

Influence of flexure and crowding on nanoscale thermal transport

by

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B.Tech. (Hons.), Indian Institute of Technology Ropar, 2016

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

Master of Applied Science

in

The Faculty of Graduate and Postdoctoral Studies

(Mechanical Engineering)

The University of British Columbia

(Vancouver)

November 2020

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Abstract

Nanoscale thermal transport has been studied by scientists for decades. Low dimensional materials have shown two significant characteristics - (1) Thermal conductivity (κ) can be dependent on the size of the system, (2) A significant reduction in κ has been observed in an array-like arrangement. Thus, it is essential to understand the mechanism to tailor material properties for different applications.

Fourier's law is an empirical relation between average thermal flux and temperature gradient. It indicates κ is an intrinsic material property, but studies have shown that it breaks down in low-dimensional systems. The heat flux (J) depends on the size of the system (N) by the relation $J \propto N^{\alpha-1}$. Traditionally, 1D studies have mostly focused on the effect of two-body interactions on κ . In this thesis, we study the effect of multibody interactions in the presence of two-body interactions on thermal transport. We use N_ℓ (number of persistence lengths) to define system size and study the asymptotic limit of NJ . The transition from ballistic to superdiffusive behaviour was observed near $100 N_\ell$ in the ordered systems. In contrast, disordered systems showed only superdiffusive transport. Coherent wave patterns emerged as thermal carriers in superdiffusive regimes. Further, modelling crowding as transverse pinning, we observe a non-monotonous transition from superdiffusive to ballistic behaviour as we increased the crowding.

While the single chain models have been extensively studied to understand the length dependence of κ , simulation studies on their bundles and forests are very few. One such example is the experimentally observed reduced heat conduction in carbon nanotube (CNT) forests compared to an isolated CNT. Here, the all-atom simulations require a significant computational expense. Therefore, we have used a coarse-grained model to study the heat flow in molecular forests by incorporating the concepts known from polymer physics and thermal transport to propose a generic picture of the reduction of κ . We show that a delicate balance between the bond orientations, the persistence length of an isolated Q1DM (Quasi-one dimensional material), and the non-bonded inter-chain interactions govern the reduction of κ .

Lay Summary

Nanomaterials have interested scientists for decades because of their tunable properties. One of these properties is the thermal conductivity (κ), which is constant in bulk materials. In nanomaterials, size dependence has been observed, i.e., large systems can have higher κ . Many models have been studied where only two-bodies can interact, like two masses connected with a spring. Multibody interactions, which can also reduce κ , have not been explored in detail. In this thesis, we introduce a three-body interaction and understand the size dependence of κ .

Further, it has been observed that the forest-like arrangement of these materials decreases κ . While simulating a forest will need substantial computational resources, we propose an equivalent model. We model millions of atoms with only a few hundreds of masses to study the reduction of κ .

Preface

The thesis discusses two models to study nanoscale thermal transport. Chapters 2 and 3 discuss a simple single chain with multibody and two-body potential. In Chapter 4, we propose a coarse-grained model for studying thermal transport in molecular forests. All the simulations have been done using the computational facility provided by the in-house computation facility at Quantum Matter Institute Cluster (LISA) and the Compute Canada Cluster. The description is as follows:

1. In Chapter 2, we study a single chain with multibody and two-body interactions. This work is under preparation: “Effect of multibody forces on the thermal transport of a single chain” by A. Bhardwaj, D. Mukherji, A. Nojeh, and A. S. Phani. Dr. Srikantha Phani proposed the idea. Aashish Bhardwaj developed and implemented the model in MATLAB, analyzed the data and produced the figures with the inputs from Dr. A. Srikantha Phani, Dr. Alireza Nojeh and Dr. Debashish Mukherji. Aashish Bhardwaj and Dr. A. Srikantha Phani are co-writing this draft.
2. In Chapter 3, we study a single chain with the pinning of transverse motion. Aashish Bhardwaj conceptualized the idea, developed the MATLAB codes and analyzed the data with inputs from Dr. A. Srikantha Phani, Dr. Alireza Nojeh and Dr. Debashish Mukherji.
3. In Chapter 4, we propose a generic coarse-grained model of the molecular forests. This work is under review, and a copy is available on <https://arxiv.org/abs/2005.10685> as: “Thermal transport in molecular forests” by A. Bhardwaj, A. S. Phani, A. Nojeh and D. Mukherji. Dr. Debashish Mukherji proposed the idea and wrote the manuscript. Aashish Bhardwaj developed the input scripts for LAMMPS simulations, ran the simulations, analyzed the data and produced the figures. All authors discussed the results and revised the content of the draft. The work has been done under the primary guidance of Dr. Debashish Mukherji, with inputs from Dr. A. Srikantha Phani and Dr. Alireza Nojeh. The simulations have also been done using the computational facility provided by UBC Advanced Research Computing.

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List of symbols

a - Non-dimensional lattice spacing ($\tilde{a}$)	$\mathbf{f}_i^b$ - Total force due to three-body interaction on i^{th} particle ($\tilde{k}_r \tilde{a}$)
α - Divergence exponent of thermal conductivity with the system size	$\mathbf{G}$ - Reciprocal lattice vector (m^{-1})
$\tilde{a}$ - Lattice spacing (m)	γ - Friction factor in Langevin bath ($\sqrt{\tilde{k}_r / \tilde{m}}$)
$C(t)$ - Autocorrelation function with 't' as time difference.	$\dot{\gamma}$ - Friction factor in Langevin bath ($1/\tau$)
C_v - Specific heat capacity (J/K/Kg)	Γ - Surface coverage ratio
d - Characteristic length scale of LJ potential (m)	Γ^* - Critical grafted density
$\mathcal{D}$ - Diameter of CNT (m)	$\mathcal{H}$ - Height of CNT forests (m)
δ_{ij} - Kronecker delta	H - Non-dimensional hamiltonian ($\tilde{k}_r \tilde{a}^2$)
$\mathcal{E}$ - Strain	$\hbar$ - Reduced Planck's constant (Js)
ε - Characteristic energy scale of LJ potential (J)	$\tilde{H}$ - Hamiltonian (J)
$\mathbf{e}_i$ - Normalized bond vector from i^{th} to $i + 1^{\text{th}}$ particle.	$I(\omega)$ - Transmittance function in harmonic limit
$\mathbf{f}_i$ - Total force on i^{th} particle ($\tilde{k}_r \tilde{a}$)	$\mathbf{J}$ - Heat flux ($\tilde{k}_r^{3/2} \tilde{a}^2 / \tilde{m}^{1/2}$)
$\mathbf{f}_i^a$ - Total force due to two-body interaction on i^{th} particle ($\tilde{k}_r \tilde{a}$)	$\dot{\mathbf{J}}$ - Heat flux ($\varepsilon / \tau / d^2$)
	J - Time average of $ \mathbf{J} $ ($\tilde{k}_r^{3/2} \tilde{a}^2 / \tilde{m}^{1/2}$)
	k_B - Boltzmann constant (J/K)
	κ - Thermal conductivity coefficient ($\tilde{k}_r^{3/2} \tilde{a} / \tilde{m}^{1/2} / \tilde{T}$)

$\kappa_{\parallel}$ - Thermal conductivity along the chain backbone in molecular forests ($\varepsilon/\tau/d^2$)	N_g - Number of grafted chains
$\kappa_{\perp}$ - Thermal conductivity perpendicular to the chain backbone in molecular forests ($\varepsilon/\tau/d^2$)	N_{ℓ} - Number of persistence lengths in the system
$\tilde{k}_r$ - Axial stiffness (N/m)	ω - Frequency ($\sqrt{\tilde{k}_r/\tilde{m}}$)
$\tilde{k}_{\theta}$ - Bending energy (J)	P_2 - Second Legendre polynomial
Λ - Mean free path (m)	ϕ - Angle of a bond vector with vector perpendicular to substrate in molecular forest (radian)
λ - Slenderness ratio of the system ($\tilde{k}_{\theta}/\tilde{k}_r/\tilde{a}^2$)	$\mathbf{p}_i$ - Non-dimensional momentum vector of i^{th} particle ($\tilde{m}\tilde{a}\sqrt{\tilde{k}_r/\tilde{m}}$)
ℓ_b - Bond length in Kremer-Grest model (d)	$\tilde{\mathbf{p}}$ - Momentum vector (Kg m/s)
$\tilde{\ell}_c$ - Contour length (m)	q - Number of pinned sites
ℓ_c - Non-dimensional contour length ($\tilde{a}$)	r_c - Cutoff radius for Lennard-Jones (LJ) potential (m)
$\tilde{\ell}_p$ - Persistence length (m)	ρ - Monomer number density (d^{-3})
ℓ_p - Non-dimensional persistence length ($\tilde{a}$)	R_g - Radius of gyration (d)
L_x - Dimension of the square plane on which monomers are grafted (d)	$\mathbf{R}_i$ - Position vector of i^{th} particle (m)
L_y - Dimension of the square plane on which monomers are grafted (d)	$\mathbf{r}_i$ - Non-dimensional position vector of i^{th} particle ($\tilde{a}$)
m - Non-dimensional mass of chain site ($\tilde{m}$)	$\Delta\mathbf{r}_i$ - Bond vector from i^{th} to $i+1^{\text{th}}$ particle ($\tilde{a}$)
$\tilde{m}$ - Mass (Kg)	R_{ee}^z - Chain end-to-end distances in z direction (d)
Δm - Disorder in mass ($\tilde{m}$)	$\sigma_{\parallel}^B$ - Virial Stress due to bonded interactions, perpendicular to the grafting surface in molecular forests (ε/d^{-3})
v - Pinning strength ($\tilde{k}_r$)	
N - Number of lattice sites	

$\tilde{T}$ - Temperature (K)	V_g - Group velocity (m/s)
τ - Characteristic time scale of LJ potential $\sqrt{\tilde{m}d^2/\epsilon}$	$\mathbf{v}_i$ - Velocity vector of i^{th} particle ($\tilde{a}/\sqrt{\tilde{k}_r/\tilde{m}}$)
$\hat{T}$ - Non-dimensional temperature (ϵ/k_B)	$ \mathbf{X} $ - Magnitude of displacement vector along chain backbone ($\tilde{a}$)
Δt - Time step ($\sqrt{\tilde{m}/\tilde{k}_r}$)	$ \mathbf{Y} $ - Magnitude of displacement vector perpendicular to chain backbone ($\tilde{a}$)
δt - Time step (τ)	$\mathbf{Z}$ - Impedance matrix
T_H and T_C - Non-dimensional temperature at hot and cold end ($\tilde{T}k_B/\tilde{k}_r/\tilde{a}^2$)	$\tilde{\zeta}_i(t)$ - A vector with both components as Gaussian random variable having zero mean and one variance.
θ_i - Total angle i^{th} with neighbouring particles (radian)	
t^* - Normalized time for different chain lengths	

Acknowledgements

I would like to first acknowledge my mother, Mrs. Vimlesh Kumari and my father Mr. Anil Bhardwaj. They have struggled a lot to see me here. It has always been their vision and hard work. I would also like to mention my little sister Shivani Bhardwaj who has been taking care of them back in India so that I can achieve what all of us dreamt of.

Then I would like to thank my research supervisors, Dr. A. Srikantha Phani and Dr. Alireza Nojeh, for giving me the opportunity to come to UBC. I cannot emphasize enough how much you two oriented me as a critical thinker. Srikanth's sincere attention to every step of my research and Alireza's direction are the stepping stones of this thesis.

I would also like to thank Dr. Debashish Mukherji, who has been an incredible guide for me. His mentoring has been extremely valuable. Be it teaching me Linux, LAMMPS, or polymer physics in general. Bearing with me despite being a novice in the field, he has guided me to a successful project.

I am thankful to my examination committee members: Dr. Joerg Rottler and Dr. Rajeev Jaiman, for generously offering their time to evaluate and constructively criticize my work.

My previous and current labmates, Ratul, Manav, Kui, Masoud, Reza, Shubham and Prabhat are the most sincere researchers I have met. They constantly motivated me throughout my stay in UBC to perform better and also taught me to stand up when I felt stuck. My friends Soham, Gorisha, Vedangi, Madhureeta, Deval, Bhavya, Kiran were always with me, through thick and thin. Sincere thanks to my roommates: Avilash and Pranav, for supporting me and being the awesome roommates you always are.

Last but not least, my teachers, especially Mrs. Renu Devgun and the late Mr. Naresh Devgun. Shaping my aspirations and motivating me to prepare for IIT, it has been a life-changing contribution.

To my family.

Chapter 1

Introduction

We deal with various materials in our daily life, each having a different combination of properties. A suitable combination of properties, be electrical or mechanical, is relevant to the application. For example, a combination of high stiffness and thermal conductivity of metals can be used for high-temperature applications. At the same time, the flexibility and insulating properties of polymers make them ideal for wearable technologies. Unfortunately, all the desired combinations cannot be accessed in bulk materials. 1D (1 Dimensional) and 2D (2 Dimensional) materials promise a lot of scope from this perspective. Some of the interesting properties are the balance between thermal conductivity (κ) and electrical conductivity, which is very relevant to electronics. High thermal conductivity and electrical conductivity are suitable for nanochip design, where thermal management is an issue [2]. In contrast, low thermal conductivity and high electrical conductivity are suitable for thermoelectric devices. Thus, there is a huge interest to tune both of these properties separately [3, 4]. Thermal conductivity (κ) in low dimension materials has interested researchers for decades as we can tune the κ by changing the size of the system. Fourier's law, which is an empirical relation between the heat flux (J) and temperature gradient in a system, breaks down [5–12]. The κ is found to be increasing with the size of the system in many systems. This behaviour, being termed as anomalous, can provide new opportunities.

It has also been observed that 1D and 2D materials generally exhibit ultrahigh thermal conductivity, which is a significant deviation from their bulk behaviour [13–17]. Since κ is the contribution of carriers like electrons, phonons, solitons, etc., it becomes necessary to understand how these carriers are affected by the system's dimensionality. In this thesis, we are only concerned with the phononic contribution. Phonons carry energy in the form of lattice vibrations. They are defined as the collective excitation of a periodic arrangement of atoms. While phonons can carry energy in a system, they can be hindered or reflected by various scattering sources in the system. Scattering can be due to anharmonicity, impurities, or boundaries and play an essential role in defining the system's behaviour. Low-dimensional systems are believed

to have less intrinsic scattering in the system, which leads to divergent κ . These materials have been studied to calculate α in relation - $\kappa \propto L^\alpha$, where $0 < \alpha < 1$ and L is the size of the system. Many experiments on 1D materials like carbon nanotube (CNT) [18], and Carbyne [19] also confirm that it is not a system-specific phenomenon. Hence, tuning κ needs understanding of the underlying mechanism. It becomes necessary to have models that can map certain properties of low dimension materials and thus have a broad application in tuning thermal conductivity for different applications.

Various Molecular Dynamics (MD) simulations and 1D chain models have been studied [20–22], to understand the divergence of κ . While MD simulations use complex potentials like AIREBO, it is difficult to separate each mode's contribution in highly non-linear regimes. Thus it is necessary to understand the impact of different modes like longitudinal, bending and twisting by having a simplified model. Simple chain models find relevance for this study. In these models, a harmonic bond is used, and then additional scattering methods are introduced. We can study the effect of each mechanism. Thus, many toy models of the 1D chain have been studied. Point masses are introduced at lattice sites, which are connected by springs. A thermal gradient is introduced with the help of thermal baths at the two ends of the chain. While the literature has reported both finite and divergent κ , depending on factors like potentials or boundary conditions, they have mostly concentrated on two-body interactions [5,6,9,23]. Only focusing on one type of interaction can hinder the understanding as many-body potentials are also present in a lattice. These potentials can lead to longitudinal, bending, and twisting modes in a lattice. Bending mode is the in-plane distortion of the included angle of particles, while longitudinal mode involves distortion of bonds. Additional modes like torsion (out of plane distortion of torsion angle) can also exist in materials. We try to study how these additional modes will affect thermal conductivity. Our aim here is to introduce a simple multibody interaction as a three-body flexural spring. These interactions are interesting because of their dispersive nature as two-body interactions, or longitudinal vibrations are non-dispersive. Thus adding this transverse degree of freedom can lead to a possible interaction between two types of waves. This interaction can provide an additional mode of scattering, which has not been explored extensively. Many questions arise, like - will thermal conductivity still be divergent? How will it affect the additional modes of wave scattering (like mass disorder)? We will come back to all the questions we are trying to answer in the next sections.

In the later part of the thesis, we will try to understand how κ is affected by interchain interactions. We have seen that these materials show interesting behaviour even when inter-

chain interactions are not considered. Another anomalous behaviour of these low dimensional materials show is - a significant knockdown in κ in array or forest arrangement. Some of the interesting effects like heat trap has been observed in CNT forests. Despite the high κ of individual CNT, the localization of heat spot was observed in a forest by [24]. The source of this localization is yet to be understood clearly. However, the interaction of CNTs is believed to be a contributor to the effect. Moreover, the defects such as kinks and the fusion of tubes may also lead to additional anharmonicities which have not been understood properly. Thus it is essential to understand how these additional scattering sources can affect the total conductivity. We first study the effect of these interactions by modelling a single chain with restricted transverse DOF. We comment on both the impact on κ as well as α , which has not been explored before. In our final section, we combine concepts of multiscale modelling with polymer physics to present a model of a forest to unveil a generic picture of κ reduction in molecular forests.

We will discuss some standard literature of the thermal conductivity and phonons as carriers.

1.1 Thermal conductivity

Thermal conductivity and thermal conductance of a material are very relevant to the discussion of thermal transport. The definitions of these properties are derived from the famous Fourier's law. The law defines the relation between J (thermal flux), A (area) and dT/dx (temperature gradient), given by

$$J = -\kappa A \frac{dT}{dx}. \quad (1.1)$$

Thermal conductivity is thus defined as heat current per unit area and unit temperature gradient. On the other hand, thermal conductance is defined as heat current per unit area per unit temperature difference applied. Thermal transport is generally studied by measuring J . It is then multiplied with system size (L) to find the behaviour of κ . This thesis assumes N lattice sites with unit spacing and studies $NJ \propto \kappa$ with the constant temperature at two ends. Thus plotting NJ vs. N , we can establish different regimes of our system. In log-log plots, we can assume $NJ \propto N^\alpha$ to find α , which indicates the process of thermal transport. The different processes of thermal transport and the respective α values are described as:

1. Ballistic transport ($\alpha = 1$) - The mean free path (MFP) of the phonons is very long compared to the size of the system.

