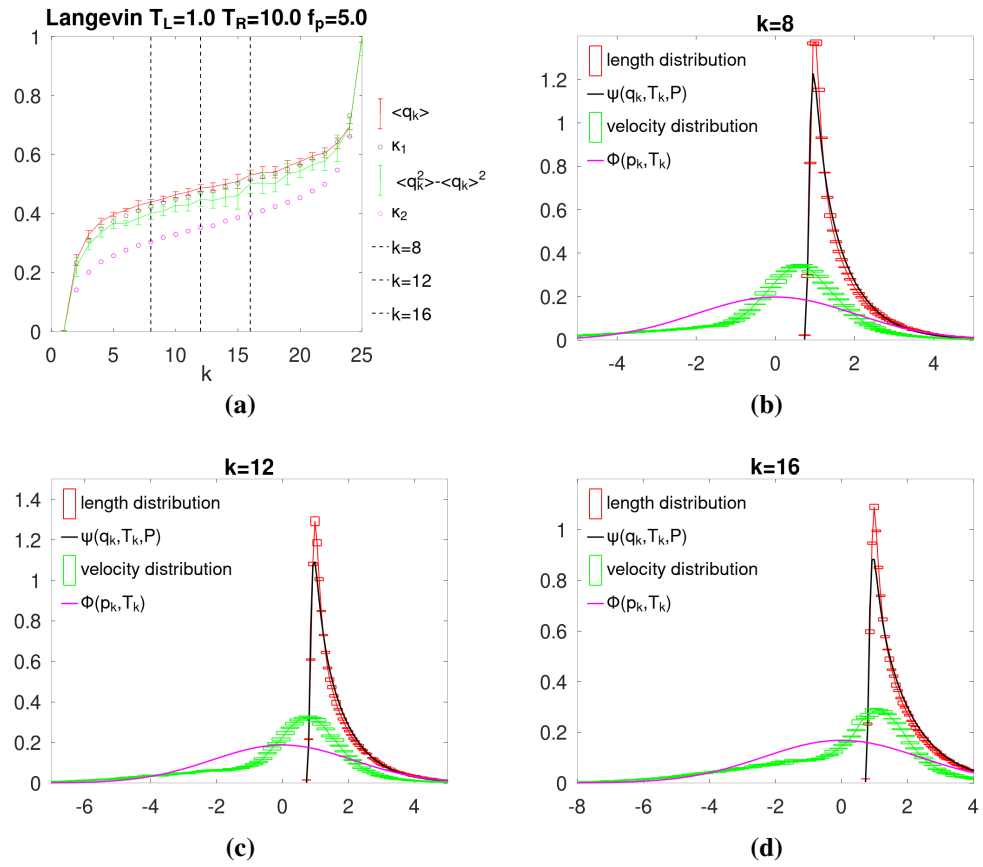


Figure B.4: Same approach with Fig. 3.11 in the main text but produced by Langevin thermostats.

Publications

- *Publication:* Sun, R, Rondoni, L, Frascoli, F, On a Microscopic Equation of State for Lennard-Jones Chains, Commun. Nonlinear Sci. Numer. Simul., **148**, 2025, p 108843
- *Publication:* Correlations and fluctuations in monodimensional chains of Lennard-Jones oscillators, submitted to Chaos Solit. Fract.
- *Publication:* Correlations and fluctuations in coupled chains, in preparation