Tagged Particle Diffusion in Stochastic One-dimensional Systems

By

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Declaration:

I hereby declare that the work reported in this thesis is entirely original. This thesis is composed independently by me at Raman Research Institute under the supervision of Prof. Abhishek Dhar. I further declare that the subject matter presented in this thesis has not previously formed the basis for the award of any degree, diploma, membership, associateship, fellowship or any other similar title of any university or institution.

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List of Publications

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1

Chapter 1

"make things simple"

1.1 Introduction

As animals, we see the world around us in different lights, classify it, and we learn by doing that. To achieve this, we are programmed to notice the contrasts and similarities. We see repeating patterns, both spatial and temporal. We measure things, to complete the description. Formal identification of measured quantities with symbols allows us to do symbolic manipulations, following certain rules and logic. The rules which the world adheres to are encoded in these allowed manipulations. The rules are called laws, and this branch of enquiry and prediction is called quantitative science.

Physics, being one of these, talks about the world around us that can be put in numbers. We

believe in what physics has to say thanks to its testability or predictive power, which has its roots in the causal, deterministic behavior of physical systems. As we said, this allows for the existence of mathematical rules, or equations which embody all the knowledge that we have about them. But this causal and deterministic behavior, or equations, need not necessarily imply predictability. We may not know or practically be able to measure what is out there. The equations need not be solvable, or the solutions might lose their predictive power due to sensitive dependence on initial conditions. Chance arises this way (of course, also modern physics has no way around an inherent stochasticity implied by the laws of quantum mechanics). So what is the way out? Is there a way out?

Since we don't see everything that is out there, we add our own assumptions about what might be there. Based on what we have seen before, we infer or imagine how something works or what lies behind the screen- a lion or a rabbit. We build models of the world, build causal connections among the parts. We test them out, see whether they predict parts of the world, and allow us to understand it, to simplify it in our minds. Since it is impossible to make one complete picture all at once, we separate it out, isolate parts of this movie that make sense. We build theories, call it science, philosophy, religion. But one shouldnt forget that it is a mishmash of what we see and what we infer, imagine. Of course the picture changes with time, and science progresses.

What if systems themselves behaved in an inherently random manner? Even if systems behaved in an apparently random manner, it was realized that averages can still be calculated, and predicted. So we give up on our program of prediction of every variable, every single time. Averages follow rules or laws that are still deterministic. This is what thermodynamics deals with, but only for averages of static quantities, that too only macroscopic quantities associated with collections of a very large number of individual particles. But its laws are derived in a purely phenomenological manner, and hence the parameters that appear in the theory are to be found out from experiment. Hydrodynamics does deal with time varying macroscopic quantities. Newton's laws are being applied to a collection of huge number of particles by treating them as a continuum. Again, forces on and between the continuum elements arising due to a large number of particles are being found in an empirical manner. As a result, one can't go to too small a time or space scale where the continuum approximation breaks down. So it is still incapable of predicting the averages of motion of an individual molecule in a fluid, say. Nor do these theories make use of the

fact that the underlying dynamics obeys laws of motion applicable to particles, neither do they mention in any form the probabilistic or random nature of the motion of the underlying particles.

How did atoms and probability enter the picture? It turns out the concept of atoms, and their random motion existed for a long long time. Attribution of heat and pressure to their motion also existed, along with other theories. It was Daniel Bernoulli (at around 1733) who came up with first derivations of gas laws from a statistical kinetic theory of billiard ball atoms. His atoms moved in all directions. From there, it took nearly a century of development for Maxwell to come up with his distribution of velocities of atoms. This inspired Boltzmann to come up with his seminal work, which paved way for the statistical mechanics as we know it today.

In the world around us, almost all objects have multiple parts of their own, which interact with each other. Like planets of the solar system. Or molecules of a gas or solid or liquid. Hence, almost all of physics has to deal with many bodies together. This poses problems for the enterprise of exact prediction of all observables. One often sees chaotic behavior, breakdown of predictability, and collapse of dreams of people after Newton. We are talking of almost all the systems in nature here. Although the errors in predictions build up, we can still predict motion of planets or satellites to some useful precision, calendars would be of no use otherwise (and bioilogical evolution as we know it would not take place, it would be interesting to imagine what would take its place, if any!).

A pendulum swinging before your eyes on a calm day in a room is predictable in its motion, to a large extent. No hurricanes or earthquakes of devastating nature are allowed. By the way, these calamitous events themselves remain largely unpredictable to date, and are expected to be inherently not amenable to long term prediction. Coming back to the pendulum, its swing slows down with time. Also, air currents affect its motion, noisily if they are turbulent, which is almost always the case. But pendulum clocks work just fine, as their pendulums are too heavy to be perturbed significantly by these feeble forces. Talking of predictability of world with living things around us, things get fairly complicated, so we will not talk about all of them in their all complexity. Living systems are full of complex and rich behavior. They are driven from outside by external energy sources, and hence are out of equilibrium. They have long time memory, relating our lives with that of dinosaurs. They learn, they are said to have purpose, like writing this thesis. We will not talk of all those things that evoke such strong emotions in us. But we are still at

liberty to explore the microscopic motion of their parts, taken one simple enough part at a time.