2. Superdiffusive transport ($1 > \alpha > 0$) - The MFP of the phonons is comparable to the size of the system.
3. Diffusive transport ($\alpha = 0$) - The MFP of the phonons is very short compared to the size of the system. It results in finite κ in bulk materials.
4. Sub-diffusive transport ($\alpha < 0$) - Extended phonon modes are localized. Thus, the system acts as an insulator.

It is interesting to know how the theory developed in the area. Fourier's law was proposed in 1811, which still holds relevance to most thermal transport problems in bulk materials. It predicts the diffusive behaviour of J as thermal conductivity in the bulk material is an intrinsic property. The first breakthrough in understanding thermal transport came when Einstein [25] in 1907 assumed each lattice point as an independent oscillator where atomic vibrations are quantized. While Dulong-Petit law [26] assumed constant vibrational energy - $3k_B\tilde{T}$, where k_B is the Boltzmann constant and $\tilde{T}$ is the absolute temperature, it was not able to address low C_v (specific heat) at the lower temperatures. Einstein's model was relatively successful as it was able to achieve the Dulong-Petit limit at high temperatures. At the same time, C_v decreased exponentially at a lower temperature. However, [27] was not able to explain the difference with values reported by [28]. Debye [29], in 1912, modified the assumption of independent oscillators to collective vibration of atoms in a lattice (phonons). He assumed that at low temperatures, only acoustic modes would be excited, which have different frequencies. On the other hand, Einstein's assumptions were more about the excitation of optical phonons, which typically have a flat frequency curve. Thus Debye suggested a T^3 dependence at low temperature. He also combined the concept of the Kinetic Theory of gases to propose an expression for κ [30]. Here each phonon mode contributes to the thermal conductivity by the expression,

$$\kappa(T) = \sum_i \frac{1}{3} C_{vi} V_g \Lambda_i, \quad (1.2)$$

where phonon mean free path(Λ), specific heat(C_v), and group velocity (V_g) are defined for i^{th} mode. This model explained the importance of the MFP of phonons in thermal conductivity. While Debye's theory was able to justify low-temperature dependence, it could not describe the decrease in κ at high temperatures. Peierls [31] in 1929 introduced the concept of the Brillouin zone to thermal transport. He presented how anharmonicity of the lattice can result

in the scattering of elastic waves. Further mentioning that two conservation laws have to be followed by phonons in a lattice:

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3, \quad (1.3)$$

$$\hbar\mathbf{q}_1 + \hbar\mathbf{q}_1 = \hbar\mathbf{q}_1 + \beta\hbar\mathbf{G}, \quad (1.4)$$

where ω_i and $\mathbf{q}_i$ is the frequency and wave vector of a phonon with wavelength λ_i . $\mathbf{G}$ is the reciprocal lattice vector where β will be non-zero if the resultant wavevector of phonon-phonon interaction is outside the first Brillouin zone. The interaction results in the reversal of phonon momentum, thus hindering thermal transport. The process is termed as Umklapp or U-process, while in Normal or N-process, there is no momentum reversal. The process is shown in Figure 1.1. Thus N-processes do not hinder thermal transport, but a chain of N-processes can generate wave vectors, leading to U-process. U-processes dominance at higher temperature was thus able to explain the decrease in κ at higher temperatures. The process is known as scattering.

Phonon scattering is the resistance in the path of phonon. The resistance causes reflection resulting in decrease in transmitted energy and thus decrease of κ . One mode of this resistance is when more than one phonons start interacting with each other as in U-process. It leads to a decrease of the mean free path and thus a reduction in κ . Other modes of scattering include boundary scattering, isotope scattering, etc. Matthiessen's rule is used to define the total resistance due to these additional modes of scattering.

Another contributor to the decrease in thermal conductivity can be the localization of extended modes. Mode Localization or Anderson localization happens when extended modes start localizing in the presence of disorder. Thus disorder results in localized vibrations, which do not contribute significantly to the thermal current. Generally, short wavelengths or high frequency are localized in disordered systems [32, 33]. For this study, we consider randomly perturbed masses as the disorder in the system.

1.2 Anomalous thermal transport in low dimensions

Fourier's law is an empirical local relation connecting the macroscopic heat flux to the spatial temperature gradient. However, the validity of Fourier's law is not universally guaranteed [34], particularly when one probes thermal transport in the nanoscale regime [8, 9]. The proof of Fourier's law has not been established mathematically. It is still an open problem in non-equilibrium statistical physics [35]. In bulk materials, κ is expected to be finite; thus, J has

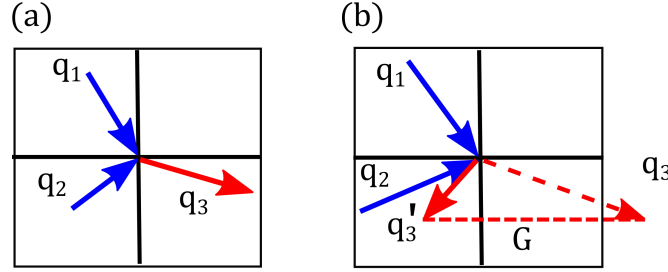


Figure 1.1: This schematic describes the two types of phonon-phonon interaction possible in a lattice (a) Normal scattering (N-process) (b) Umklapp scattering (U-process). Here $\mathbf{q}_1$ and $\mathbf{q}_2$ represent the incident wavevectors. $\mathbf{q}_3$ is the resultant wavevector, which is in N-process is still inside the Brillouin zone. In U-process the $\mathbf{q}_3$ has been mapped back to the first Brillouin zone by shifting it by a reciprocal lattice vector ($\mathbf{G}$). As a result, N-process conserves total phonon momentum, while U-process does not.

a diffusive behaviour. On the other hand, a wide range of simulations and experiments have shown that diffusive behaviour is not visible in many low dimensional systems. Fourier's law breaks down, where the mean free path of phonons is comparable to the characteristic length of the system [36]. It has been shown in both 1D lattices [23, 32, 37, 38] and quasi 1D materials such as polymers that thermal transport is superdiffusive or anomalous.

To understand the anomalous transport, we have to start with a 1D harmonic chain with no transverse motion. The thermal transport is ballistic - $J \propto (T_H - T_C)$, where T_H and T_C are the temperatures of the hot and cold reservoirs. There is no scattering source in the system, and no temperature gradient is established. Also, conductivity cannot be defined. When there is scattering in the system but is insufficient to lead to diffusive behaviour, we can see a superdiffusive or anomalous behaviour. In these systems, the increase in the chain's size leads to the participation of additional long-wavelength modes, resulting in divergence. While 1D systems with 2 body potentials have been studied extensively, multibody potentials have not been explored. Only one set of studies is available for multibody potentials [39, 40]. We will brief the 1D literature (also summarized in Table 1.1) to emphasize the gap that is existing between the study of the effect of these 2 potentials on thermal conductivity.

Several studies have been done to understand if there is a particular property of the system or interaction that causes this divergence in a 1D model with 2 body interactions. Momentum conservation, integrability, onsite pinning, and non-linearities have been studied to a great extent. Among these properties, non-integrability was expected to lead to diffusive behaviour as phase space restrictions are removed from the system. However, it turned out to be necessary

but not a sufficient condition. Similarly, non-linearity or anharmonicity was also studied to understand if it can lead to a diffusive behaviour. Non-linear lattices like FPUT (Fermi-Pasta-Ulam-Tsingou) [5, 41–44] lattices, diatomic Toda [45] lattices have shown anomalous behaviour while Toda lattices [46] have ballistic behaviour. [42] further showed that any 1D non-linear lattice where the acoustic branch is present would show anomalous transport. The behaviour can be different in the presence of optical phonons. Thus, literature has focused on other properties and have resulted in three broad observations:

1.2.1 Chaos is not a necessary but sufficient condition for diffusive transport

Chaos or unpredictable trajectories in a system leads to the exploration of additional phase space, leading to diffusion. While chaos was initially believed as responsible for diffusive behaviour [47], systems like Triangle Billiard Gas channels [48] showed that systems with zero Lyapunov exponents can also show Fourier behaviour. It showed that chaos is sufficient for Fourier's behaviour. However, not a necessary condition as mixing can be possible due to other factors, like disorder. Triangle Billiard Gas channels showed mixing at irrational angles in which Fourier like behaviour was observed.

1.2.2 Momentum conservation is not necessary for anomalous transport

Momentum conservation or translation invariance has shown to prevent the diffusive transport in [5, 41–45]. On the other hand, many non-momentum conserving lattices like [49–51] have shown a finite conductivity. Some authors probed the underlying physics, and Levy walk distribution for energy correlation was observed in momentum conserving lattices rather than Gaussian distribution for diffusive behaviour [52]. In one of the cases, [53] replaced the onsite potential by harmonic interactions. There despite momentum conservation, we see a finite conductivity. Some other exceptions, like rotor models [54, 55], have momentum conservation but show finite conductivity. One of the most common lattices studied under this category is the FPUT lattice. Several studies have been done [5, 41, 41–44] where $\alpha = 1/3$ to 0.4, have been reported. Renormalization group theory [23] also has predicted $\alpha = 1/3$ for these lattices. While there have been many exponents debated for these non-linear potentials, there seems to be a generic exponent depending on the type of non-linearity in the system. It has been shown that [44] using Mode Coupling Theory (MCT) $\alpha = 1/3$ is expected when the leading non-linearity is cubic, and $\alpha = 2/5$ can be expected for quartic one.

1.2.3 Non-Integrability is necessary but not a sufficient condition for diffusive transport

Non-Integrability of a dynamical system can expand the limited phase space of a system resulting in diffusive transport. While other properties have been explored, the system's non-integrability has proved to be a necessary but not a sufficient condition. [56] studied ϕ^4 and FPUT lattices, both of which are non-integrable. While the former has finite conductivity, the latter has divergent behaviour. It was observed that in ϕ^4 lattices, site potential leading to non-momentum conservation was causing scattering, sufficient enough for diffusive transport. On the other hand, in FPUT lattice, the interaction of solitary waves is not enough, and momentum conservation enforces divergent behaviour. Thus, non-integrability is necessary to have a thermal gradient in the system but not necessarily leads to diffusive transport. Some other exceptions with non-integrability and anomalous behaviour are diatomic lattices [43, 45] and disordered lattices [10, 57].

1.2.4 Onsite pinning is not necessary for diffusive transport

As we have mentioned earlier, non-integrability is a necessary condition for diffusive transport; the nature of pinning can affect the system's integrability. It is well known that a harmonic chain with harmonic pinning is completely integrable and thus shows anomalous behaviour. This system prevents momentum conservation but still holds anomalous behaviour. [62] has studied Toda lattice both at high and low temperatures as well as harmonic and quartic pinnings. It has been observed that Toda lattice shows the transition from anomalous to finite conductivity from low to high temperatures. It is because Toda lattice is approximated as a harmonic chain at low temperatures. Ultimately it is the integrability of the system that directs the behaviour, not onsite pinning. Similar behaviour can be observed for Sine-Gordon lattice [61], which is integrable and shows anomalous behaviour despite the presence of onsite pinning. Sinh-Gordon [61], on the other hand, being non-integrable shows finite conductivity.

From this discussion, we can observe that there is no concrete property that can help us indicate if the lattice will show diffusive behaviour. For 1D chain with transverse motion the problem has not been explored. The literature is quite vacant there. Since all these studies have been done with a 1D chain and 1 DOF (degree of freedom), the interaction of only one type (longitudinal) of waves has been studied in detail. We add a slow-moving flexural wave with quadratic dispersion relation; thus, it differs from the very nature of longitudinal non-dispersive

Potential	Boundary condition	Method	Bath	α	Ref.
Double Well ^{■◦}	Pinned	NESS	Langevin	0.5, 0.33	[41]
1D fluids ^{■◦}		RG theory		0.33	[23]
FPU β ^{■◦}	Periodic	Green-Kubo	Nosé Hoover	0.4	[5]
FPU α ^{■◦}	Periodic	MCT		0.33	[44]
FPU β ^{■◦}	Periodic	MCT		0.4	[44]
Harmonic ^{■◦△★}	Pinned	NESS	Langevin	-0.5	[6]
Harmonic ^{■◦△★}	Free	NESS	Langevin	0.5	[6]
Diatomic toda ^{■◦}	Maxwell/ periodic	Green Kubo	Maxwell/ Langevin	0.35	[45]
Diatomic 1D gas ^{■◦}			Maxwell	0.35	[43]
1D hard point gas ^{■◦}			Maxwell	0.2	[58]
MCDL ^{■◦}	Periodic		Langevin	0	[53]
Lorentz Gas ^{■•}			Maxwell	0	[47]
Triangle Billiard ^{■•}			Maxwell	0	[48]
Alternate mass-core ^{■•△}			Maxwell	0	[59]
hard potential channel					
Ding-a-Ling ^{■•△}		Green Kubo	Maxwell	0	[50]
1D Rotor ^{■◦}	Pinned	Green-Kubo	Nosé Hoover	0	[54]
1D Rotor ^{■◦} with peri- odic potential	Pinned	Green Kubo	Langevin	0.26,0	[55]
Frenkel Kontorova ^{■•}			Nosé Hoover	0	[51]
ϕ^4 ^{■•}	Independent		Nosé Hoover	0	[56,60]
Sinh-Gordon ^{■•△}	Free Free	Green Kubo	Langevin	0	[61]
Sine-Gordon ^{□•△}	Free Free	Green Kubo	Langevin	>0	[61]
Toda ^{■•△}	Pinned	NESS	Langevin	> 0,0	[62]

Table 1.1: A literature review of 1D lattices with two-body potentials. Methods have been categorized as Non-Equilibrium Stationary State simulations (NESS), Green Kubo calculation, and Mode Coupling Theory (MCT). Here open square and open circular markers are for integrability and momentum conservation in a lattice, respectively. Filled markers represent the opposite. Triangular markers represent onsite pinning, and star markers represent mass disordered systems. It can be observed that non-integrability is necessary for normal transport but not a sufficient condition. All the other properties do not show any conclusive results. Here, we have only presented literature of 1D models. Despite being extensively studied, understanding the reason of anomalous thermal transport is still a challenge. This problem is relatively less explored for multibody interactions with only one set of study available [39,40]. Thus, it is necessary to explore the multibody interactions. These interactions are an integral part of the real systems and their presence can affect the thermal transport.

waves. The presence of such slow flexural waves has been recently shown to give rise to four-phonon interactions in Graphene [63], and other material systems [64,65]. These interactions in a 1D chain can lead to additional scattering. Thus ballistic behaviour cannot be expected in the thermodynamic limit. To explore this interaction [39,40] added a bending potential to the 1D chain and reported $\alpha = 0.4$ for weak coupling and $\alpha = 1/3$ for strong coupling. While several combinations of $\tilde{k}_\theta$ (bending energy), T_C (the temperature at the cold end) and T_H (the temperature at the hot end) have been considered, $\alpha = 0.5$ and logarithmic divergence were also observed at some parameters. They have observed different exponents in superdiffusive behaviour when size is defined by the length of chain. We try to understand if there exists an asymptotic behaviour of κ with respect to the additional length scale - Persistence length (ℓ_p), that enter as parameters. ℓ_p is a measure of flexibility of the chain and is defined as the length over which the correlation in the direction of tangent is lost. Thus, for a piece of a system smaller than ℓ_p system acts like a beam for longer sizes, it can be described statistically or three dimensional random walk. Additionally, we probe the effect of mass disorder, which has not been explored in these models. We simulate a chain with pinned boundary conditions and a temperature range, which removes the requirement of any additional smoothing potentials. Large longitudinal fluctuations can result in a collision and will necessitate the use non-linear potentials near such singularity. They could introduce a potential scattering source. Thus, reducing the clarity in understanding of the effect of multibody interactions. Further, we introduce transverse pinning to study the effect of crowding in these systems, which has not been explored yet.

We can make a few observations and identify a few gaps in the literature of a single chain with multibody potential. They are listed as below:

1. What is the difference in the frequency-dependent contribution of flexural and longitudinal modes to thermal transport in the harmonic limit? Disordered systems have not been studied for a chain with multibody potential.
2. In the presence of persistence length, is it possible to define a new length scale - N_ℓ (number of persistence lengths in the system) to study the asymptotic limit? How will the scaling change in the system with ordered and disordered masses?
3. What will be the effect of crowding on κ of a single chain with multibody potential? How significant is the effect on the divergence of thermal conductivity?

Thus, we observe that the effect of multibody potentials have not been understood in detail.

We will try to address some of the gaps.

1.3 Thermal transport in crowded environment¹

Understanding heat transport in quasi-one dimensional materials (Q1DMs) is a scientifically major problem [67, 68], and becomes even more challenging when dealing with arrays of Q1DMs, such as forests [24, 69–72], bundles [73], sheets [74], and fibers [21, 75]. Here, the complex molecular structure of an array introduces entropic disorder and thus controls its physical properties. One such intriguing phenomenon is strong heat localization in CNT forests [24]: while a single CNT exhibits $\kappa_{||} > 10^3 \text{ Wm}^{-1}\text{K}^{-1}$ [14, 18, 76], CNT forests show a drastic reduction in $\kappa_{||}$. Here, $\kappa_{||}$ is the thermal conductivity along the molecular backbone. This “heat trap” effect was observed at a very high temperature of $T > 10^3 \text{ K}$. However, room temperature experiments have also yielded relatively low values, such as $\kappa_{||} \simeq 0.5 - 1.2 \text{ Wm}^{-1}\text{K}^{-1}$ for CNT forests [72], $\kappa_{||} \simeq 100 \text{ Wm}^{-1}\text{K}^{-1}$ for CNT bundles [73] or $\kappa_{||} \simeq 43 \text{ Wm}^{-1}\text{K}^{-1}$ for CNT sheets [74]. We note that the observed influence of crowding on $\kappa_{||}$ in CNT forests and sheets may not be a system specific phenomenon. Here, the other examples include nanowire (NW) arrays [70, 71, 77], polyethylene (PE) fibers [75], crystalline-like assemblies of PE [21] and poly-3,4-ethylenedioxythiophene (PEDOT) [78], and composite materials [79].