1.1.1 Parts are simpler than the whole

A calm day in your room. You are sitting in your armchair. The air is still. Your brain is thinking, or dreaming. Heart is pumping blood. Cells are working. Molecules in your body are moving. They are not sitting still. Air molecules are also moving. But their motion is much simpler in a sense when the air in the room is still, i.e. there are no drafts or currents. We say the air is in equilibrium. We are disregarding the fact that light of a much higher temperature is coming in, and your body is perhaps radiating heat and evaporating water, which is diffusing away. Walls, roof, floor and objects in the room are also perhaps not at the same temperature. Still we are allowed to treat parts of this whole system as if tghey are in equilibrium due to a number of properties of the system in question. First, the temperature differences are small, and hence currents are small. Further, even in presence of these small currents, there is the concept of local equilibrium that allows us to talk of a local temperature at every point in space. So there still exists a relatively simple description, we can talk about most of the many particle systems in terms of a small number of local parameters.

We can extend this to the regions inside our body. It might be possible to view a macromolecule moving in a cell as a pollen grain bouncing about in water. We can do this most of the time for many of the molecules, we treat them as boring Brownian walkers. They could be doing exciting things. But those could be transitions that happen when they attach themselves to other molecules. Or they could be having internal degrees of freedom, internal structure. This makes it a Hepatitis virus, or a protein. We need not care about it if only thing we are interested in is the motion of its centre of mass. We say the particle has this or that diffusivity, everything else is irrelevant. We have again extracted/separated a relevant parameter from all the complexity. This may not always be possible, the ambient medium can have substructure. Or the medium could be being reshaped, and hence changing with time. But as long as the change is not too fast, or the substructure again gives rise to only an effective diffusivity to our particle, we are fine. But there are circumstances under which the fundamental nature of the motion itself will change, giving rise to sub or superdiffusion. This is a case we will talk about.

1.1.2 The program of statistical mechanics

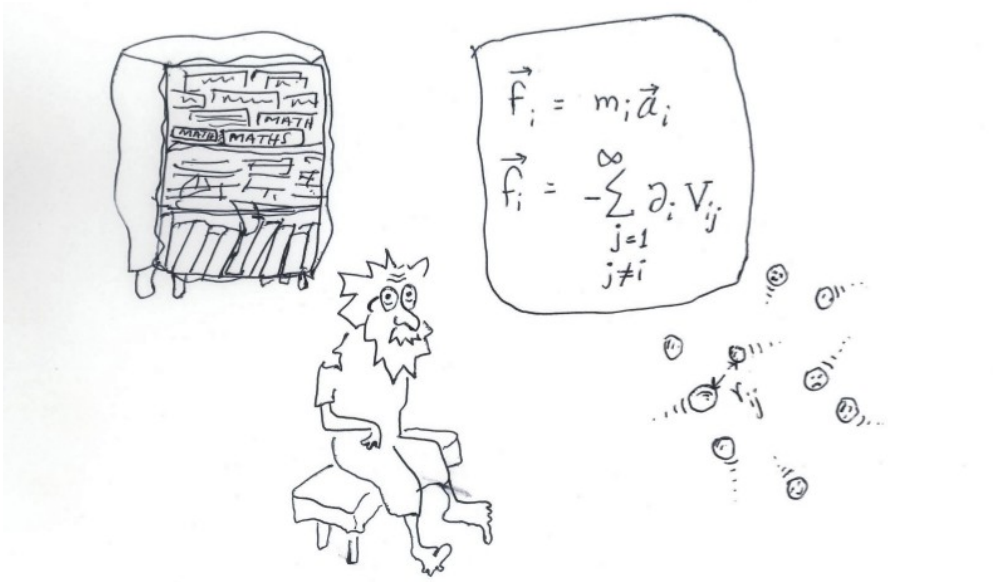
The seemingly random motion of bodies, the so called chaotic motion, has been exploited by observers of materials in nature, especially the ones concerned with thermal motion and properties arising out of that. These people came up with a wise device, ergodic hypothesis, to explain the equilibrium properties of materials. This allows one to carry out the full program of equilibrium statistical mechanics, allows us to derive the thermodynamics behavior. The amazing fact that there is a single characterizing parameter called temperature, in the sense that all the parts of all materials have a single universal distribution of energies characterized solely by this one parameter, that gives us a lot of relief. The fact that it needs free energy dissipation to maintain currents also tells us that on an average, there can't be currents in equilibrium. Also, Ergodicity ensures that it is equally likely to have v or $-v$ as the velocity, either of a region in fluid or of a particle. Then time reversibility of the microscopic dynamics tells us that currents should vanish on an average in equilibrium. Also, once established, currents usually die out due to dissipation, save for superfluids or superconductors. Also, distributions allow for a local temperature within a flow. Of course turbulent flows still pose problems. Ergodic hypothesis, whether right or wrong, gives us the observed equilibrium properties, well, whenever we manage to solve for partition function.

Can all this say something for the random motion of individual particles? Yes, of course. We have detailed balance in equilibrium. This says that net probability current between any two states in a system in equilibrium vanishes. Very often, one also models stochastic processes as having a one step memory, which are called as Markov processes. For example, a diffusing particle has a very short memory of its velocity. The Markov approximation allows us to solve many time-dependent problems. Of course, what allows for this is the fact that noise that kicks the particle around has very short correlation in time.

The fact is that in spite of all this kicking around, the system stays in equilibrium. This gives rise to the so called fluctuation dissipation relations, which relate the response of the system to the correlation of noise. Then recognizing that the response of the system to an internal forcing- a thermal kick or noise- would be same as that to an external force allows one to infer the linear out of equilibrium properties of the system.

1.1.3 Diffusion- normal and anamolous

Most of the microscopic bodies seen around us seem to undergo diffusion, a sort of random walk, if they are suspended in a fluid. Is this true for all bodies? In all media? Obviously not. A particle stuck in a glass or a very dense medium does not appear to undergo diffusion. This might be a caged diffusion, or a caged diffusion at short timescales followed by a jump from one cage to a neighboring cage. The cage itself might be rearranging or deforming slowly.



Experience, experiments, and simulations suggest that many generic short range interactions, of course including the ones often encountered in the real world, also give rise to normal diffusion many a times. But there are important exceptions. Apart from the obvious examples of solids and glasses, there are other places where one encounters anomalous diffusion. For a bead diffusing in F-actin networks, a power law waiting time distribution between jumps gives rise to anomalous diffusion [18][19]. Interiors of cells are one place where we get to see anamolous diffusion, where particles have memories of their motion intact, thanks to the surrounding medium in which they are moving. This medium is mostly viscoelastic(it could also be active), and hence remembers

the deformations it has undergone, as the stresses in these media do not relax quikly as in others. This gives rise to anomalous diffusion.

Here one can distinguish between two kinds of stochastic motion. One is the fundamental and hard problem of statistical mechanics: We are given a Hamiltonian, the bodies evolve and interact deterministically according to Newton's laws or Schrodinger equation, but the resultant motion looks effectively stochastic. It is quite hard to understand and calculate features of these systems from the microscopic equations of motion. Another is where we are looking at parts of a big and effectively infinite system. Here the parts undergo an effectively stochastic motion as they are coupled to other parts of the big system, whcih acts as the source of the stochasticity. There is no attempt made to derive the sochastic motion of the source from the microscopic dynamics. This is the bath-system paradigm. Most of the problems one attempts to solve in statistical mechanics are of this second type. Fortunately, they are not just much simpler to solve, but also real enough to allow us an understanding of the world around us at this level.

In dilute fluids in three dimensions, usually the correlations induced between particles due to collisions decay quickly, and a given particle diffuses normally. However, if you look at molecules in narrow tubes, such as in zeolites or nanotubes or pores in cell membranes, it is easy to see that movements of particles are highly correlated. We are talking of tubes that are so narrow that the molecules can't cross each other. You need to push your neighbors farther and farther to spread in space, to diffuse. In turn, they will have to push their neighbors. Seen in a different manner, the number of particles that will have to do a concerted movement increases, the length to which the individual particles have to move in a given direction also increases. This results in a diffusion of the tagged particle that is slower and slower as time progresses. Or in other words, the particle is subdiffusive.

1.1.4 Dissipative Force

A simple way of heuristically understanding the motion of a heavy particle of mass M in a bath of lighter particles of mass m is the following: consider any one component of motion of the heavy particle, say x. As the particle moves through the fluid with a velocity V, it encounters other lighter particles. Also, due to thermal motion, the lighter particles impinge on it. Given

that the bath is at a temperature T, the rms velocity of smaller particles is $v \sim \sqrt{k_B T/m}$. If the density of gas is ρ, the avg. distance between particles is $a \sim (m\rho)^{-1/3}$. Average number of collisions of smaller particles with the bigger particles per unit time is $\sim (v+V)/a$ from the front and $\sim (v-V)/a$ from the back. Assuming $M >> m$, the particles from front, upon collision, go back with a velocity $v+V$, and that from back, $-v+V$. Hence, change in momentum per particle is $m(2v+V)$ and $m(-2v+V)$ resp. Now, rate of change of momentum of the bigger particle due to these collisions is,

$$\frac{dP}{dt} = -m(2v+V)(v+V)/a - m(-2v+V)(v-V)/a. \tag{1.1}$$

Simplifying,

$$f = -\frac{6mv}{a}V \tag{1.2}$$

is the dissipative force on the bigger particle due to the bath of smaller particles. See that this linear in V, the velocity of the bigger particle.

1.1.5 Noise and Random Walk

We try to model the noisy part of the motion now. We start with a random walker, who is walking on a lattice. The walker moves one step at a time, and the steps are unbiased as well as uncorrelated. So after every time step of duration τ, the walker moves to either left or right a distance a with equal probability. Now, probability of being at x, t is

$$P(x,t) = \frac{1}{2}[P(x-a,t-\tau) + P(x+a,t-\tau)]. \tag{1.3}$$

Subtracting $P(x,t-\tau)$ from both sides and dividing by τa^2 on both sides,

$$\frac{P(x,t) - P(x,t-\tau)}{\tau} = \frac{a^2}{2\tau}\frac{P(x-a,t-\tau) - 2P(x,t-\tau) + P(x+a,t-\tau)}{a^2}. \tag{1.4}$$

Now, in the limit of $a, \tau \to 0$ such that $2D = a^2/\tau$ is finite, we get the diffusion equation

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}. \tag{1.5}$$

See that $a, \tau \to 0$ such that $2D = a^2/\tau$ is finite can be interpreted as follows: the walker receives impulses every timestep, resulting in a velocity with magnitude a/τ, and a displacement a. As $\tau \to 0$, the strength of the impulse, and resulting velocity diverges as $\sqrt{D/\tau}$. So the force due to the collision, if we imagine it to last for a time τ, would be of a magnitude $|\zeta| \sim m\sqrt{D/\tau^3}$. As $\tau \to 0$, requiring the velocity to damp out in a time τ would imply $\gamma \sim m/\tau$. Now uncorrelated noise in the limit $\tau \to 0$ implies $\langle \zeta(t)\zeta(t')\rangle \sim \gamma^2 D\delta(t-t')$, which is the noise correlation that one uses in Langevin equation.