The heat transport in an isolated Q1DM has been studied extensively [67, 68, 80–82]. Moreover, a few studies have also investigated the effects of crowding on κ , where individual molecules are randomly orientated in a sample [83–86]. These studies have modelled junctions that lack the full picture of kinks and interfaces that can form in a forest. In these studies, the non-bonded van der Waals (vdW) contacts between different Q1DMs strongly influence their thermal behaviour, especially when the molecular lengths are smaller than the sample dimensions. This vdW-based interaction also leads to a low κ [83]. Another study by [87] simulated cross-linked functionalized polyethylene chains to single-walled and double-walled CNTs. They reported a significant decrease in κ by increasing the number of pinned sites and weight percentage of functional groups. In the case of double-walled CNTs, sensitivity was less. This simulation was done for individual CNTs. However, a molecular forest is inherently anisotropic where many types of interactions can arise that are difficult to predict. In these forests, a delicate balance between the bonded interactions and molecular entanglements dictate $\kappa_{||}$ along the molecular

¹A version of this text is available online [66]. [Bhardwaj, A., Phani, A. S., Nojeh, A., & Mukherji, D. (2020). “Thermal transport in molecular forests”. *arXiv preprint arXiv:2005.10685*.

orientations. In the lateral directions, $\kappa_{\perp}$ is dominated by the weak vdW interaction. Generally, κ between pure bonded neighbours is about 50–100 times larger than that between the non-bonded neighbours [75]. Therefore, it is rather challenging to predict a priori how crowding can account for a drop in $\kappa_{\parallel}$ [21, 24, 70, 71, 74, 78].

Thus, a scheme to understand the decrease in κ in a forest is absent in the literature.

1.4 Summary

This chapter briefly reviewed the anomalous behaviour of κ in low dimensional materials and the decrease in thermal transport in a crowded environment.

Fourier’s law breaks down in these materials and κ can be length dependent. While many properties of the system like non-linearity, momentum conservation, integrability, and onsite have been considered, there is still no conclusive answer to this anomalous behaviour. Non-linear systems like FPUT show anomalous behaviour, while Toda lattices show ballistic behaviour. Momentum conservation also is not a strong driver for anomalous behaviour as exceptions such as rotor lattices exist. The non-integrability of the system, also seems to be a necessary but not a sufficient condition. While non-integrability leads to the temperature gradient in the system, lattices like FPUT still show anomalous behaviour. Onsite potentials also can affect the integrability of the system. Here, we have only presented literature of 1D models. Despite being extensively studied, understanding the reason for anomalous thermal transport is still a challenge. This problem is relatively less explored for multibody interactions with only one set of study available [39, 40]. The asymptotic limit of the model with persistence length as length scale has not been explored. Moreover, the effect of pinning and disorders have also not been explored. Thus, raising the necessity to explore the multibody interactions. These interactions are an integral part of the real systems and can affect the thermal transport.

We further discuss the thermal transport in molecular forests. We saw that a decrease in $\kappa_{\parallel}$ has been reported in the literature in crowded environments. This knockdown is the result of additional interactions like vdW forces, which scatter the phonons. Although some simulations have been done in literature where random networks of CNTs have been studied, they have been limited to studying junctions. A model that can simulate whole forest still lacks in the community. This model can help in understanding the thermal transport in molecular forests. This thesis uses a coarse-grained model that gives insight into some of the complex issues of bond orientations and density in a forest.

1.5 Objectives and outline

After a comprehensive review of the literature, the following gaps have been addressed:

1. In Chapter 2, we make a non-dimensionalized model with multibody and two-body forces. We first understand the difference in frequency wise contribution of each mode to thermal current in the harmonic limit. We further extend our analysis with Non-Equilibrium simulations to explore the effect of the coupling of modes on the divergence of κ .
2. In Chapter 3, we modify the model developed in Chapter 2 to include transverse pinning. We use transverse pinning to understand the effect of density and defects on the divergence of thermal transport in a crowded environment.
3. In Chapter 4, we use a coarse-grained model for simulating molecular forests using the Kremer-Grest model of a polymer. We study the effect of crowding on κ as a function of the forest's density.
4. In Chapter 5, we list important findings and directions for future work.

Chapter 2

Anomalous thermal transport in single chain with multibody forces

In this chapter, in Section 2.1, we will describe a non-dimensionalized model with multibody forces that we will be using for our analysis. Then in Section 2.2, we will try to understand the difference in transmittance function (frequency spectrum) of longitudinal and flexural modes in the harmonic limit. We observe that longitudinal modes have a higher contribution from high frequencies. In contrast, flexural modes have symmetric contribution centred at half of the maximum frequency. With this insight, we further probe the effect of disorder in the spectrum. As the disorder is expected to localize high frequencies, longitudinal modes are observed to localize at a shorter system size than flexural modes. In the next half of this chapter, in Section 2.3, we explore the effect of anharmonicity and non-linearities. We analyze the 1D chain model with Non-Equilibrium simulations. Langevin baths being stochastic, have been used to excite thermal vibrations and achieve Non-Equilibrium Stationary States (NESS). NJ vs. N plots, which have been useful for two-body interactions, have been scaled to NJ^* vs. N_ℓ plots. These plots were observed to transition from ballistic to superdiffusive behaviour in the asymptotic limit. Disordered systems were also observed to have superdiffusive behaviour in the range of parameters in our simulations. We observe coherent patterns emerging as energy carriers in superdiffusive limit by observing the magnitude of the longitudinal and transverse displacements.

2.1 Modelling of 1D chain with both flexural and longitudinal modes

As we are interested in the interaction of multibody and two-body interactions, we start by considering a Hamiltonian with a stretching and a (non-linear) bending energy term:

$$\tilde{H} = \sum_{i=1}^N \left\{ \frac{\tilde{\mathbf{p}}_i \cdot \tilde{\mathbf{p}}_i}{2\tilde{m}_i} + \frac{1}{2} \tilde{k}_r (|\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_{i+1}| - \tilde{a})^2 + \tilde{k}_\theta (\cos \theta_i + 1) \right\} \quad (2.1)$$

where $\tilde{k}_r$ is the axial stiffness, $\tilde{k}_\theta$ is the bending energy and $\tilde{a}$ is the lattice spacing. Bending term is obtained from unit vectors of two adjacent bonds connecting a particle with its neighbours as:

$$\cos \theta_i = -\mathbf{e}_{i-1} \cdot \mathbf{e}_i \quad \mathbf{e}_i = \frac{\Delta \mathbf{r}_i}{|\Delta \mathbf{r}_i|}, \quad \Delta \mathbf{r}_i = \mathbf{r}_{i+1} - \mathbf{r}_i. \quad (2.2)$$

In the above equation, the bond vector $\Delta \mathbf{r}_i$ between the particles i and $i+1$ is shown in Figure 2.1. Bending is common in many structural and biological problems [88–90]. Note that using $1 + \cos \theta_i$, like in [88, 89], one recovers the bending energy of a classical Euler-Bernoulli beam for small $\theta_i - \pi$. Thus, the bending energy is proportional to the square of the change in the angle between adjacent bonds in that limit.

With transverse motion in 1D chain, bending energy introduces additional length scales of lattice spacing and persistence length (ℓ_p). These scales can be relevant to thermal conductivity as thermal excitation can be significant at these length scales. Thus it is useful to re-scale the dimensional Hamiltonian. To non-dimensionalize the equation (2.1), we take $\tilde{k}_r \tilde{a}^2$ as the energy

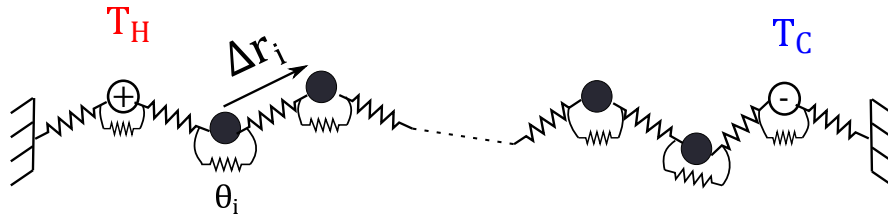


Figure 2.1: Schematic of a single chain model with both axial and flexural springs and Langevin thermal baths at the two ends. Here $i \in [0, N+1]$ where the two end particles are pinned. Langevin baths have been added at $i=1$ and $i=N$ with temperatures T_H and T_C respectively. θ_i represents the relative angle made by two links at one common chain site (i). $\Delta \mathbf{r}_i$ represents the vector along the link from i^{th} site to $i+1^{\text{th}}$ site.

scale, $\sqrt{\frac{\tilde{m}_i}{k_r}}$ as the time scale, $\tilde{m}_i$ as the mass scale. Dividing (2.1) by energy scale, we can get a dimensionless Hamiltonian (H) as:

$$H = \sum_{i=1}^N \left\{ \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2} + \frac{1}{2} (|\mathbf{r}_i - \mathbf{r}_{i+1}| - 1)^2 + \frac{1}{\lambda} (\cos \theta_i + 1) \right\} \quad (2.3)$$

where

$$\lambda = \frac{\tilde{k}_r \tilde{a}^2}{\tilde{k}_\theta}. \quad (2.4)$$

Slenderness ratio (λ) is thus introduced. It allows us to move from an extremely low bending energy (rope like) regime to extremely high bending energy (rod like) regime. The value of λ as a parameter will determine the persistence length ($\tilde{\ell}_p$) in the system depending on the temperature ($\tilde{T}$). Thus we first define ($\tilde{\ell}_p$) as:

$$\tilde{\ell}_p = \frac{\tilde{k}_\theta a}{k_B \tilde{T}}. \quad (2.5)$$

Further non-dimensionalizing $\tilde{\ell}_p$, we get:

$$\ell_p = \frac{\tilde{\ell}_p}{\tilde{a}} = \frac{1}{\lambda T} \quad (2.6)$$

where

$$T = \frac{\tilde{T}}{\frac{\tilde{k}_r \tilde{a}^2}{k_B}} \quad (2.7)$$

is the non-dimensional temperature. We will proceed with λ as a parameter and ℓ_p as an additional length scale in the system for our analysis.

Now we have clearly defined our model parameters. We will study the model in the harmonic limit first and then move to the Non-Equilibrium simulations in the next section.

2.2 Flexural and longitudinal modes in the Harmonic limit

As we have seen in the previous section, it will be interesting to understand how these two phonons will affect the system. However, before moving to the complexity of interactions, we

should first compare some of the characteristics of both modes in the harmonic limit. Longitudinal modes are non-dispersive with the constant group velocity. At the same time, flexural waves are dispersive, and group velocity depends on the wavenumber. Here with the harmonic limit, we emphasize that the $|\mathbf{r}_i - \mathbf{r}_{i+1}| \approx 1$ in the (2.3). This can only be possible at low temperatures or with high stiffness. Changes in length are not significant to introduce geometric non-linearities. In other words, $\ell_p \rightarrow \infty$. Both modes will be uncoupled in this limit, and we can analyze them separately for each system. For our analysis, we have taken two systems - Ordered and Disordered Harmonic chain.

Ordered Harmonic chain

For an ordered harmonic system, $J(N)$ has been worked out by [91] for two-body harmonic potential, where $J(N) \propto (T_H - T_C)$ for $N \rightarrow \infty$. Thus the thermal current scales linearly with temperature difference. This behaviour is ballistic, as no temperature gradient is visible in the system. The system's temperature profile is constant at value - $\frac{T_C + T_H}{2}$ throughout the chain except at the ends. The profile also changes exponentially near the ends due to applied thermal baths. As a result, thermal conductivity cannot be defined for these systems.

Since the expression is independent of mass and stiffness matrices, its independence on N can be expected for longitudinal and flexural modes. Thus we will focus more on disordered systems to compare these two modes.

Disordered Harmonic Chain

In a periodic system, when the disorder is introduced, the extended modes can localize. This phenomenon is also known as Anderson localization. Thus in a disordered system, all modes will not be able to contribute to thermal current. It has been shown by [7, 33, 92, 93] that in the presence of disorder, short wavelengths start localizing and thus reduce J . The disorder is not relevant for long wavelengths, and thus these modes can continue contributing to thermal transport. The study for disorder in these simple toy models is only available for two-body interactions. Literature is not available for simple multibody potentials.

To understand the localization of longitudinal and flexural modes, we will start with a more general expression of J , which can be used for both in the harmonic limit. The expression has been given by [94] . In this model, the lattice of $N + 2$ beads is pinned at two ends and the Langevin baths have been applied at the two ends, with the coupling strength γ . The expression

for J is given as:

$$J(N) = \gamma \frac{T_H - T_C}{\pi} \int_{-\infty}^{+\infty} \underbrace{\omega^2 |\mathbf{Z}(\omega)_{1,N}^{-1}|^2}_{I(\omega)} d\omega \quad (2.8)$$

where,

$$\mathbf{Z}(\omega) = \mathbf{K}_{N \times N} - \omega^2 \mathbf{M}_{N \times N} - i\omega \mathbf{M}_{N \times N} \mathbf{L} \text{ and} \quad (2.9)$$

$$\mathbf{L}_{ii} = \gamma(\delta_{i1} + \delta_{iN}). \quad (2.10)$$

Here $I(\omega)$ in (2.8) is known as the transmittance function, which we can use to understand the frequency-wise contribution of each mode to thermal transport. Since this expression is applicable to any harmonic system, we will use it to study the spectrum of both modes. In the harmonic limit we will define respective $\mathbf{M}$ and $\mathbf{K}$ matrices. The bending force ($\mathbf{f}_i^b$) and axial spring force ($\mathbf{f}_i^a$) are calculated for the net force $\mathbf{f}_i$. Linearizing (2.3), we separate x and y motions for longitudinal and flexural modes, respectively for the pinned boundary condition.

Longitudinal mode

We linearize the longitudinal motion form (2.3) as:

$$\mathbf{f}_i^a = -(x_i - x_{i-1}) + (x_i - x_{i+1}), \quad (2.11)$$

$$\mathbf{f}_i^a = -x_{i-1} + 2x_i - x_{i+1}. \quad (2.12)$$

Rearranging the coefficients, it can be transformed into the stiffness matrix $\mathbf{K}$ give as:

$$\mathbf{K} = \begin{bmatrix} 2 & -1 & 0 & . & . & . \\ -1 & 2 & -1 & 0 & . & . \\ 0 & -1 & . & . & . & . \\ . & 0 & . & . & -1 & 0 \\ . & . & 0 & -1 & 2 & -1 \\ . & . & . & 0 & -1 & 2 \end{bmatrix}. \quad (2.13)$$

Flexural mode

For bending energy, we define third term in (2.3) as V_i . We neglect the higher order terms in the expansion of $\cos \theta$ term for analyzing the flexural mode. Thus we expand V_i as:

$$V_i = -\cos(\theta_i - \pi) + 1 = -\cos(\Delta\theta_i) + 1 = \Delta\theta_i^2 + \Delta\theta_{i-1}^2 + \Delta\theta_{i+1}^2 + \dots \quad (2.14)$$

Converting angles to transverse displacements, we get:

$$V_i = [(2y_{i-1} - y_i - y_{i-2})^2 + (2y_{i-2} - y_{i-1} - y_{i-1})^2 + (2y_{i+1} - y_i - y_{i-1})^2] + \dots \quad (2.15)$$

$$\mathbf{f}_i^b = [y_{i-2} - 4y_{i-1} + 6y_i - 4y_{i+1} + y_{i+2}]. \quad (2.16)$$

Finally we rearrange the terms considering pinned boundary conditions to get a stiffness matrix as:

$$\mathbf{K} = \begin{bmatrix} 5 & -4 & 1 & . & . & . \\ -4 & 6 & -4 & 1 & . & . \\ 1 & -4 & . & . & . & . \\ . & . & . & . & -4 & 1 \\ . & . & 1 & -4 & 6 & -4 \\ . & . & . & 1 & -4 & 5 \end{bmatrix} \quad (2.17)$$

We will use the respective $\mathbf{K}$ matrices for calculation using (2.8), where $\mathbf{M}$ will be a diagonal matrix with each value as the mass corresponding to that site.

2.2.1 Flexural vs longitudinal modes - Transmittance function

To understand the spectrum of frequencies contributing to J in both modes, we must understand the transmittance function. We start by plotting the transmittance function for both longitudinal and flexural modes. Here we have used equation (2.3) with all the parameters as unity for the ordered chain. While for the disordered system, we have varied the masses independently as $-\Delta m$ from a uniform distribution $[-0.2, 0.2]$ with zero mean and unit variance. The mass of each site is thus $1 + \Delta m$. The spectrum has been plotted in Figure 2.2.

Ordered system

In an ordered system, it can be noted that for longitudinal vibrations, the distribution has higher contribution from higher frequencies of its spectrum (Figure 2.2). However, flexural modes have a symmetrical spectrum centred around half of the maximum frequency. Besides, we observe that longitudinal modes contribute in frequency range $-0 < \omega \leq 2$, which can be related to the dispersion curve of a monoatomic chain as $\omega = 2\sqrt{\sin(k/2)}$, where k is the wavenumber. Longitudinal modes have high density of states at higher wavenumber. The decrease in group velocity is compensated resulting in high contribution. On the other hand, flexural modes with dispersion curve as $\omega = \sqrt{6 - 8\cos(k) + 2\cos(2k)}$ have $-0 < \omega \leq 4$ as contributors. The modes have low group velocity and high density of states at small wavenumber but vice-versa at large wavenumber. Thus leading it to a more symmetric contribution. It highlights the difference

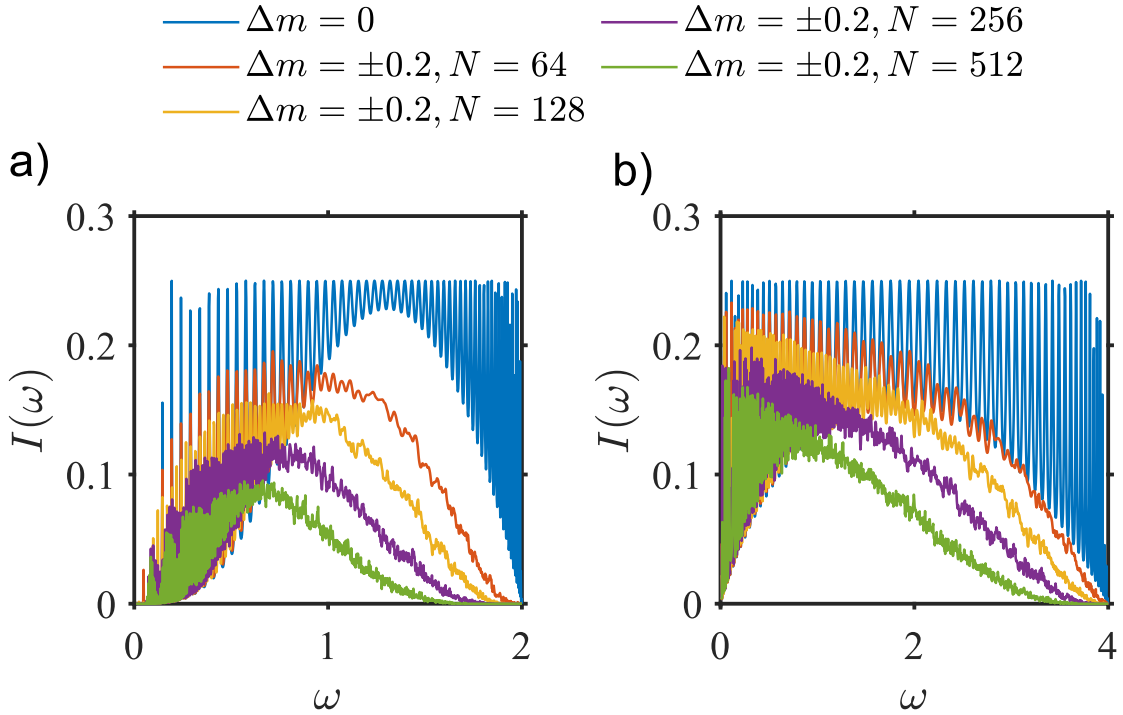


Figure 2.2: Transmittance function $I(\omega)$ showing the contribution of each frequency to total thermal conductivity κ in the harmonic limit for a) Longitudinal and b) Flexural modes. Both disordered and ordered cases have been plotted. The ordered chain spectrum is independent of system size, and thus N value has not been shown. Localization of high-frequency waves can be observed in both modes where longitudinal modes start localizing at smaller system sizes.

in characteristics of both modes and we can scale these frequencies to tailor total spectrum when both modes are present (Figure 2.3).