1.1.6 Fokker Planck Equation

In presence of an external force and a noise, the dissipative and noise part add to the deterministic Hamiltonian part of the equation of motion to give

$$m\dot{v} = -\gamma v + f^{ext} + \zeta. \tag{1.6}$$

From here, like we did in case of diffusion equation, one can derive the Fokker -Planck equation, which is the governing equation for the time-evolution of the probability density. It reads

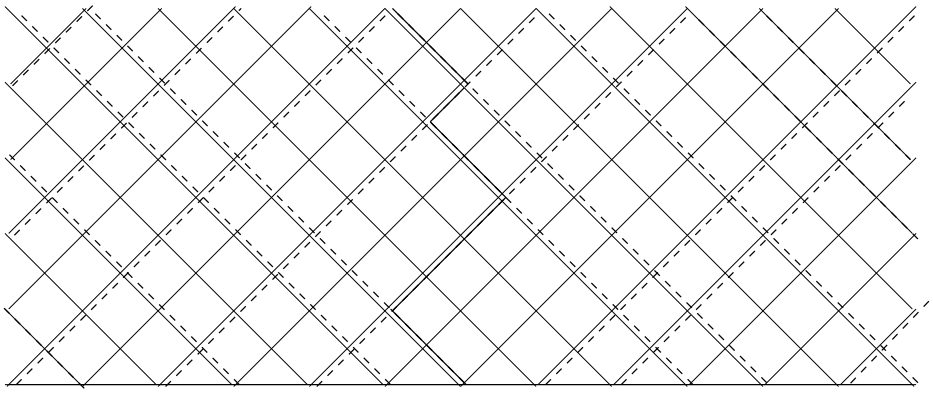


FIGURE 1.1: Equal mass particles start from their initial positions on a one-d lattice with one of the two possible velocities, v and $-v$. They collide elastically to reverse their velocities. One realization of trajectories is shown in dashed lines. One of the particle trajectories is shown in bold.

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} - \frac{\partial}{\partial x}\left(\frac{fP}{\gamma}\right). \tag{1.7}$$

1.2 Two simple examples

In some sense the most natural model to imagine for a classical gas is a collection of hard disks in 2-D or spheres in 3-D. But unfortunately, the problem of solving for the motion of all or even one particle is not a simple one. You will realize this if you consider all the possible outcomes of a collision between two balls, depending on the impact parameter. However, such complications do not arise in one dimension, since impact parameter itself is not a variable. If we let the balls in a tube collide whenever they try to cross- by making the tube narow, or making the balls slide on a frictionless wire, an amazing simplification occurs. Modeling them as hard particles in one dimension, when they have equal masses, the collisions result in an interchange of velocities, and hence trajectories. Trajectories just pass through each other as if the collisions didn't occur at all. Using this property, we will give an exactly solvable model which gives a realistic motion to the tagged particle.

We consider a system of identical point particles (Fig. 1.1). All the particles start with a velocity v or $-v$ with equal probability. They also start from their positions on a lattice of spacing a. For

simplicity, we will take $v, a = 1$. The figure shows one realization of motion of a tagged particle. Now, once the motion starts, it is very clear that the motion of the tagged particle will always be on the diagonal square lattice made of probable trajectories of all the particles. At every lattice point that it goes to, the particle either suffers a velocity reversal or goes ahead with the same velocity as before. Hence it recieves a displacement noise of ± 1 every unit interval of time (and space). Hence $x(t) = x(t-1) + \zeta(t)$ where $\zeta(t) = \pm 1$ with equal probability, is the equation of motion of the tagged particle. Probability of ending up at x after time t is same as that of a random walker.

$$P(x,t) = \frac{t!}{\left(\frac{t+x}{2}\right)!\left(\frac{t-x}{2}\right)!2^t}, \tag{1.8}$$

See that the particle stays within the triangle made by its allowed initial velocities, i.e. the probability of finding it outside this triangle is zero at any point of time. For $t, t-x >> 1$, the above distribution can be cast in a large deviation form. Using Stirling's approximation,

$$P(x,t) = \frac{1}{\sqrt{4\pi t}} e^{-\frac{t}{2}\left[\left(1+\frac{x}{t}\right)\ln\left(1+\frac{x}{t}\right)+\left(1-\frac{x}{t}\right)\ln\left(1-\frac{x}{t}\right)\right]}, \tag{1.9}$$

which is in a large deviation form. For $x << t$,

$$P(x,t) = \frac{1}{\sqrt{4\pi t}} e^{\frac{-x^2}{4t}} \tag{1.10}$$

The problem has a straightforward extension. Instead of lattice, we start the particles from random initial positions. Now the kicks received by the tagged particle are at random times. Consequently, the displacements caused by the kicks are going to have the same distribution as the interparticle distances. For the uniform distribution, where each particle is placed with uniform density throughout the system, these intervals are Poisson distributed. Now, within Gaussian approximation, diffusivity of the tagged particle is going to be dependent on the mean interparticle distance ρ^{-1}. At unit velocity, and at unit mean density of particles, the Gaussian distribution is going to be identical with Eq. (1.10). For a general density ρ and speed v of particles,

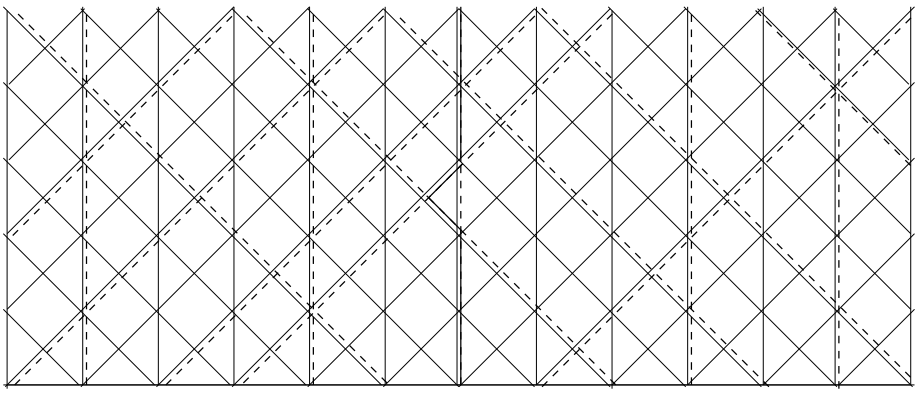


FIGURE 1.2: Equal mass particles start from their initial positions on a one-d lattice with one of the three possible velocities, $v.-v$ and 0. The three particle collisions are assumed to effect velocity reversal of the outer two particles, and the middle particle continues unaffected. A realization of velocities is shown in dashed lines. A tagged particle trajectory is shown in bold.

$$P(x,t) = \frac{1}{\sqrt{4\pi vt/\rho}} e^{\frac{-x^2}{4vt/\rho}}. \tag{1.11}$$

So far any given noninteracting trajectory(a straight line) collided with the tagged particle only once, hence the kicks that the tagged particle recieved were uncorrelated. Suppose we have three possible velocities for each particle (Fig. 1.2). Now the one collision condition no more holds, and we are forced to take into account the correlations of the kicks or noise felt by the tagged particle.

Simulation results for the three velocity case show that the tagged particle motion is diffusive, so one needs to see how is that coming about. Typically, an exponentially decaying memory makes the motion effectively memoryless over timescales. But our simple uncorrelated noise calculations no more serve us to show this. Also, moving to a more realistic continuum velocity distribution like Gaussian, we will not be able to derive the PDF with these methods either.

1.2.1 Motion of a tagged particle under a constant applied force

Newton's equations of motion imply a constant acceleration in presence of a constant external force for a particle. What do they imply for a particle that is among a crowd of other particles? The question had an answer when we were giving a heuristic answer in case of a heavy particle

in a bath of lighter particles. There we said it experiences a dissipative force proportional to its velocity. For a particle that is identical to the bath particles, i.e. comparable in mass, such a simple estimate eludes us. Nevertheless, if we go to one dimenson, some heuristics can again be tried.

Broadly, two class of interactions can be considered. One, the hard particle limit, and two, the particle chain limit. Once again, there is another important classification, particles which are interacting with each other according to a given Hamiltonian, and particles which themselves are already in a bath of other particles. For simplicity, let us consider particles sitting on a line with density ρ at zero temperature.

In the Hamiltonian identical hard particle case, the chosen particle of mass m on which the external force f is acting ends up colliding with its neighbor. The velocity is transferred to its neighbor, and the tagged particle momentarily comes to rest, but starts moving again thanks to the external force. After a time t, we have roughly $\rho vt/m$ particles, all moving with an average velocity v. Now, from Newton's second law, $\rho v^2 t = ft$, from which we infer that $v = \sqrt{f/\rho}$. Alternatively, $v = f\tau/m$, where $\tau = m/\sqrt{\rho f}$ is the mean free time between collisions. This also gives the same expression for the steady state velocity of the tagged particle. One can also use energy conservation, that also yields the same scaling.

In the overdamped hard particle case, all the particles in motion after time t are experiencing a dissipative force proportional to their velocity. Force balance gives $f = x\rho(\gamma v)$, where x is the distance covered by the tagged point particle in time t, and γ is the damping coefficient for each particle, and ρ is the number density of particles on the line. Solving for x we get, $x \sim \sqrt{ft/(\gamma\rho)}$. This means that $v \sim t^{-1/2}$.

Hence the overdamped and Hamiltonian cases are eveidently very different. We will get to the particle chains in the third chapter, where we will give scaling arguments based on local equilibrium to infer the tagged particle motion.

1.3 Chapter II. Tagged particle motion in an identical hard particle single file

After all this, we still have not managed to come up with a method to derive the PDF for the tagged particle in one-dimensional overdamped systems of hard particles. We do this in the second chapter. The fact that the particles are identical once again allows a mapping from the interacting system to noninteracting one, as we saw in the ballistic particle case. The N-particle propagator turns out to be a sum of permuted products of non-interacting particle propagators. The nested integrals over the initial and final positions of particles become products of individual integrals thanks to the permutation symmetry of the N-propagator. Then the task of finding the tagged particle PDF or MSD is accomplished by summing this series. In past, this has been accomplished in the large N limit by using asymptotic long-time properties of Bessel functions [3], [10]. We carry out the sums in large N limit using a technique developed in [13]. This allows us to arrive at long-time limits of the tagged particle MSD in both infinite and finite sized systems. At shorter times, a simple one-dimensional numerical integration allows us to reproduce the MSD. Results are found to be in excellent agreement with the brownian dynamics simulations that we perform.