Disordered system

On observing closely, in both longitudinal and flexural modes, disorder localizes the higher frequencies or short wavelengths. The effect of disorder is more prominently visible in longitudinal mode than the flexural mode (Figure 2.2). We see a significant localization at $N = 50$ in longitudinal mode, while flexural modes start deviating at higher lengths. As longitudinal modes have a heavily weighted contribution from higher frequencies, it becomes apparent that these modes are more sensitive to disorder. However, flexural modes have a symmetric contribution in ordered case. This characteristic makes flexural mode less sensitive to disorder than longitudinal modes. We have to be very cautious as this spectrum is still in the harmonic limit and is only to understand the different characteristics these modes have. It might not be accurate to expect the

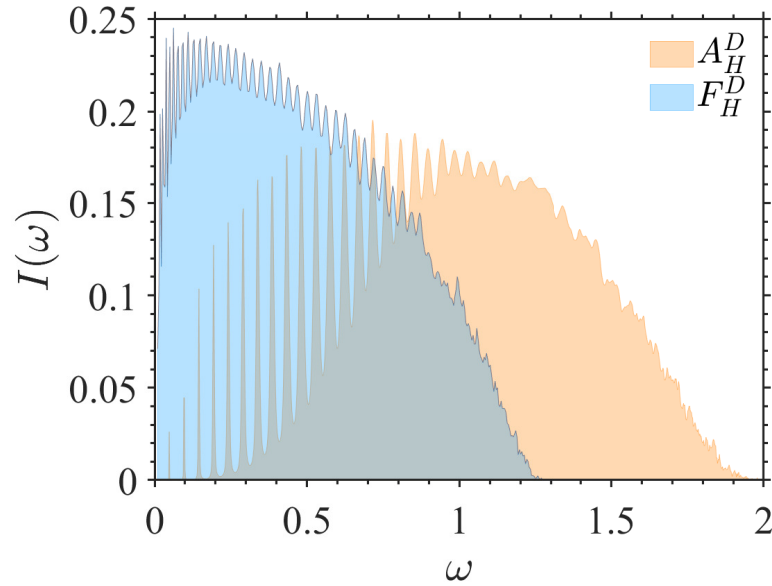


Figure 2.3: Mode-wise frequency contribution of longitudinal and flexural modes to J , according to (2.8) for $\lambda = 10$ in the harmonic limit. Here A_H^D and F_H^D represents the $I(\omega)$ or transmittance function of the longitudinal and flexural modes in a system with the mass disorder. This highlights that the presence of both modes can help us in exploiting different frequency ranges to tailor thermal properties.

same behaviour when non-linearities take over. Thus, as a summary, we establish that the two modes have different thermal transport characteristics in the harmonic limit.

2.3 Effect of coupling of longitudinal and flexural modes - Non-Equilibrium Simulations

In the previous section, we saw that within the harmonic limit, i.e., $\Delta \mathbf{r}_i \approx 1$, the modes are linearly independent. In this limit, fluctuations are not significant, and the contour length (l_c) $\approx N$. This independence does not provide additional interaction between these modes. If we have suitable parameter values in the Hamiltonian (2.3), then there is a possible interaction between these modes. It can lead to scattering by the transfer of energy from flexural to longitudinal modes and vice versa. Thus we can expect a deviation from ballistic behaviour even without the disorder. The coupling is related to the transverse motion, which depends on the slenderness ratio (λ). In this section, by using N_ℓ as a measure of the system's size, we can observe a superdiffusive behaviour in the asymptotic limit for both ordered and disordered systems. We set a temperature gradient in the system with Langevin baths at $T_C = 0.008$, $T_H = 0.01$ for different λ and calculate J when Non-Equilibrium Stationary State (NESS) is reached. Thus we will start by discussing the implementation of the model.

2.3.1 Non-Equilibrium simulations

This section will discuss the simulation set up for a single chain multibody and two-body forces. We will also discuss the implementation of Langevin baths and the calculation of J . As we discussed in Section 2.1, we have a chain with both bending and stretching potentials. The model with Langevin baths at two ends of the chains is shown in Figure 2.1. As a summary, dimensional parameters - $\tilde{k}_r$, $\tilde{k}_\theta$, $\tilde{a}$, $\tilde{\ell}_p$, $\tilde{M}$, $\tilde{T}$ condense to $\lambda (\sim 1 - 100)$, $\ell_p (\geq 1)$, $T (\sim 10^{-2})$, N_ℓ as non-dimensional (ND) parameters in our model. The code has been written in MATLAB and both model and langevin bath implementation have been validated as shown in Section A.1.

2.3.1.1 Force calculation

We know that a particle will be experiencing forces due to 2 types of potentials in this system - Two-body potential and Three-body potential. The bending force ($\mathbf{f}_i^b$) and axial spring force ($\mathbf{f}_i^a$) are calculated for the net force $\mathbf{f}_i$. For the calculation of these forces, the bond orientations

are calculated at each time step. Thus the vectors $\Delta \mathbf{r}_i$ and θ_i has been computed at each step. Two-body interactions are easy to calculate as they involve the nearest neighbors. Changing bond direction causes force along both longitudinal and transverse directions. We calculate the forces as:

$$\mathbf{f}_i^a = (|\Delta \mathbf{r}_i| - 1) \cdot \mathbf{e}_i - (|\Delta \mathbf{r}_{i-1}| - 1) \cdot \mathbf{e}_{i-1}. \quad (2.18)$$

For three-body interaction, we use the bending energy V_i denfined in last chapter as:

$$V_i = \frac{1}{\lambda} (\cos \theta_i + 1)$$

. Now differentiating the above equation with relation to θ we get the moment:

$$\frac{dV_i}{d\theta_i} = M_i = \frac{-\sin(\theta_i)}{\lambda}. \quad (2.19)$$

With these expressions, we use the same methodology developed in [95]. We will scale the moment by respective lengths to get the force on each connected link. The direction of the force will be perpendicular to the link on $i-1^{\text{th}}$ and i^{th} link. Thus the two internal forces will become:

$$\mathbf{f}_{i-1}^b = \frac{M_i}{|\Delta \mathbf{r}_{i-1}|}, \quad (2.20)$$

$$\mathbf{f}_{i+1}^b = \frac{M_i}{|\Delta \mathbf{r}_i|}. \quad (2.21)$$

Since, both of these forces are internal forces, we place an equal and opposite force on i^{th} bead i.e.:

$$\mathbf{f}_i^b = -\mathbf{f}_{i-1}^b - \mathbf{f}_{i+1}^b, \quad (2.22)$$

resulting in total force as $\mathbf{f}_i = \mathbf{f}_i^b + \mathbf{f}_i^a$.

2.3.1.2 Velocity Verlet method

Once the forces have been calculated, we integrate the equations of motion by Velocity Verlet method [96]. where force on each particle is given by:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{f}_i. \quad (2.23)$$

The steps for integrating the equations of motion have been implemented in the N body simulation as follows:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{f}_i(t)}{2m_i}\Delta t^2, \quad (2.24)$$

$$\mathbf{v}_i(t + \Delta t/2) = \mathbf{v}_i(t) + \frac{\Delta t \mathbf{f}_i(t)}{2m_i}, \quad (2.25)$$

$$\mathbf{f}_i(t + \Delta t) = \mathbf{f}_i(\mathbf{r}_i(t + \Delta t)), \quad (2.26)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) + \frac{\Delta t \mathbf{f}_i(t + \Delta t)}{2m_i}, \quad (2.27)$$

where $\mathbf{f}_i$ and $\mathbf{v}_i$ are the force and velocity vectors of each particle and Δt is the time step.

2.3.1.3 Stochastic thermostat - Langevin bath

To simulate the system with a temperature gradient, we apply a thermostat on two ends of our chains. This temperature is established by enforcing the kinetic energy of the particles to be equal to:

$$T_i = m_i \frac{v_i^2}{2}. \quad (2.28)$$

A friction factor γ is inserted, which increases or decreases the particle's kinetic energy at each step. Different thermostats calculate this friction factor in different ways. The most common are Nosé Hoover and Langevin thermostat. While Nosé Hoover is deterministic and easy to implement, but literature has shown that it fails to excite all the modes in the harmonic system [97, 98] in some systems. Thus, stochastic Langevin baths, have been used. The equations are written as:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{f}_i - \gamma m_i \mathbf{v}_i + \sqrt{\frac{2k_B T \gamma}{\Delta t}} \boldsymbol{\zeta}_i(t), \quad (2.29)$$

where

$$\langle \boldsymbol{\zeta}_i(t) \rangle = 0, \quad (2.30)$$

and

$$\langle \tilde{\zeta}_{i,\alpha} \tilde{\zeta}_{i,\beta}(t) \rangle = \delta_{\alpha,\beta}. \quad (2.31)$$

$\tilde{\zeta}_i(t)$ is a vector with both components as a Gaussian random variable having zero mean and one

variance. We have implemented these forces in MATLAB with the same algorithm that is used in the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The equations have been combined with velocity verlet for particles with bath as:

$$\mathbf{v}_i(t + \frac{\Delta t}{2}) = \mathbf{v}_i(t) - \frac{\Delta t}{2} \left(\frac{-\mathbf{f}_i}{m_i} + \gamma \mathbf{v}_i(t) \right) + \sqrt{\frac{\Delta t k_B T \gamma}{m_i}} \tilde{\zeta}_i, \quad (2.32)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \Delta t, \text{ and} \quad (2.33)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) - \frac{\Delta t}{2} \left(\frac{-\mathbf{f}_i}{m_i} + \gamma \mathbf{v}_i(t + \Delta t/2) \right) + \sqrt{\frac{\Delta t k_B T \gamma}{m_i}} \tilde{\zeta}_i. \quad (2.34)$$

Here we have to generate random vector $\tilde{\zeta}_i$ for each particle at each integration step.

2.3.1.4 Heat flux calculation

For multibody potential, the relation has been simplified to $\mathbf{J}_i = \frac{d}{dt}(\mathbf{r}_i H_i)$ by [39]. To simplify it for N body simulation, we rewrite the local energy H_i again as used by [39] as:

$$H_i = \frac{1}{4} (|(\Delta \mathbf{r}_{i-1} - 1)^2 + (\Delta \mathbf{r}_i - 1)^2|) + \frac{1}{\lambda} (\cos \theta_i + 1) + \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i}, \quad (2.35)$$

and write the flux calculation as:

$$\begin{aligned} \tilde{m}_i \mathbf{J}_i = & -(\Delta \mathbf{r}_i (\mathbf{p}_i + \mathbf{p}_{i+1}) \cdot \mathbf{g}(i)) \\ & -(\Delta \mathbf{r}_{i-1} (\mathbf{p}_i + \mathbf{p}_{i-1}) \cdot \mathbf{g}(i-1)) \\ & +(\Delta \mathbf{r}_{i-1} (\mathbf{p}_i \cdot \mathbf{w}(i-2, i-1, i-1))) \\ & +(\Delta \mathbf{r}_i (\mathbf{p}_i \cdot \mathbf{w}(i+1, i+1, i))) + \mathbf{p}_i H_i. \end{aligned} \quad (2.36)$$

Here, $\mathbf{g}(i) = \frac{1}{4} (|\Delta \mathbf{r}_i| - 1) \mathbf{e}_i$, $\mathbf{w}(i, j, k) = \frac{1}{\lambda} (\mathbf{e}_i + \mathbf{e}_k \cos \theta_j / |\Delta \mathbf{r}_k|)$, and $\mathbf{e}_i$ is the unit vector. We use this expression to calculate the heat flux in this paper. We can observe from this expression that each term in $\mathbf{J}_i$ is scaled by density. Since the vibrations at a higher temperature will introduce density variation between sites, this current will be different from what we can expect with the expression given in [7].

Finally, we use $\lambda = 5, 10, 15, 20, 80, 100$ to compare the effect of slenderness on power

law. We restrict our analysis to $\lambda = 100$ as it corresponds to $\ell_p = 1$ for our temperature range. Due to computational limitations, we only go to $N = 8192$. With a time step of $\Delta t = 0.1$, the system was stabilized for $10^8 - 3 \times 10^8$ time steps to reach a Non-Equilibrium Stationary State. J is $\langle |\mathbf{J}| \rangle$ where $|\mathbf{J}|$ is averaged over 10^8 time steps and $\langle . \rangle$ is the time average with units $(\tilde{k}_r^3/\tilde{m})^{1/2}\tilde{a}^2$. Finally, NJ vs. N has been plotted in Figure 2.4 and Figure 2.5 where the error is smaller than the size of markers.

2.3.2 Effect of slenderness ratio on coupling

Ordered systems

As we know, the thermal current will depend on the magnitude of longitudinal vibrations and transverse fluctuations. If we keep the temperature constant, transverse fluctuations are only governed by λ . A higher value of λ leads to large transverse fluctuation amplitude. It leads to coupling between longitudinal and flexural modes and thus leads to scattering. Thus we can expect more deviation from ballistic behaviour, with an increase in λ .

On plotting NJ vs. N , in Figure 2.4(a) we observe that with the increase in λ , a decrease in NJ is observed. Also, the plot starts deviating from Ballistic behaviour. Transition to superdiffusive behaviour becomes evident when we measure the system size with ℓ_p as length scale rather than $\tilde{a}$ as unit length. N is divided by each system's persistence length to define a new system size given by N_ℓ . In Figure 2.4(b), NJ values have been normalized by an arbitrary number and plotted against N_ℓ . An exponent α is observed as different curves in Figure 2.4(a) collapse to a master curve. We fit a straight line with the last 4 data points for $\lambda = 100$ and extend that line to lower N_ℓ values. For clear representation, we have drawn a parallel line in the plot. This helps us in comparing two extremes of our system - rod and rope regimes ($\lambda = 5, N = 128$ and $\lambda = 100, N = 8192$). Near rod regime, we see that exponent is very close to $\alpha = 1$, which is the ballistic regime. On the other hand, in the rope regime ($N_\ell > 100$), the system is asymptotically approaching a subdiffusive regime. We cannot simulate for all N_ℓ at each λ . However, there seems to be a smooth transition region, supporting a collapse to the same exponent. The transition from ballistic to superdiffusive behaviour is also visible in the temperature profile plotted in Figure 2.6 where the thermal gradient develops in the rope limit. No logarithmic divergence is visible here, which has been observed by [40] in one of the cases. Thus, we can get a superdiffusive behaviour with a multibody potential in a single chain. We can expect the system to asymptote to a power law with exponent α , provided we have enough persistence lengths in

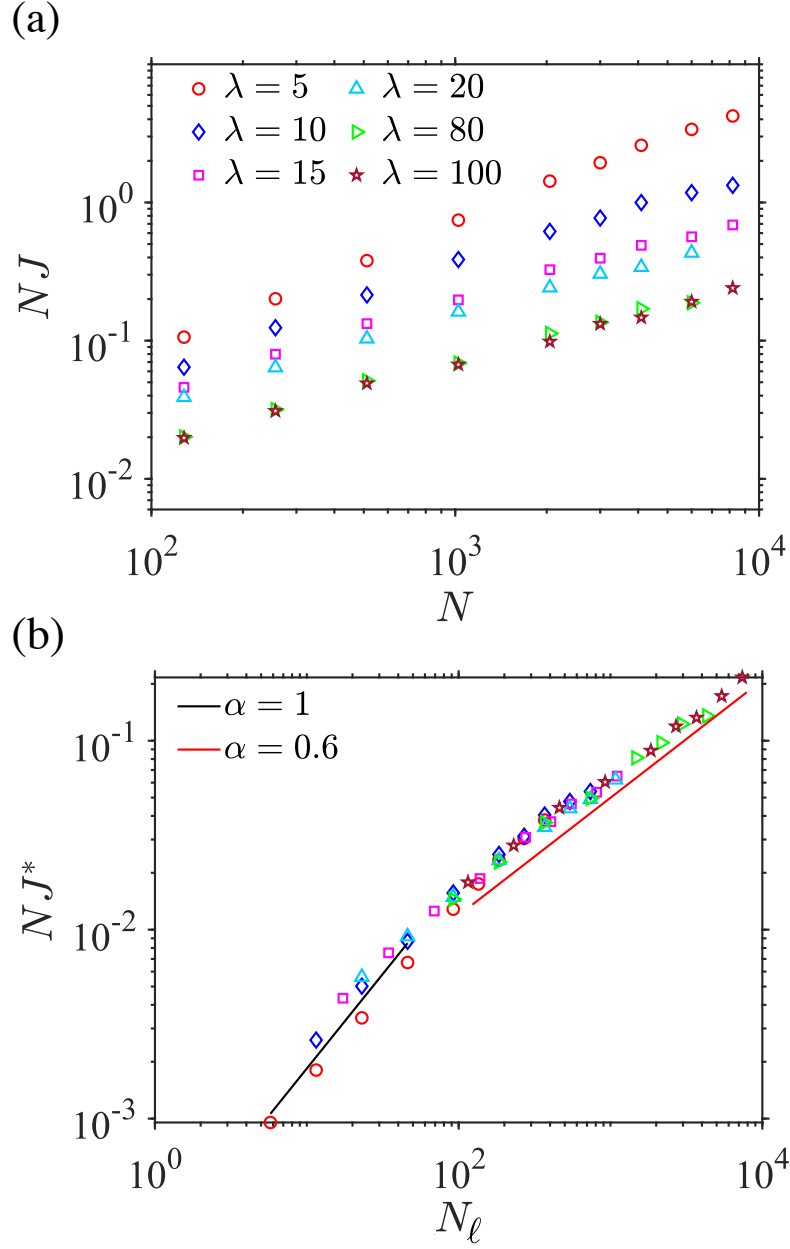


Figure 2.4: (a) Shows the divergence of NJ with the size of system in a mass ordered system with Langevin baths and unit spacing. (b) The X axis has been scaled as the number of persistence lengths in the system (N_ℓ), while Y axis has been scaled by different numbers to find a master curve for power law. The line has been fitted using the last four points for $\lambda = 100$ and has been extended to lower N_ℓ values. For clear representation, a parallel line has been drawn and a superdiffusive behaviour can be seen with transition around $N_\ell = 100$ from ballistic behaviour. $T_H = 0.01$, $T_C = 0.008$.

the system.

Disordered systems

Since we have seen the effect of multibody potential in an ordered system, we want to further study the power law in the presence of mass disorder. The disorder can localize extended modes in a system, leading to an insulating chain. While [1] observed a perfect insulator with only two-body interactions, the localization was destroyed in the presence of non-linearity. As we are interested in NJ at the asymptotic limit where geometric non-linearities take over, delocalization of modes is possible. Thus, we introduce an independent mass disorder to the system like in Section 2.2. The two plots have been plotted similarly as in the ordered case. We can observe from Figure 2.5 that the magnitude of NJ is an order less than the ordered system. This is expected as we have an additional source of scattering. Apart from that in Figure 2.5, the exponent is similar through all the values of N_ℓ explored. We do not see a transition region from ballistic to superdiffusive regime. These features are also visible in the temperature profile plotted in Figure 2.6 where the thermal gradient is present in the system in both rod and rope limit. It can be possible that the transition region has shifted to short system sizes because of additional scattering, or mass disorder is a dominant source of scattering for our range of parameters. The exponents that we get are slightly lower than the ordered case. However, the superdiffusive behaviour with N_ℓ in the asymptotic limit seems to exist.

2.3.2.1 Displacement amplitude projection

As the asymptotic limits show signs of a superdiffusive behaviour in both ordered and disordered systems, we try to understand the physics behind it. Since this is an extremely non-linear regime, plotting modal projections or understanding Eigenvalues might not give an accurate perspective. Thus, we plot the magnitude of longitudinal ($|\mathbf{X}|$) and transverse displacements ($|\mathbf{Y}|$) for each chain site (i) along with the normalized time (t^*). Here $i = 1$ corresponds to the hot end and $i = N$ corresponds to the cold end. The positions have been recorded after the system has reached NESS. Time (t^*) has been recorded for $2 \times 10^4 \times \frac{N}{128}$ steps for both rope limit ($N = 128, \lambda = 5$) and rod limit ($N = 6000, \lambda = 100$). It can be observed from Figure 2.7(a) that as we move from rod to rope regime, $|\mathbf{Y}|$ show coherent wave packets travelling from one end to the other. This pattern is recurring, and we believe that the shift in types of waves carrying energy leads to superdiffusive behaviour. These patterns have to be investigated further and are outside the

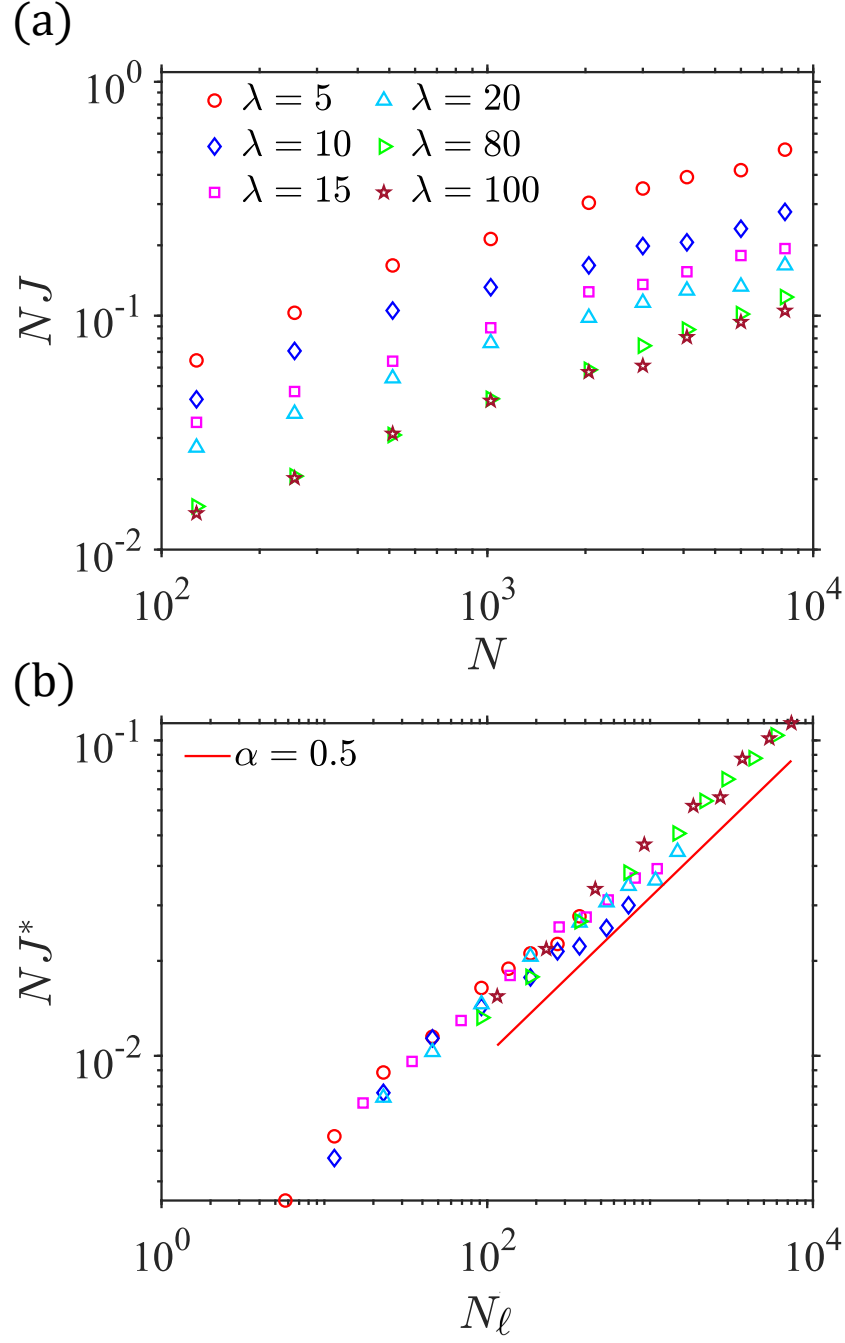


Figure 2.5: (a) NJ vs N plot showing divergence of NJ with the size of the system in a mass disordered system with Langevin baths and unit spacing. (b) The X-axis has been scaled as number of persistence lengths in the system (N_ℓ), while Y-axis has been scaled arbitrarily to find a master curve for power law. No transition region has been observed and the system is superdiffusive throughout the range of the simulations. $T_H = 0.01$, $T_C = 0.008$.

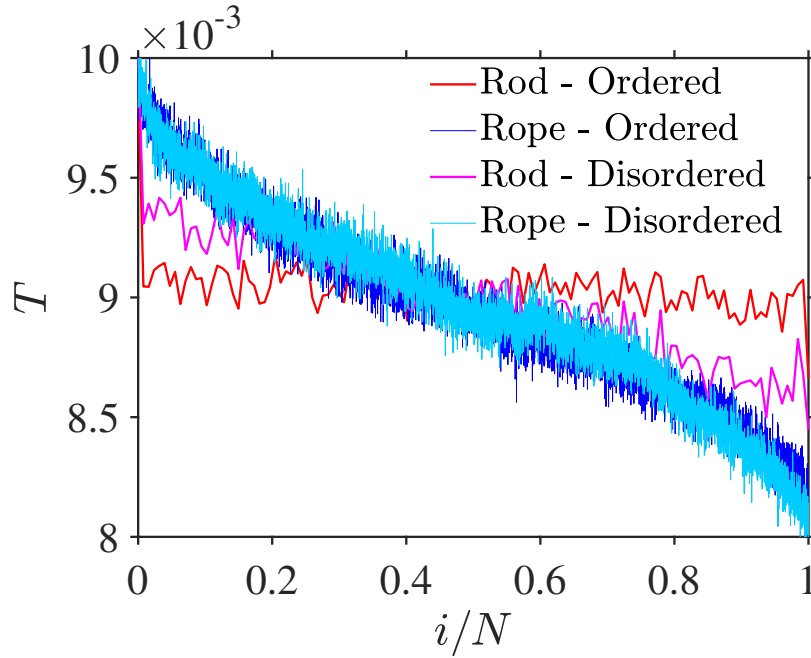


Figure 2.6: Temperature profiles of the ordered and disordered systems in the rod ($N = 128$, $\lambda = 5$) and rope limit ($N = 6000$, $\lambda = 100$). Here i is the chain site. For both systems we see a well developed temperature gradient in the system. Except rod limit of ordered system all other systems have a temperature gradient showing deviation from ballistic behaviour. $T_H = 0.01$, $T_C = 0.008$.

scope of this thesis. Moreover, this recurring pattern is also visible when there is a mass disorder in the system in Figure 2.7(b) for both rod and rope regime. Since these patterns exist in all three regimes of ordered and disordered cases where superdiffusive behaviour is visible, we believe these are correlated. Further investigation is needed.

2.4 Summary

In this chapter, we have first characterized both flexural and longitudinal modes in the harmonic limit using transmittance function. In longitudinal modes, a significant contribution was found to be observed from higher frequencies, while flexural modes had symmetrical contributions centred around half of the maximum frequency. Since, the disorder can localize higher frequency, we observed that the contribution of longitudinal modes to the J decreased at shorter system sizes compared to the flexural mode.

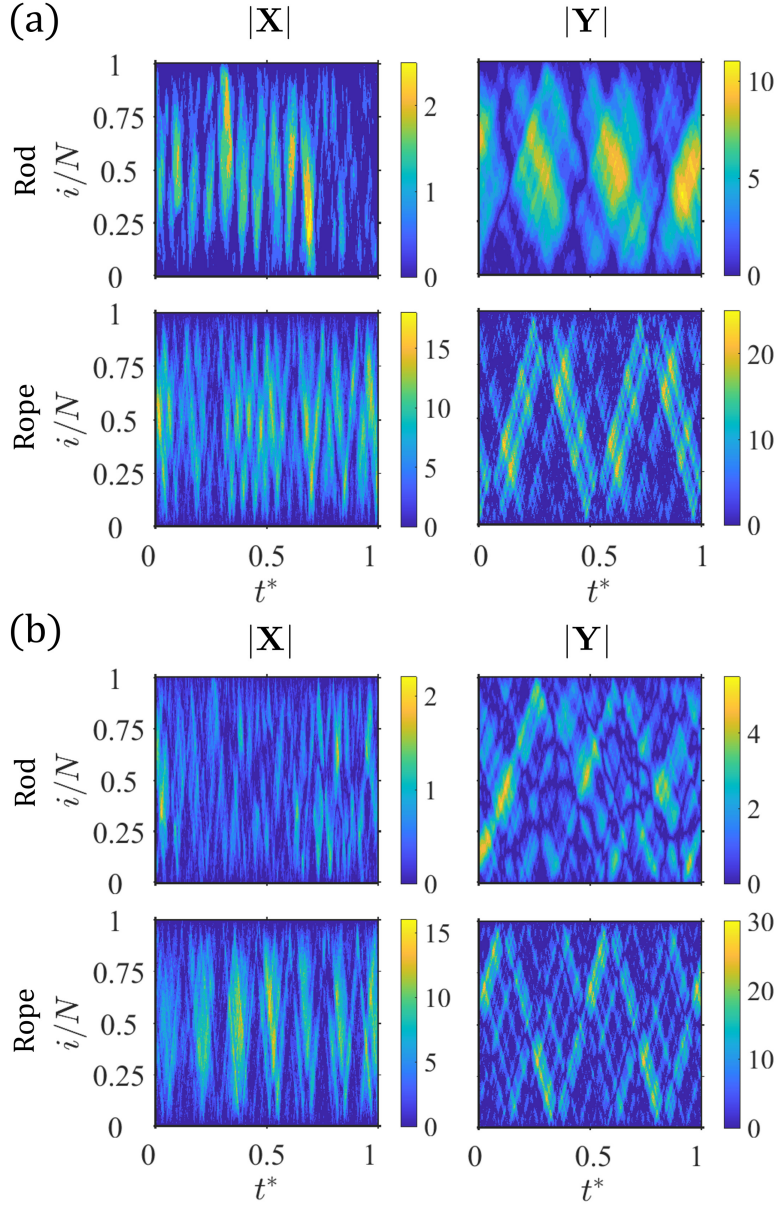


Figure 2.7: Projected longitudinal($|X|$) and transverse displacements($|Y|$) of (a) Ordered system (b) Disordered system in the rod and rope limit. Here i represents the chain site, where $i = 1$ is the hot end and $i = N$ is the cold end. The positions have been recorded after the system has reached NESS for $2 \times 10^4 \times \frac{N}{128}$ time units for both rope limit($N = 128, \lambda = 5$) and rod limit ($N = 6000, \lambda = 100$). Here $t^* = 0$ and $t^* = 1$ corresponds to the starting and ending time of recording. Coherent patterns are visible in $|Y|$ of all 3 regimes showing super diffusive behaviour (rope limit of the ordered system and both limits of the disordered system).

For the analysis in the non-linear regime, we use NESS simulations. We have analyzed a non-dimensionalized Hamiltonian with multibody forces and pinned boundary conditions. Both ordered and disordered mass systems have been studied to establish a superdiffusive behaviour in the system. N_ℓ as a measure of system size has been used to study the asymptotic limit of NJ and characterize the behaviour of our chain for both systems. While there is a visible transition around $N_\ell = 100$ for an ordered system from ballistic to superdiffusive behaviour, the disordered system has shown a continuous superdiffusive behaviour. This can be due to the dominance of the mass disorder as a scattering source for our range of parameters in the multibody system. Displacement amplitude plots were used to get insight into superdiffusive behaviour. Recurring patterns of wave reflection from one to the other end are visible in all three regions (ordered and disordered systems) where superdiffusive behaviour is seen. These coherent patterns reflect a change in the energy carriers when the behaviour changes from ballistic to superdiffusive behaviour. We believe that this change of the carriers is responsible for imposing superdiffusive behaviour.

Chapter 3

Effect of pinning transverse motion on thermal transport of a single chain having multibody potential

In this chapter, we study the effect of transverse pinning on a single chain with multibody potential. While studies have been available for two-body interactions, literature for simple multibody potential with pinning is missing. We use the concept of transverse pinning to model the effect of crowding in an array or forest-like arrangement on κ .

We briefly discuss the literature showing reduction of κ in Section 3.1. In Section 3.2, we discuss the computational limitations of modelling an array with multibody potential. We describe our model shown in Figure 3.1 in the same section. In section Section 3.3, we discuss the effect of pinning on ordered and disordered systems. The ordered systems show up to 70% decrease in κ with only $\sim 0.3\%$ of pinned points. On the other hand, no considerable effect was visible in the presence of mass disorder. Finally, in Section 3.4, we study the tradeoff between increasing scattering points and decreasing non-linearity in a single chain by increasing

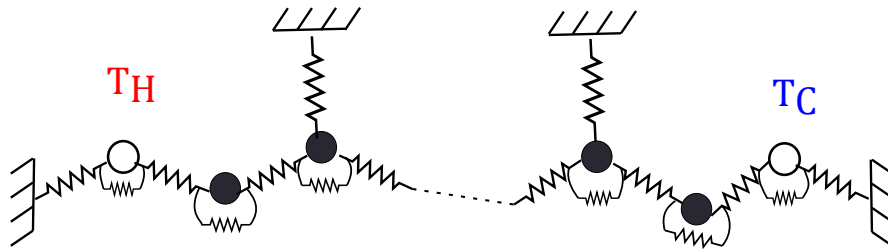


Figure 3.1: Schematic of single chain model in a crowded environment, modelled as the pinning of transverse motion. Here $i \in [0, N + 1]$ where the two end particles are pinned. Langevin baths have been added at $i = 1$ and $i = N$ with temperatures T_H and T_C respectively. Additional springs with stiffness $-v$ are added to restrict the transverse motion.

the number of pinning sites. We observe a non-monotonous trend from superdiffusive to the ballistic regime. It indicates that a critical density can exist in arrays, leading to a transition from a superdiffusive to a ballistic behaviour.

3.1 Reduction in κ of a Q1DM in an array-like arrangement

We have observed that an additional vibration mode can lead to a transition from superdiffusive to ballistic behaviour in a single chain. The motion in the transverse direction is the only source of non-linear coupling in a single chain. Heat transfer also is only along the backbone in an isolated chain. When multiple chains are placed side-by-side, the heat can also transfer in the transverse direction. The heat transfer to surrounding chains can be due to non-bonded interactions like vdW forces or fusing of two chains during manufacturing. These interactions can introduce a coupling between adjacent chains, resulting in scattering and heat leakage. Some interesting results have been observed by [24] where a knockdown in κ , has been observed. They observed that heat gets localized in a CNT forest despite individual CNT's high thermal conductivity along the axis. This phenomenon is intriguing as κ even along the chain's backbone is decreased. The inter-chain interaction we have discussed before can be observed in these forests. The CNTs are not perfectly aligned, and interactions like fusion and entanglement can be observed. It can also lead to kinks or bends along the backbone, which can decrease κ .