1.4 Chapter III. Tagged particle motion in one-dimensional systems: scaling relations using local equilibrium

Although there have been a number of works on the tagged particle correlations in one-dimensional systems, the involved nature of calculations usually doesn't allow for a clear physical understanding. For example, the ease with which the variance or even distribution function for a random walk is obtained is missing when one comes to interacting particle systems. The subdiffusive nature of the motion in dimensions smaller than three hence remains shrouded in mystery. The strongly interacting nature of particles leading to caging poses problems. But we note that local equilibrium is a feature found in almost all overdamped systems and Hamiltonian systems when started from stochastic initial velocities. We also note that there are hydrodynamic density modes

present in most of these systems. This allows one to come up with a length scale for the size of the system in equilibrium with the tagged particle after time t. Hence, we mange to derive scaling relations for time dependence of the tagged particle motion in systems with fixed topology of interactions.

We connect the free energy of a finite sized system with time dependence of tagged particle motion. We note that the treatment is valid for overdamped systems with diffusive density modes as well Hamiltonian systems with sound modes. We extend the argument to exclusion processes, including the driven asymmetric case, where kinetic waves are the dominant contributors to equilibration, when started from a staedy state distribution. We then move on to asymmetric initial conditions, and successfully calculate the drift and diffusion of the tagged particle. We apply the arguments to a 2D harmonic lattice, and recover the logarithmic diffusion seen in the simulation. We note that this also explains the similar behavior seen in 2D hard disks in overdamped systems.

We notice that local equilibration is a feature seen even when there is a constant external force acting on the tagged particle. This allows us to calculate the response of the tagged particle to an constant force, and also verifies a generalized fluctuation-dissipation relation.

From here, we move to topologies other than the 1D chain. Extensivity of the free energy allows us to calculate the MSD and force response of a particle connected to many linear chains. After this, we go on to hierarchical structures composed of chains of chains. Here we simulate overdamped and Hamiltonian combs with harmonic and quartic interactions, and see that the Percus relation relating the MSD of a particle to MSD of a tagged particle in a chain of such particles still holds true. From here, we propose that it is possible to obtain a whole series of power-laws for MSD of tagged particles in these hierarchical structures. We connect this fact with previously known results about response of tagged particles in overdamped harmonic chains, and diffusion of a particle on hierarchical lattices.

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Chapter 2

2.1 Introduction

Diffusion in many particle systems is an intersting yet simple to observe phenomenon, with a range of behaviors available for study for the experimentalists as well as theorists. Like the very first observation of Brownian motion, the observations could be of a heavy particle in a sea of smaller particles, or like in colloids, there could be many heavy particles interacting with each other, with a thermal background of smaller particles. As is obvious, these scenarios arise in many physical, biological, or chemical systems. One could be interested in the motion of a given kind of particle, or might want to understand the environment in which this particle is moving. Hence tagged particle dynamics is an interesting problem in its own right as well as a probe for the underlying many particle dynamics. In many of these systems, particles exhibit anamolous diffusion or subdiffusion. In such systems interaction of a tagged particle with its neighbors has non-trivial

consequences for its motion, possibly resulting in subdiffusion or/and crossovers from one behavior to the other. However, dimensionality plays a crucial role in deciding how interactions show up in the diffusive behavior. These interaction effects reach their extreme in one-dimension, where a particle can't overtake its neighbors and is always caged by its two neighbors. This makes the one-dimensional problem a separate beast as compared to its higher dimensional versions. As we will see, this also paves way for a unique method of solution.

The problem is of interest to biologists studying motion of molecules in pores or ions in pumps on the cell-membrane, with applications in drug delivery[1], to chemists for its role as a model for motion of molecules in pores of catalysts such as zeolites [2] [3] or in nanotubes. It is not hard to imagine this system playing an important role in nanofluidics in coming years. There have also been experiments on specially set up systems such as beads in an optical ring trap[14] or colloids in etched channels[5] to test the behavior of such a system.

Harris[6] was the first to study this system theoretically. He showed that for an infinite system with finite density of diffusive point particles, a tagged particle is subdiffusive at long times, with the mean square deviation(MSD) in position going as $t^{1/2}$. He also showed that the distribution of the displacement is gaussian. Thereafter Jepsen[7] came up with a mapping of a system of ballistic point particles to one without collisions, and was able to derive asymptotic behavior of the tagged particle, i.e. distribution of the displacement as well as velocity autocorrelation for infinite system size. Lebowitz and Percus[8] studied the position and velocity joint autocorrelation at short and long times for particles of finite size. Later Lebowitz and Sykes[9] investigated the effect of system size on the velocity autocorrelation. Thereafter the next step was the work of Rodenbeck et al.[3], who used the noninteracting particle mapping in the diffusive system for tagged particle behavior at long times for the infinite system size. Later Lizana and Ambjörnsson[3] used the same mapping to derive these results for a finite system with reflecting boundaries in the limit of large but finite number of particles. They were able to get accurate results for all times, although the resulting expressions were rather complicated had to be evaluated numerically. Anjan Roy et al.[13] used the same mapping, but a simpler mathematical method, to derive some results for finite and infinite systems of ballistic particles.