A decrease in thermal conductivity due to crowding has also been reported in other literature [24, 70–72, 77]. Thus, this inter-chain interaction is not limited to CNT forests. It has to be noted that there is no model with a simple two-body and three-body interaction that can study the effect of crowding on power law. Thus it becomes interesting to understand how these interactions can affect the system.

3.2 Modelling of inter-chain interactions as transverse pinning

As we have seen, two body potentials have been studied for power law and thermal conductivity. The analysis can be limited by the computational power [99] in the case of 2D networks as the number of sites increases as $N \times M$, for M number of chains. It is computationally expensive to go to larger system sizes, which is necessary to observe power law. Thus we model this interaction as pinning of transverse DOF of a single chain. We add harmonic springs with

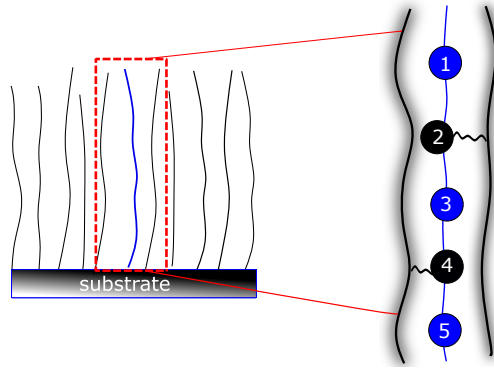


Figure 3.2: Representation of interaction of a single chain in a crowded environment, like forest. Zoomed view of a single chain shows the cylindrical wall potential.

pinning strength of v in the Hamiltonian, (2.3) as:

$$H = \sum_{i=1}^N \left\{ \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2} + \frac{1}{2} (|\mathbf{r}_i - \mathbf{r}_{i+1}| - 1)^2 + \frac{1}{\lambda} (\cos \theta_i + 1) + v_i y_i^2 \right\} \quad (3.1)$$

The number of pinning sites (q) can be related to the forest's density, where chains interact with the surroundings. In this model, pinning sites were equally spaced. Thus this simple model can give an insight into the thermal transport of a single chain in a cylindrical potential as shown in Figure 3.2. The figure shows a chain in the influence of nearby chains where few sites are close enough to be in cutoff radius for interaction. The potential due to neighbouring tubes has been represented as wall potential. Here we can vary the value of v to probe two extremes possibilities of the interaction. $v = 0.01$ can represent a weak interaction, while $v = 1$ can be a fusion of two chains while manufacturing. A simplified model has been shown in the Figure 3.1. The system's size - N was fixed as 4096. This size was chosen as we observed deviation from ballistic behaviour at this system size in the last chapter. Moreover, it saves the computational cost required for larger system sizes.

3.3 Effect of pinning on thermal transport in ordered and disordered systems

Adding pinning to the system destroys translational invariance as well as introduces band gaps in the system. Thus it can affect the magnitude as well as divergence of κ in the system. The pinning has been studied of two-body interactions by [7] in a disordered system of harmonic axial interactions. It has been shown that when all the sites are pinned, the J can decrease exponentially with the system's size, depending on the pinning strength. Our system is quite different as there are two DOF in our system, and we are pinning only one DOF. Thus we start by analyzing the effect of the increasing number of pinning sites for both ordered and disordered systems in Figure 3.3. It can be seen that in an ordered system, the κ decreases by more than 70% for strong pinning and about 20% for weaker pinning. It has to be noted that we have pinned only $\sim 0.3\%$ of the total sites. Disordered case, on the other hand, is less sensitive to pinning. Since there is already a huge reduction in κ due to disorder, additional pinning does not

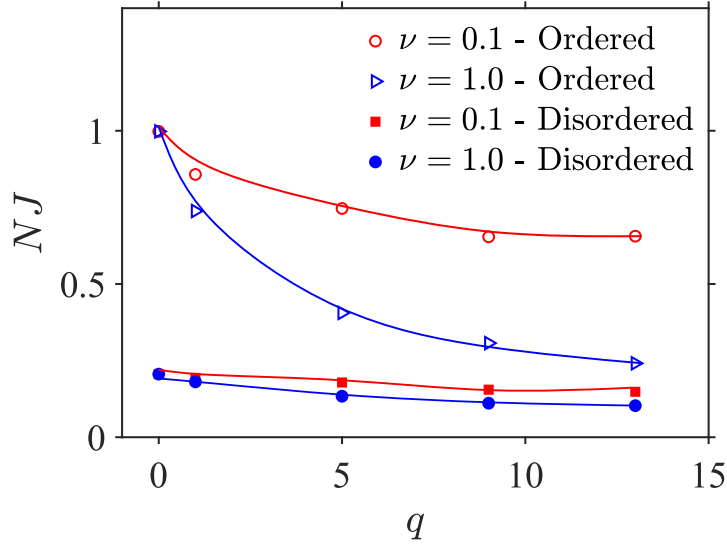


Figure 3.3: Comparison of the decrease in the thermal conductivity for the ordered (empty markers) and disordered systems (filled markers) with increase in the q (number of pinned points). These pinned sites are equally spaced. Ordered systems show up to 70% drop in NJ with only $\sim 0.3\%$ of the number of sites pinned. Disordered systems are less sensitive as the mass disorder is a dominant source of scattering. $\lambda = 10$, $T_H = 0.01$, $T_C = 0.008$, $N = 4096$

affect the system. In a nutshell, we can see that an ordered system is more sensitive to pinning than a disordered mass system. The mass disorder seems to be a dominant scattering source for this system.

3.4 Effect of the number of pinning points on κ

In the previous section, we have seen that transverse pinning decreases the κ in a chain with multibody and two-body interactions. It has to be noted that the number of pinning points were $\sim 0.3\%$ of the sites available. Thus the effect of pinning sites can be quite significant. The addition of pinning sites is also interesting as it introduces two opposite drivers. On the one hand, we are increasing scattering sites in the system. On the other hand, we are arresting one degree of freedom, thus reducing the transverse fluctuation. It can reduce non-linearity in the system. This effect can lead to the decoupling of axial and flexural modes. Thus, under these conditions, we can expect anomalous behaviour. In such a case, despite adding a scattering mechanism, we can see a transition to the ballistic regime. It should be a non-monotonous behaviour, as we can see from Figure 3.4. The κ first decreases when the number of scattering sites increases but increases when more than 25% sites are pinned. This behaviour is quite visible in Figure 3.5 where the temperature gradient first increases from $q = 1$ to $q = 13$, while at $q = N$, we see a flat profile corresponding to ballistic transport. This observation indicates a possibility of a transition region in a crowded environment where the behaviour can shift from anomalous to ballistic.

Here $v = 0.01$ is a very weak interaction. It can be analyzed as the effect of vDW forces ($\sim k_B \tilde{T}$), which are approximately two orders less than a C-C bond ($\sim 80 k_B \tilde{T}$). On the other hand, $v = 1$ can be analyzed as the fusion of two chains. It can be observed that fusion can have a more drastic effect on NJ than vDW interactions. We also would like to highlight that our chains are pinned at two ends, which can be different from the chains grafted on a surface (forests). One free end can lead to additional kinks and transverse interactions and thus lead to additional scattering. It can lead to an additional reduction of NJ with fusion, which is already showing a huge reduction.

3.5 Summary

In this chapter, we studied the effect of pinning of transverse motion of a single chain with multibody potential on κ . The model can be used to study the crowding of chains in a forest-like environment. We observed that even 0.25% pinned sites can lead to a 70% decrease in κ of an ordered chain. This effect is not significant in the presence of mass disorder, which itself is a dominating scattering source in reducing the transport. We further studied the impact of adding pinning points in an ordered system. It leads to two counter effects in the system; we are adding scattering sources as well as decreasing the transverse motion of the chain. It has been observed that the decrease in κ is thus non-monotonous from superdiffusive to ballistic transport with an increase in the number of pinned sites. This transition is visible in the temperature profiles for the respective number of pinning. It seems possible to observe a transition from superdiffusive to ballistic behaviour in a crowded environment.

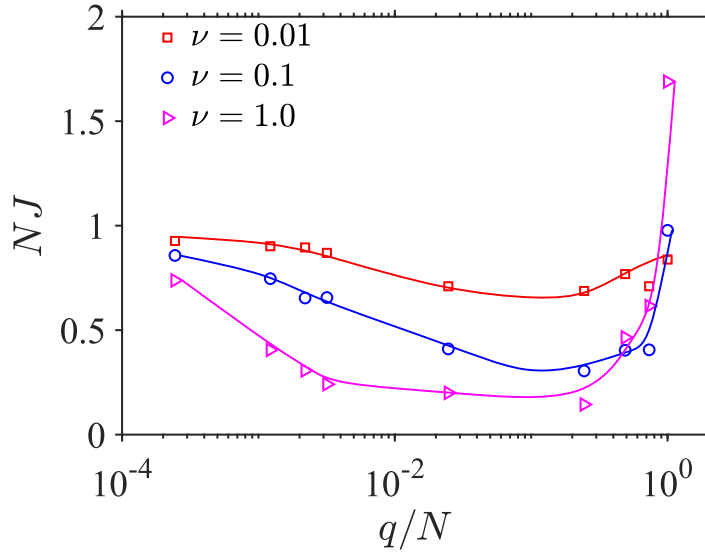


Figure 3.4: Non-monotonic behaviour of the thermal conductivity from superdiffusive to ballistic transport with increasing q (number of pinned points). There is an interplay of the addition of scattering sites and the straightening of the chain backbone which leads to this transition. $\lambda = 10$, $T_H = 0.01$, $T_C = 0.008$, $N = 4096$

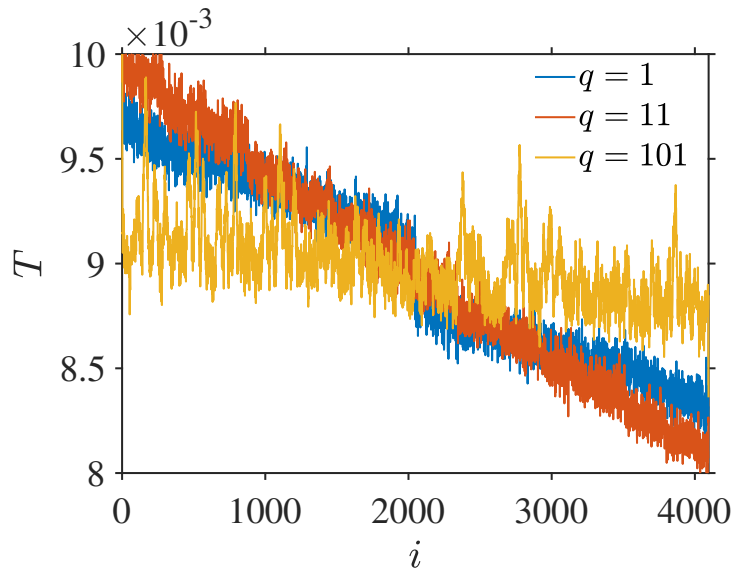


Figure 3.5: Temperature profiles showing the non-monotonous transition from superdiffusive to ballistic behaviour with an increase in q (pinned points). Here i is the site. $\lambda = 15$, $T_H = 0.01$, $T_C = 0.008$, $N = 4096$. Increasing q adds scattering points but also removes non-linearity due to the flexibility of the system. Thus, leading to a non-monotonous behaviour.

Chapter 4

Thermal transport in molecular forests²

In this chapter, we study the anisotropic heat flow in molecular forests using a multiscale molecular simulation approach. For this purpose we devise a generic scheme to map the nanoscale physics onto a coarse-grained (CG) model in Section 4.1. We discuss the effect of crowding on reduction of $\kappa_{\parallel}$ of a single chain in Section 4.2. Finally, we develop a microscopic understanding of the reduced heat transport in molecular forests in Section 4.3. We thus, show how a broad range of materials can be modelled within one unified physical concept. To achieve the above goals, we combine molecular dynamics simulations of a generic polymer brush model [100] with known theoretical concepts from polymer physics [101] and thermal transport [77, 102].

4.1 Modelling

We consider a Q1DM as a linear polymer chain, where the inherent flexibility is dictated by its persistence length $\tilde{\ell}_p$. For example, a linear molecule behaves as a rigid rod when the contour length $\tilde{\ell}_c \simeq \tilde{\ell}_p$, while it follows a self-avoiding random walk statistics for $\tilde{\ell}_c \gg \tilde{\ell}_p$ [101]. In this context, a recent experiment has measured that $\tilde{\ell}_p$ of an isolated single wall CNT is about $50 - 60 \mu\text{m}$ for a CNT diameter of $\mathcal{D} \simeq 1.0 \text{ nm}$ [103]. Furthermore, $\tilde{\ell}_p \simeq 5 \mu\text{m}$ for a NW with $\mathcal{D} \simeq 1.0 \text{ nm}$ [104], $\tilde{\ell}_p \simeq 0.65 \text{ nm}$ for PE [105] and $\tilde{\ell}_p \simeq 1.0 \text{ nm}$ for PEDOT [106]. Using these $\tilde{\ell}_p$ estimates, we can now analyze different molecular forests. For example, the typical heights $\mathcal{H}$ of CNT forests or arrays of NWs range within $0.1 - 2 \text{ mm}$ [24, 107], while in some cases can also be 6 mm [72]. Furthermore, for the bundles of PE [75] or PEDOT [78], $\mathcal{H} \simeq 100 \text{ nm}$. Therefore, it is evident that $\mathcal{H} \simeq 2 - 200\tilde{\ell}_p$ in most cases. This observation provides an

²A version of this chapter is available online [66]. [Bhardwaj, A., Phani, A. S., Nojeh, A., & Mukherji, D. (2020). “Thermal transport in molecular forests”. *arXiv preprint arXiv:2005.10685*.

important length scale in our simulations and suggests that a long Q1DM can be modelled as a flexible polymer chain, and hence a molecular forest as a polymer brush (Figure 4.1).

Here it is important to note that the bonded monomers along an isolated chain backbone impart almost crystalline-like structure, while a polymer brush is amorphous-like in all directions. This is very similar to the situation in molecular forests [21, 24, 70, 71, 74, 78]. It should be emphasized that, while a simple polymer model is certainly not appropriate to describe all the complex properties of Q1DMs, our aim is to investigate if a CG model can explain the anomalies in thermal behavior observed in experiments [24, 73, 74]. Furthermore, CNTs and NWs have rather large $\tilde{\ell}_p \simeq 5 - 50 \mu\text{m}$ even when their $\mathcal{D} \approx 1.0 \text{ nm}$. Here, we map one $\tilde{\ell}_p$ onto a monomer bead. This simple mapping scheme is chosen to capture the molecular bending for $\tilde{\ell}_c \geq \tilde{\ell}_p$, which is essential in dictating the phonon mean-free path and thus $\kappa_{||}$ in the molecular forests.

For this study, we employ the Kremer-Grest polymer model [100]. In this model, individual

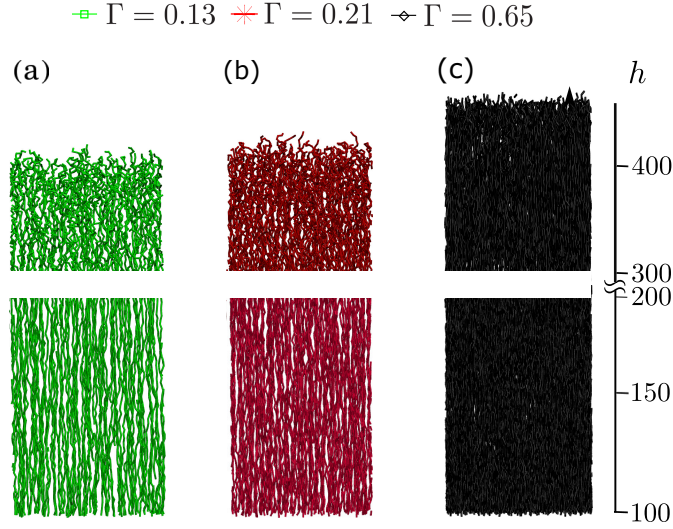


Figure 4.1: (a-c) show simulation snapshots for $\Gamma = 0.13$ (green), $\Gamma = 0.21$ (red) and $\Gamma = 0.65$ (black), where Γ is the ratio of the total area occupied by all tethered monomers and the surface area of the plane. d is the length scale in reduced LJ units. The bottom panels of the snapshots are the enlarged views of brushes between $100d < h < 200d$ and the top panels show the top layer for $h > 340d$. The arrow at the right corner points at the direction of brush height h . We can observe the variation in height of equilibrated configurations where h increases with Γ . The visualization is done using VMD package [108].

monomers interact with each other via a repulsive 6–12 Lennard-Jones potential with a cutoff distance $r_c = 2^{1/6}d$. $V_{LJ} = 0$ for $r > r_c$. The bonded monomers in a chain interact with an additional finitely extensible nonlinear elastic (FENE) potential:

$$U_{LJ} = 4\epsilon \left(\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right) + \epsilon \quad (r < 2^{1/6}d) \quad (4.1)$$

$$U_{FENE} = -33.75\epsilon \log \left[1 - \left(\frac{r}{1.5d} \right)^2 \right], \quad (4.2)$$

which is also shown in (Figure 4.2).

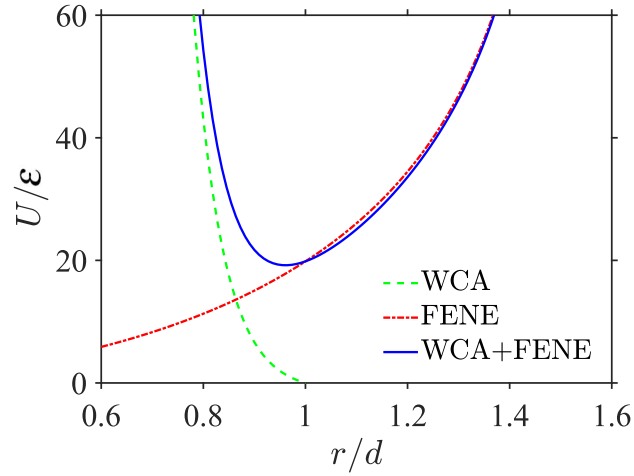


Figure 4.2: Weeks-Chandler-Andersen (WCA), Finite Extensible Non-Linear Elastic (FENE) potential and WCA+FENE potential (Kremer-Grest model).

The results are presented in the unit of LJ energy ϵ , LJ distance d and mass m of individual monomers .

This leads to a time unit of $\tau = d(m/\epsilon)^{1/2}$. We consider chains of length $N = 500$. Note that $\tilde{\ell}_p$ of the fully flexible polymer model is about one bead, thus in our case $N \simeq 500\tilde{\ell}_p$. Here the bond length $\ell_b \simeq 0.97d$. Furthermore, the first monomer of every chain is tethered randomly onto a square plane with lateral dimensions $L_x = L_y \simeq 36.5d$ and the chains are oriented normal to the surface, in the z direction. The surface coverage Γ is varied up to 0.65. Here, Γ is calculated as the ratio of the total area occupied by all tethered monomers and the surface area of

the plane. Γ values chosen here are much larger than the critical grafting density defined as $\Gamma^* = (d/2R_g)^2$ with R_g being the radius of gyration of the chain. Periodic boundary conditions are applied in the x and y directions. One set of single chain simulations have also been performed where the chain is tethered at both ends forming a fully stretched configuration.

4.1.1 System details

The polymer brush configurations are generated by randomly tethering the first monomer of each chain onto a plane with lateral dimensions $L_x = L_y \simeq 36.5d$ and then chains are created normal to the plane, i.e., along the z direction. Here, it is important to note that our protocol to generate a brush configuration reasonably mimics the experimental reality of synthesizing a CNT forest [24, 72], gradually grown upward starting from catalyst nanoparticles on a substrate and normal to the substrate, using the process of chemical vapor deposition. The striking similarity between the original system [24, 72] and the model system presented here is highlighted by the presence of kinks along the molecular backbone that effects heat propagation along the chain. Once the chains are grown normal to the substrate, the excluded volume interaction between the non-bonded monomers are increased from $0d$ to $1d$ with a step of $0.01d$ during a warmup stage. During each stage of warmup, system is equilibrated for 10^4 MD steps with and time step of $\delta t = 0.01\tau$. This protocol generates a sample without any unphysical particle-particle overlap, while also ensuring that the system is equilibrated (Figure 4.1). We have chosen a chain length of $N = 500$ and five different grafting densities Γ . The details of these system sizes are presented in Table 4.1. All Γ values are much larger than the critical grafting density Γ^* of a polymer chain of $N = 500$ onto a plane. Here, $\Gamma^* = (d/2R_g)^2$, i.e., one chain grafted within an area of πR_g^2 and defines the transition from mushroom to brush regime. For an isolated chain of $N = 500$, the gyration radius $R_g \simeq 18.0d$. The brush height $\mathcal{H}$ is calculated based on the monomer density profile ρ shown in Figure 4.3.

4.1.2 Stress and thermal conductivity calculations

The virial stress is calculated using the standard subroutine in LAMMPS [109] as:

$$\sigma_{ij} = \frac{1}{V} \left(\frac{1}{2} \sum_{n=1}^{n=N_p} (r_{1i}F_{1j} + r_{2i}F_{2j}) + \frac{1}{2} \sum_{n=1}^{n=N_b} (r_{1i}F_{1j} + r_{2i}F_{2j}) \right) \quad (4.3)$$

Γ	Γ/Γ^*	N_g	NN_g	$\mathcal{H}$
0.06	77.8	100	50000	350d
0.13	168.5	225	112500	360d
0.21	272.3	361	180500	380d
0.29	375.8	484	242000	420d
0.65	842.4	1089	544500	460d

Table 4.1: A table listing the system size details used for the simulations. For this purpose a chain length of $N = 500$ is chosen. We give details of the grafting density Γ , the critical grafting density Γ^* , the number of grafted chains N_g , the total number of particles NN_g , and the brush height $\mathcal{H}$.

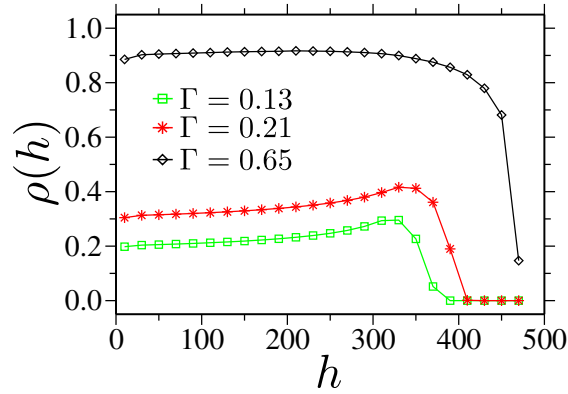


Figure 4.3: Monomer number density ρ as a function of height h along the z -direction. Data is shown for three different surface coverages, Γ . We observe that with the increase in Γ , the brush height increases.

where N_p and N_b are the total number of particles with pairwise and bonded interactions of an atom. $\mathbf{F}_1$ and $\mathbf{F}_2$ are forces on particle 1 and 2 due to each other and V is the volume. Height h dependent stress profile is calculated by dividing the brush height $\mathcal{H}$ into different slabs of width $50d$, see Figure 4.6(b).

For the calculation of the anisotropic thermal conductivity coefficients κ , we have used the Kubo-Green formalism [110] implementation in LAMMPS [109]. The equation of motion are integrated in the microcanonical ensemble, while an estimate of the heat flux autocorrelation function,

$$C(t) = \langle \dot{\mathbf{J}}(t) \cdot \dot{\mathbf{J}}(0) \rangle, \quad (4.4)$$

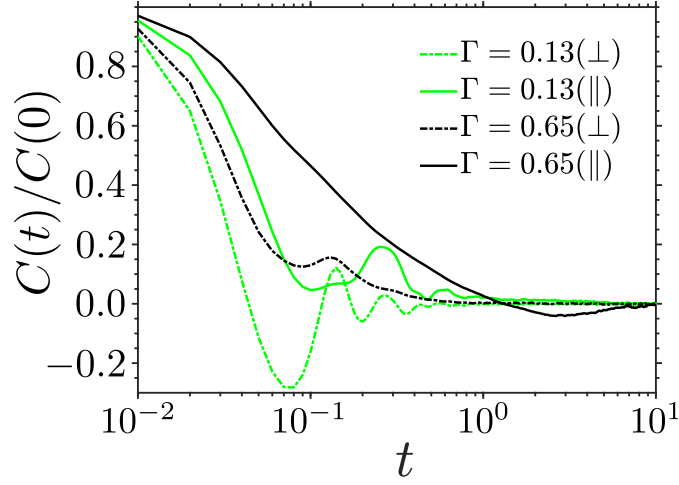


Figure 4.4: Normalized heat flux autocorrelation function $C(t)/C(0)$. Data and shown for two different surface coverages Γ and for both components. Here we have considered a slab centered on $125d$.

is obtained by sampling the system's heat flux vector $\mathbf{J}(t)$ over simulation time. Here we choose a sampling period of $10^{-3}\tau$ to determine the correlation function over a time frame of $0 \leq t \leq 2 \times 10^3\tau$, which is one order of magnitude larger than the typical de-correlation time. During a total simulation of $2 \times 10^5\tau$, we accumulate correlation data and compute a running average of the heat flux correlation function $C(t)$. In Figure 4.4 we show the typical $C(t)$ data for a couple of our simulation runs. Finally, κ values are calculated by taking the plateau value of the Green-Kubo integral for the component along the chain,

$$\kappa_{\parallel} = \frac{V}{k_B \hat{T}^2} \int_0^{\infty} \langle \mathbf{J}_z(t) \cdot \mathbf{J}_z(0) \rangle dt, \quad (4.5)$$

and in the lateral directions, i.e., x or y -directions,

$$\kappa_{\perp}(t) = \frac{V}{2k_B \hat{T}^2} \int_0^{\infty} \left[\langle \mathbf{J}_x(t) \cdot \mathbf{J}_x(0) \rangle + \langle \mathbf{J}_y(t) \cdot \mathbf{J}_y(0) \rangle \right] dt. \quad (4.6)$$

For the single chain and single chain in brush data, we have used V of a single chain, see Figure 4.5. Furthermore, for the calculation of slab-wise κ , v is taken as the volume of a slab with thickness $50d$.

Simulations are carried out in two stages: the initial equilibration and the thermal transport

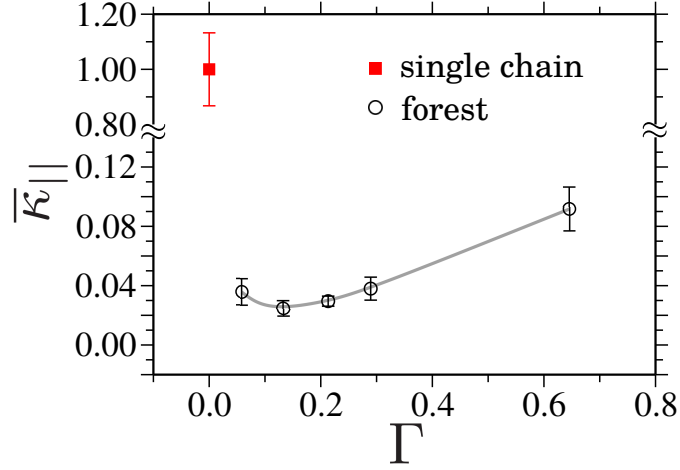


Figure 4.5: Normalized thermal conductivity along a chain backbone $\bar{\kappa}_{||} = \kappa_{||}(\Gamma)/\kappa_{||}(0)$ as a function of surface coverage of polymers Γ . $\kappa_{||}(0)$ corresponds to the single chain data (i.e., $\Gamma \rightarrow 0$), where the chain is tethered at both ends. For the simulations under crowded environments, we have only calculated $\kappa_{||}$ of a single chain in a brush configuration, such that a chain experiences a cylinder-like confinement. Note that normalization volume in the Kubo-Green formula is taken as the volume of one chain, i.e., $v = v_m N$ with v_m being the volume of one monomer. The gray line is a polynomial fit to the data that is drawn to guide the eye.

calculations. Initial equilibration is performed under the canonical ensemble with a time step of $\delta t = 0.01\tau$ for 2×10^7 MD time steps. The equations of motion are integrated using the velocity Verlet algorithm [96]. The system is thermalized via a Langevin thermostat with a damping constant $\dot{\gamma} = 1\tau^{-1}$ and $\dot{T} = 1\varepsilon/k_B$, where k_B is the Boltzmann constant. After this step, the components of κ are calculated using the Kubo-Green method in microcanonical ensemble [110].

4.2 Effect of crowding on $\kappa_{||}$ of a single chain

In Figure 4.5 we summarize the normalized thermal conductivity along a chain backbone $\bar{\kappa}_{||} = \kappa_{||}(\Gamma)/\kappa_{||}(0)$ as a function of Γ . Here, $\kappa_{||}(0)$ corresponds to the single chain data (i.e., $\Gamma \rightarrow 0$). Note that for the calculation of $\kappa_{||}$ in a brush we only consider one chain in the crowded environment. It can be seen that, within the range $0.05 < \Gamma < 0.30$, $\kappa_{||}$ reduces by a factor of 25–30 in a brush compared to a single chain. This sharp decrease is reminiscent of the reduced $\kappa_{||}$ in CNT forests [24, 73] and sheets [74]. What causes such a dramatic decrease

in $\kappa_{||}$? It is particularly puzzling given that $\Gamma \gg \Gamma^*$ in all cases (Table 4.1) and therefore individual chains in a brush are expected to stretch significantly [101]. Here, $\kappa_{||}$ is expected to be dominated by the bonded interactions. In this context, a closer investigation reveals that a monomer of a chain in a crowded environment has two different modes of heat dissipation: (a) two covalently bonded neighbors and (b) n non-bonded neighbors governed by the vdW interactions. Furthermore, the vdW interaction strength is less than $k_B \tilde{T}$, while the bonded interactions can be typically of the order of $80k_B \tilde{T}$ (a number representative of a C-C covalent bond) [111, 112]. The stronger bonded interaction also leads to about two orders of magnitude higher stiffness [113, 114]. Moreover, given that κ is directly related to the stiffness (we will come back to this point later) [77, 102], we will now investigate how a 25–30 times reduction in $\kappa_{||}$ is observed in Figure 4.5 and in experiments [24, 72–74]. For this purpose, we will now investigate the influence of microscopic chain conformation on $\kappa_{||}$.

4.3 Effect of microscopic chain conformation on $\kappa_{||}$.

We start by calculating the second Legendre polynomial P_2 of the bond orientation vector using $P_2 = (3 \langle \cos^2(\phi) \rangle - 1) / 2$. Here, ϕ is the angle of a bond vector with the z axis and $\langle \cdot \rangle$ represents the averages over all bonds and the simulation time. Here, $P_2 = 1.0$ when all bonds are oriented along the z axis, $P_2 = 0.0$ when bonds are randomly oriented and $P_2 = -1/2$ when all bonds are perpendicular to the z axis. In Figure 4.6(a) we show the variation of P_2 with the forest height h for three different values of Γ . It can be seen that $P_2 \simeq 0.92$ for a single polymer with about 5% fluctuation. This is expected given that a single chain is fully stretched and all bonded monomers are arranged in an almost perfect one-dimensional crystalline-like structure along the z axis. This is also consistent with a large $\kappa_{||}$ value for a single chain (Figure 4.5).

For $\Gamma = 0.13$ and $\Gamma = 0.21$ in Figure 4.6(a), it can be seen that P_2 decreases rather sharply with h , as known from the structure of polymer brushes [115]. This is consistent with the tethering constraint that the chains are significantly more stretched near the tethered points and become more randomly oriented as h increases, see also simulation snapshots in Figure 4.1. Furthermore, the individual chain end-to-end distances are $R_{ee}^z \simeq 370d$ (for $\Gamma = 0.13$) and $R_{ee}^z \simeq 380d$ (for $\Gamma = 0.21$) (Table 4.1 and Figure 4.3), and thus are only about 75% of the chain contour length $\tilde{\ell}_c = N\ell_b \simeq 485d$ for $N = 500$. This incompatibility between R_{ee}^z and $\tilde{\ell}_c$ indicates a significant chain bending (via the flexural vibrations) and introduces kinks along the chain contour, as shown in the lower panels of the simulation snapshots in Figure 4.1. With increasing

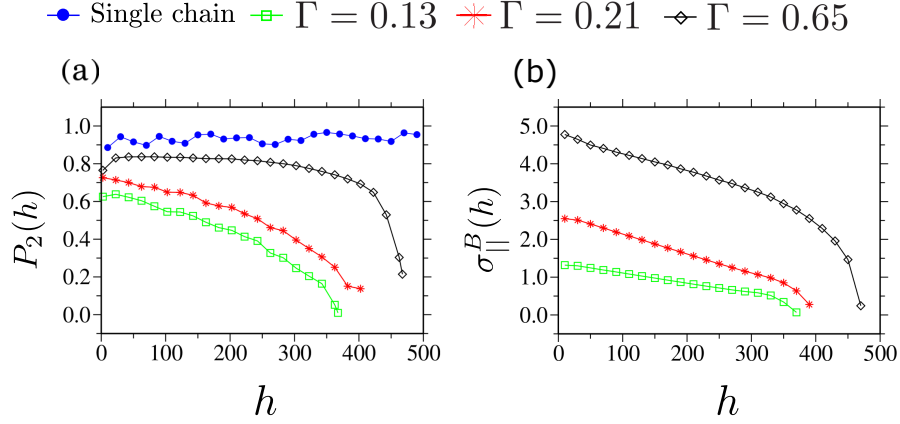


Figure 4.6: (a) shows the second Legendre polynomial of the bond orientation vector P_2 as a function of the brush height h along the z axis. Data is shown for a single chain and for three different surface coverage concentration - $\Gamma = 0.13$ (green), $\Gamma = 0.21$ (red) and $\Gamma = 0.65$ (black). (b) is the stress along the chain backbone $\sigma_{||}^B$. The lines are drawn to guide the eye. We can observe that orientation of bonds is changing in parallel direction which is also reflected in the stress.

h , chain bending (or kinks) become more-and-more prominent, see the upper panels of the simulation snapshots in Figure 4.1. In this context, it is important to note that in a fully stretched chain (as in our case of the single chain), phonon-like wave propagation carries a heat current along the chain backbone because of the periodic arrangement of monomers. When kinks appear along a chain backbone due to the flexural vibrations dictated by $\tilde{\ell}_p$ (as in the cases of $\Gamma = 0.13$ and 0.21), the longitudinal phonon propagation is impacted. Here, each kink acts as a scattering center for phonon propagation and thus reduces the phonon mean free path. The larger the number of kinks for a given N , the higher the resistance to heat flow, i.e., the lower $\kappa_{||}$ (Figure 4.5). This observation is consistent with the recent simulation study of a single PE chain, where it has been shown that increasing the number of kinks also decreases κ [116]. For $\Gamma = 0.65$, bonds are significantly more oriented and also the chains are more stretched with $R_{ee}^z \simeq 450d$ (Figure 4.6), resulting in an approximately three fold increase of $\kappa_{||}$ in comparison to $\Gamma = 0.13$ or 0.21 , see Figure 4.5

Chain bending also reduces the longitudinal chain stiffness and thus κ . Therefore, to achieve a better quantitative relationship between P_2 (or an estimate of bending), local stiffness, and κ , we will now look into how P_2 can be related to stiffness (or stress). For this purpose, we have calculated the h dependent bonded contribution to the virial stress $\sigma_{||}^B$. The data is shown in Figure 4.6(b). It can be seen that the data for $\Gamma = 0.13$ and 0.21 not only show a rather large

variation with h , consistent with the variation of P_2 in Figure 4.6(a), but that this is significantly lower than $\sigma_{||}^B \simeq 5.0\epsilon d^{-3}$ for $\Gamma = 0.65$, see Figure 4.6(b). We highlight that the monomer arrangements in our model system of forests are amorphous in all directions (as evident from the Figure 4.6 and Figure 4.3), while it is periodic for an isolated single chain. The amorphous-like structures ordinate due to the molecular kinks along the z -direction (i.e., the direction of chain orientation). This is reflected in the variation of $\kappa_{||}$ with temperature T in Figure 4.7, which does

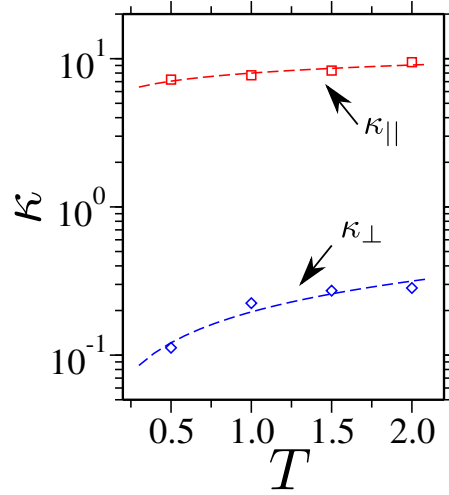


Figure 4.7: The parallel $\kappa_{||}$ and perpendicular $\kappa_{\perp}$ components of the thermal conductivity coefficients as a function of temperature $\hat{T}$. The data are shown for the surface coverage concentration $\Gamma = 0.13$. The lines are power law fits to the data that are drawn to guide the eye.

not show a $\hat{T}^{-1}$ scaling reminiscent of the standard heat transport in crystals [31, 36]. Instead we observe an increase of $\kappa_{||}$ with $\hat{T}$, as known for amorphous materials [76] where heat propagates because of the local fluctuations. Furthermore, while phonons carry a heat current in crystalline materials [31, 36], such a compact phonon picture is absent in amorphous materials [117, 118] as in the case of molecular forests. In this context, a forest with the typical height much larger than the $\tilde{\ell}_p$ of a Q1DM, such as CNT or NW, will also exhibit kinks and thus lead to amorphous like arrangements.