There have also been approximate methods to get Gaussian features of both overdamped and Hamiltonian systems. Barkai and Silbey[9] have used central limit theorem for the number of non-interacting particles crossing the tagged particle position to derive long-time results for many diffusive systems including one with an external harmonic potential.There are also approaches where the system is approximated by a system of masses connected by harmonic springs, and subjected to viscous damping and delta-correlated noises. Later, one either takes the particle index to be a continuous variable and comes up with uncoupled harmonic modes [1] or solves the harmonic discrete particle system as it is [16][3] to derive the tagged particle behavior. Kollmann[14] has considered single file systems with short range and hydrodynamic interactions. By projection operator techniques, he has been able to show that MSD goes as $t^{1/2}$, independent of the form of the interaction.

In this chapter, we use the method developed in [13] to calculate the above quantities for finite and infinite diffusive systems. Our approximations for large number of particles and calculation methods are transparent, simple, and straightforward, and resulting expressions are much simpler and compact compared to earlier works, and agree well with simulations. The method allows us to derive asymptotic results for systems with particles whose free propagators are Gaussian, but with arbitrary time dependence for the MSD.

2.2 System, and our analytical approach

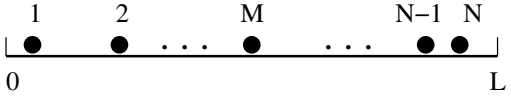

FIGURE 2.1: system

We consider a system of N point particles diffusing in a one-dimensional box with reflecting boundaries at $x = 0$ and $x = L$. The particles diffuse freely till they encounter each other, upon

which they act as reflecting walls for each other. The free diffusion of an individual particle in absence of walls and other particles is assumed to be described by the Gaussian propagator

$$G^f(x_2,t;x_1,t=0)=\frac{1}{\sqrt{4\pi Dt^\alpha}}e^{-(x_2-x_1)^2/4Dt^\alpha} \tag{2.1}$$

where $G^f(x_t,t;x_0,t=0)$ is the probability that the particle reaches a point x_2 at time t, given that it starts at x_1 at $t=0$.

Given this system, we are interested in calculating the mean square deviation(MSD) of a given(tagged) particle as a function of time, and possibly the distribution of the displacement at time t. Our calculation method relies on the fact that any given interacting system trajectory, if one ignores the particle labels, can be identified with a set of noninteracting system trajectories. In other words, on collision, two particles pass through each other, with a label exchange. To evolve the interacting system, one evolves the corresponding noninteracting system, and relabels the particles at the time of interest according to their position, since the order of particles is conserved in the interacting system (Fig. 2.2). Thus, when one looks at noninteracting trajectories, the i'th tagged particle is the one which has $i-1$ particles to its left and $N-i$ to the right at time $t=0$ and at time t.

In this work we choose initial conditions corresponding to the equilibrium N-particle joint probability density. For convenience, we take N to be odd and set it to be $N=2M+1$, and the middle particle at $i=M+1$ to be the tagged particle. Consider a trajectory of the tagged particle starting at x_0 at $t=0$ and ending at x_t after time t, possibly with many collisions on the way. The corresponding trajectories in the non-interacting system are the ones with a particle starting at x_0 with same number of particles on its left and right as in the interacting system. But now, unlike in the interacing system, this particle can go anywhere. For the tagged particle, we again need a particle at x_t at time t, again with the same number of particles on its left and right in the noninteracting system(NS). But now in NS, this particle need not be the one that started at x_0. Denoting the probability of the tagged particle starting at x_0 at $t=0$ and ending up at x_t at time t by $P_N(x_0,x_t,t)$, we have contributions to this from two cases in NS: (i) where the same particle that started at x_0 ends up at x_t (probability of which

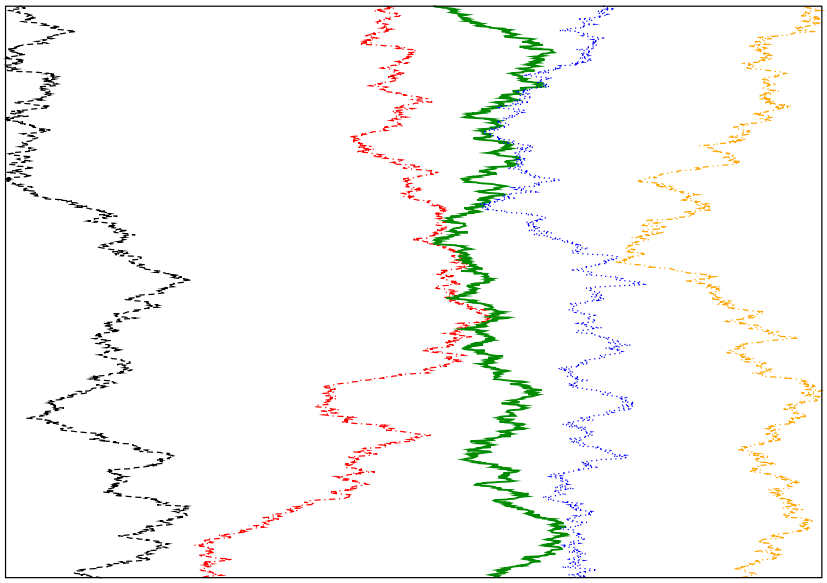

Figure 2.2: Order of particles is retained in the interacting system. Corresponding trajectories in the noninteracting system do not conserve the order, hence we need to relabel the particles according to their position at the time of interest. Trajectory of the middle particle in the interacting system is shown in bold.