Figure 4.6 also suggest that there is an inherent h dependent anisotropy in the chain orientation, i.e., the chains are more stretched very close to $h \rightarrow 0$ due to tethering and become more random with increasing h [101, 115]. Consequent anisotropy is reflected in $\kappa_{||}/\kappa_{\perp}$ in Figure 4.8, where $\kappa_{\perp}$ is the thermal conductivity along the x & y directions. For $\Gamma = 0.13$

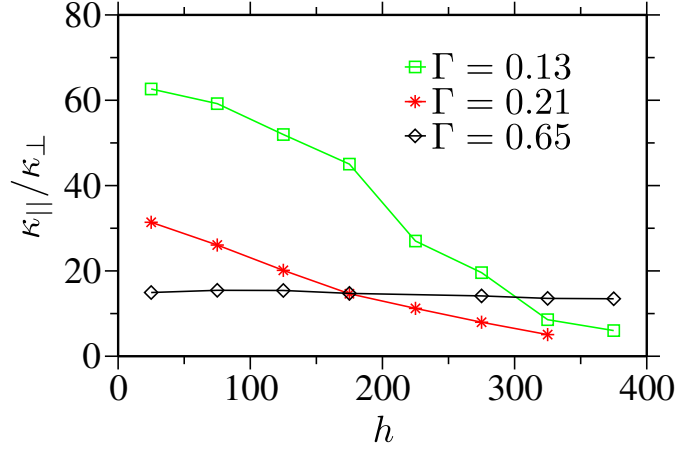


Figure 4.8: $\kappa_{||}/\kappa_{\perp}$ as a function of the brush height h . Here, $\kappa_{||}$ and $\kappa_{\perp}$ are the parallel and the perpendicular components of the thermal conductivity, respectively. Data are shown for three different surface coverage concentrations Γ . The lines are drawn to guide the eye.

we observe that heat flow is: highly anisotropic for $h < 200d$ ($\kappa_{||}/\kappa_{\perp} \simeq 50 - 60$), moderately anisotropic for $200d < h < 350d$ ($\kappa_{||}/\kappa_{\perp} \simeq 10 - 40$), and weakly anisotropic for $h > 350d$ ($\kappa_{||}/\kappa_{\perp} < 10$). With increasing Γ , the relative anisotropy in $\kappa_{||}/\kappa_{\perp}$ decreases (see the red and black data sets in Figure 4.8). The values of $\kappa_{||}$ and $\kappa_{\perp}$ are plotted in Figure A.3. The anisotropy trend is predominantly because of the increased particle number density ρ that induces a faster increase in $\kappa_{\perp}$ than $\kappa_{||}$ with ρ (Figure 4.3). Here, considering that $\tilde{\ell}_p \simeq 1d$ in our model, this also gives a comparable estimate of the relevant length scales (in terms of $\tilde{\ell}_p$) that are needed to make a direct experimental comparison. In this context, most experiments on CNT forests deal with $\Gamma \leq 0.10$, $1 < \mathcal{D} < 10$ nm (can even be several 10 nm in some cases) and also relatively small $\mathcal{H} \leq 2$ mm [24]. Therefore, the conditions typically fall within the range when $\mathcal{H}$ varies from a few $\tilde{\ell}_p$ to about $40\tilde{\ell}_p$ (i.e., for $\mathcal{D} \simeq 1.0$ nm and $\mathcal{H} \simeq 2$ mm) [103]. This will then lead to a rather anisotropic regime [24, 74]. Here, experiments on CNT forests yielded a $\kappa_{||}/\kappa_{\perp} \simeq 10 - 100$ [24, 72], for CNT sheets $\kappa_{||}/\kappa_{\perp} \simeq 500$ [74], and for PE fibers $\kappa_{||}/\kappa_{\perp} \simeq 1000$ [75]. Furthermore, our simulations show $\kappa_{||}/\kappa_{\perp} \simeq 10 - 60$ for $h < 200\tilde{\ell}_p$ and with varying Γ , see Figure 4.8. This further suggests that our simple CG model captures the relevant physics of the problem.

Lastly, we would like to investigate the dependence of $\kappa_{||}$ on the material's stiffness [77]. Figure 4.9 shows $\kappa_{||}$ as a function of an estimate of the elastic modulus along the direction of

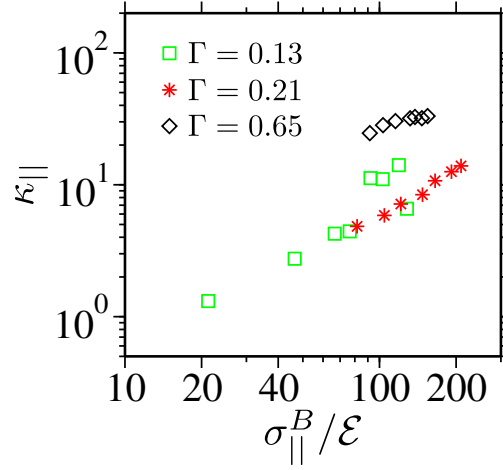


Figure 4.9: The parallel component of the thermal conductivity $\kappa_{||}$ as a function of an estimated elastic modulus along the chain orientation $\sigma_{||}^B / \mathcal{E}$. Here, $\sigma_{||}^B$ and $\mathcal{E}$ are the longitudinal bonded components of the stress and strain, respectively. Data are shown for three different surface coverage concentrations Γ .

the chain orientation $\sigma_{||}^B / \mathcal{E}$. Note that the elastic modulus is directly related to the sound wave velocity. Here, $\mathcal{E}$ is strain. We estimate $\mathcal{E}$ from the stretching of the bond vector along the z direction, which is only about 1.0% for $\Gamma = 0.13$, 1.1% for $\Gamma = 21$ and 3.0% for $\Gamma = 0.65$. These small $\mathcal{E}$ values are expected given that a bond is rather stiff [100]. It can be appreciated that the data in Figure 4.9 is constant with an understanding that κ is directly related to the stiffness [77, 102].

4.4 Summary

In conclusion, combining molecular dynamics simulations with known concepts from polymer physics and thermal conductivity, we have studied the microscopic, generic behavior of anisotropic thermal conductivity in molecular forests. As a model system, we have used a generic coarse-grained polymer brush. We provide a possible explanation for the reduced thermal conductivity in molecular forests, i.e., the observation that, while a single linear molecule can have very large thermal conductivity along the molecular backbone $\kappa_{||}$, the same molecule in a forest shows a drastic reduction in $\kappa_{||}$. Typical experimental systems include nanotube and nanowire forests and macromolecular fibers. Our analysis reveals that the reduced $\kappa_{||}$ is due to

the lateral chain bending and vdW interactions with other chains hinders the longitudinal heat flow along the molecular backbone. These results point to a general principle of flexible tuning of κ by changing density, molecular flexibility and forest height. Therefore, they may pave the way towards the design of advanced functional materials with tunable thermal properties.

Chapter 5

Conclusion and Future Work

5.1 Conclusion

This thesis investigates the effect of multibody potential and crowding on nanoscale thermal transport. We studied two different models - single chain with multibody potential and molecular forests. The first model gives us an insight into the effect of multibody forces. Divergence of κ of a single chain in an isolated environment and a crowded environment has been studied in Chapter 2 and Chapter 3, respectively. In Chapter 4, we propose a multiscale simulation method to study thermal transport in molecular forests. The significant findings are:

1. In the harmonic limit, longitudinal and flexural modes have different frequency spectrum (transmittance function) of contribution to thermal transport. This behaviour can be expected, as both modes differ fundamentally. Longitudinal modes have a higher contribution from higher frequencies. In contrast, flexural modes have symmetric contributions centred around half of the maximum frequency. Hence, disorder leads to the localization of longitudinal modes at a shorter system size. *Thus, flexural and longitudinal modes differ fundamentally on frequency-wise contribution to thermal transport in the harmonic limit.*
2. A single chain with multibody and two-body interactions show deviation from ballistic behaviour at large system sizes. Additional length scale - ℓ introduced due to multibody potential, has been used to measure system size as - $N\ell$. In the asymptotic limit, superdiffusive behaviour is observed. The phenomenon is thus independent of the system parameters, given sufficient $N\ell$ in the system. Mass-disordered systems also show the same superdiffusive behaviour. It is different from chains with only longitudinal motion and 1DOF, which are insulators. Finally, from longitudinal and transverse displacements, we observe coherent wave patterns in superdiffusive regimes. We believe that change in carriers is responsible for superdiffusive behaviours. *Thus, we establish that the pres-*

ence of multibody potential introduces superdiffusive behaviour, given sufficient N_ℓ in the system. A change of carriers was observed in the superdiffusive regime.

3. Pinning transverse motion of a single chain with multibody potential shows 70% knock-down of κ by $\sim 0.3\%$ of pinned sites. This result can be useful in understanding the decrease in κ of forests. While the decrease is significant in ordered systems, disordered systems are less sensitive. Moreover, we observe a non-monotonous transition from superdiffusive to ballistic transport on increasing the number of pinned points. It is because of the tradeoff between the increase in scattering points and straightening of the chain backbone to decrease nonlinearity. It highlights that a critical density can exist in a crowded environment where a similar transition can be observed. *Thus, we establish a non-monotonous transition from superdiffusive to ballistic transport by increasing crowding around a single chain. Significant knockdown in κ was observed in the ordered system. However, the mass disorder was a dominant scattering source than pinning for our range of parameters.*
4. A coarse-grained model has been used combining the concepts of polymer physics and thermal transport. Using the Kremer-Grest model for molecular chains, we propose a possible explanation of $\kappa_{||}$ knockdown in forests. We observe that lateral chain bending results in phonons' interaction, decreasing heat flow along the molecular backbone. *The results highlight the role of density in introducing anisotropy in the system, thus proposing a way to simulate forests with millions of atoms at a fraction of computational cost.*

5.2 Future work

While we were able to study various aspects of thermal transport successfully, there are still many directions that we could not explore here:

1. Single chain with multibody potential has only been studied at a constant temperature. Increase in temperature can introduce additional scattering which can lead to the transition to superdiffusive regime at shorter system sizes. Though there is one set of simulations available in Section A.2, the effect on α with change in temperature has also not been studied.

2. Single chain with multibody potential has two DOFs. Additional modes like twisting can be introduced when three DOFs are considered. Twisting modes can couple with the bending modes, and the effect on κ can be studied on Q1DM like CNTs.
3. Single chain with multibody potential is a phenomenological model. It cannot be mapped directly to a real system.
4. Coherent patterns emerging in the superdiffusive regimes have not been studied in detail. These carriers have to be studied to characterize them and understand their emergence.
5. We have qualitatively observed the non-monotonous transition from superdiffusive to the ballistic regime with pinning of transverse mode. The divergence exponent (α) can be calculated for each value of q , and transition can be verified.
6. In the molecular forest model, we have not studied the time evolution of energy when a spot is heated. It can help us understand the evolution of the temperature profiles in the "heat trap" effect [24]. The effect of disorder and fusion of two chains can also be explored to simulate the defects in a real forest.

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Appendix A

A.1 Code validation

A.1.1 Force calculation validation

The single chain model has been validated by comparing the frequencies of the first four modes of a beam calculated by the equation:

$$\rho A \frac{\partial^2 w}{\partial t^2} = -EI \frac{\partial^4 w}{\partial x^4}, \quad (\text{A.1})$$

where $E = 2000$ GPa, $I = 2.08e - 09$ m⁴, $A = 2.5e - 04$ m², $L = 50$ mm and $\rho = 1000$ kg/m². In the model, an impulse is given at one point the displacements have been recorded at the other point. Fast Fourier Transform has been done to find the first four frequencies and the values are compared with the analytical expression for nth mode, which is given by:

$$\omega_n = n^2 \sqrt{\frac{EI}{\rho AL^4}}. \quad (\text{A.2})$$

Calculated	2.55	10.25	23	40.08
Analytical Expression	2.56	10.25	23.06	41.01
Percentage error	0.39	0	0.29	0.51

Table A.1: Comparison of analytically and numerically calculated frequency (Hz) of first four modes. The error is less than 1% and thus validates the force calculation in our model.

A.1.2 Langevin bath's implementation validation

The NJ values have been compared with [1] for different anharmonicities in a 1 DOF mass disordered system. Here μ is the parameter for the quartic anharmonicity given in [1]. The calculated values have been plotted in: which are in good agreement as in [1]. This validates the Langevin bath implementation.

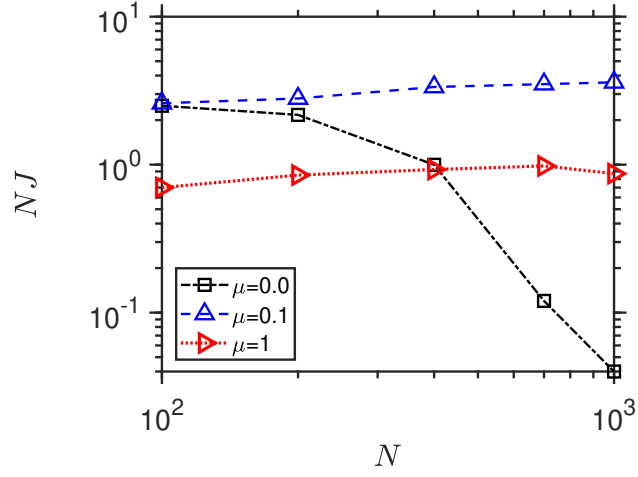


Figure A.1: Calculated NJ for different strength of anharmonicity (μ) in a single chain with 1 DOF and mass disorder. The values and trend is in good agreement as in [1].

A.2 Effect of temperature in the single chain model

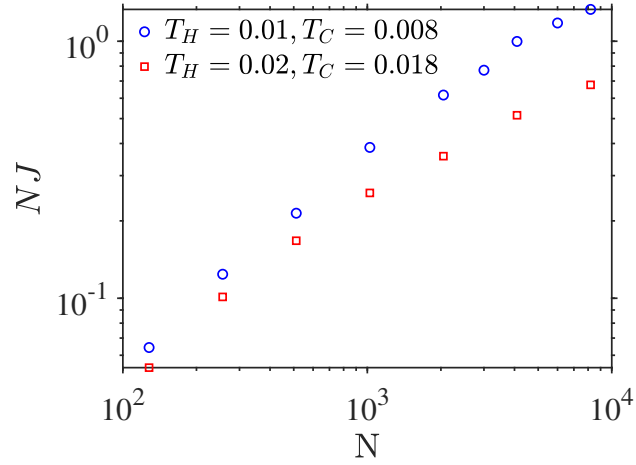


Figure A.2: Dependence of thermal conductivity on temperature with both axial and flexural modes (2.3) in an ordered system. Increasing temperature leads to the decrease in thermal conductivity of the chain as expected. Since Figure 2.4 was already showing a transition from the ballistic to the superdiffusive regime, the transition is more apparent at higher temperatures. $\lambda = 10$, $T_H = 0.01$, $T_C = 0.008$, $a = 1$

Since we have analyzed the effect of flexibility in the system, we know that the coupling of

these modes will deviate the system from ballistic behavior. This coupling can be expected to be stronger at higher temperatures in the Hamiltonian given in (2.3). As the coupling scales with the instantaneous length of the links, high temperatures will amplify the vibration amplitudes, thus increasing coupling. Thus we expect a decrease in NJ which is visible from Figure A.2

A.3 Variation of thermal conductivity within a brush

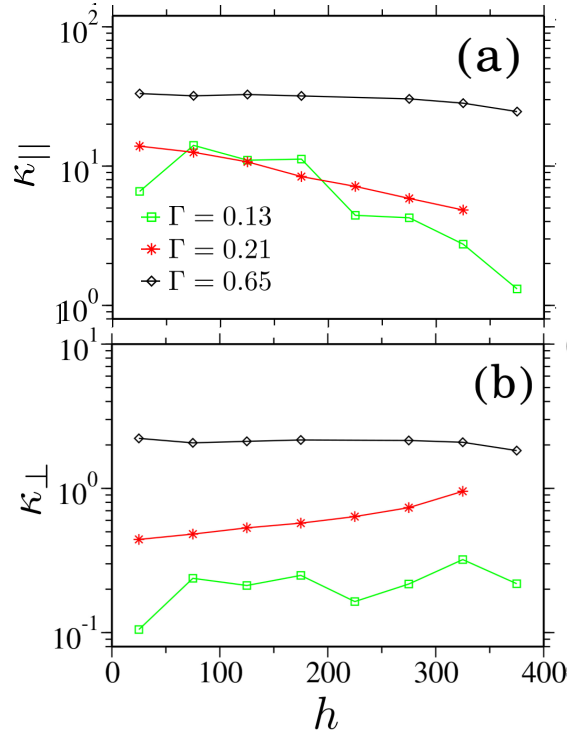


Figure A.3: The parallel $\kappa_{||}$ (a) and perpendicular $\kappa_{\perp}$ (b) components of the thermal conductivity coefficients as a function of height h along the z direction. Data is shown for three different surface coverage concentrations Γ . We can see that $\kappa_{||}$ is two orders of magnitude higher for the largest Γ compared to the lowest value of Γ . The decrease in $\kappa_{||}$ with increase in h is due to change in bond orientations. Higher density leads to increased chain alignment throughout the height of the brush, leading to a flat profile of $\kappa_{||}$ vs. h . On the other hand we see an increase in $\kappa_{\perp}$ with increase in h . This is because, the brush is less anisotropic at the top than at the bottom. The thermal transport due to bonds is increasing in the perpendicular direction.