is $P_N^{(1)}(x_0, x_t, t)$) (ii)where a different particle which started on left or right of x_0 ends up at the x_t ($P_N^{(2)}(x_0, x_t, t)$). To proceed further we make a few definitions. There are four contributions to $P_N^{(2)}(x_0, x_t, t)$ depending on whether the particle that started at x_0 goes to the left (whose probability density is $p_{0-}(x_0, x_t, t)$) of x_t or to the right($p_{0+}(x_0, x_t, t)$), and whether the particle that reaches x_t came from the left($p_{-t}(x_0, x_t, t)$) of x_0 or from the right($p_{+t}(x_0, x_t, t)$). We also define $p_{-+}(x_0, x_t, t)$ as the probability that a noninteracting particle starts to the left of x_0 at $t = 0$ and ends up to the right of x_t at time t and so on. $P_{kl}^{mn}(x_0, x_t, t)$ is the probability that $k(l)$ particles start on the left(right) of x_0 at time $t = 0$ and $m(n)$ particles end up on the left(right)

of x_t at time t. In terms of these we have:

$$P_N^{(1)}(x_0, x_t, t) = NG^f(x_t, t; x_0, t = 0)P_{M,M}^{M,M}(x_0, x_t, t) \quad (2.2)$$

$$P_N^{(2)}(x_0, x_t, t) = N(N-1)\Big(p_{0-}p_{-t}P_{M-1,M}^{M-1,M} + p_{0-}p_{+t}P_{M,M-1}^{M-1,M} + p_{0+}p_{+t}P_{M,M-1}^{M,M-1} + p_{0+}p_{-t}P_{M-1,M}^{M,M-1}\Big) \quad (2.3)$$

where the factor N arises as there N (noninteracting)particles to choose from for the tagged middle particle, and $N-1$ factor due to $N-1$ particles left after tagged particle is chosen, out of which one is chosen to go from left or right of x_0 to x_t. To calculate $P_{M,M}^{M,M}(x_0, x_t, t)$ etc., we see that to get a specified number M of particles on each side of x_t, given that M started on each side of x_0, there are many ways. One could have m of these crossing over from the opposite sides of x_0. Also, there are many ways of choosing these m particles out of M particles which were on that side of x_0. Hence we have

$$P_{M,M}^{M,M}(x_0, x_t, t) = \sum_{m=0}^{M}(p_{--}p_{++})^m(p_{-+}p_{+-})^{M-m}\frac{(N-1)!}{M!}\left(\frac{M!}{m!}\right)^2 \quad (2.4)$$

One can see that, as expected, the expression on the right involves only the noninteracting single particle probabilities. Next we need to sum this series. So far, past works have expressed it in terms of Bessel functions/Legendre polynomials to derive asymptotic expressions in the limit of large N and large/small t [10] [3]. However we express the above sum in a different manner, following [13]:

$$P_{M,M}^{M,M}(x_0, x_t, t) = \sum_{\sum n = N-1} p_{--}^{n_1}p_{-+}^{n_2}p_{++}^{n_3}p_{+-}^{n_4}\delta_{n_1 n_3}\delta_{n_2 n_4}\frac{(N-1)!}{n_1!n_2!n_3!n_4!}$$

$$= \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}[p_{--}e^{i\phi} + p_{++}e^{-i\phi} + p_{-+}e^{i\theta} + p_{+-}e^{-i\theta}]^{N-1}\,d\theta\,d\phi \quad (2.5)$$

where the integral representation of the delta function has been used. Hence we have managed to express the above sum as a double integral. The treatment till now is valid for any number of particles N. To proceed further, we look at the limit of large number of particles, $N >> 1$. Denoting the quantity in square brackets by f, as $\lim_{N\to\infty}(f-1)N$ is finite for the case we are interested in(see (5), and using $N = L\rho$), using $\lim_{N\to\infty}(1 + r/N)^N = e^r$ where now $r = f - 1$,

we can approximate the above integrand as

$$\exp[(N-1)[(p_{--}+p_{++})(\cos\phi-1)+(p_{-+}+p_{+-})(\cos\theta-1) \\ +(p_{--}-p_{++})(i\sin\phi)+(p_{-+}-p_{+-})(i\sin\theta)]]$$

Now, depending on which of the $(p_{--}+p_{++})$ and $(p_{-+}+p_{+-})$ are of $O(1)$, we can expand the corresponding cos and sin terms to quadratic order, and expand the range of integration to $(-\infty,\infty)$. Performing the resulting Gaussian integrals gives us the probability density for the middle particle to start from x_0 and reach x_t in time t. If only one Gaussian integral results, we will have to evaluate the other integral numerically. This will be the case, for example, for diffusive particles at short times $(Dt^\alpha \sim (L/N)^2)$. The results till now are valid for any form of the noninteracting particle propagator, as we have not made use of any specific form for the propagators. Now we go to specific propagators to derive further results.

2.3 Diffusive propagator, infinite system size limit

For a system of diffusive particles, at short times $(Dt^\alpha << L^2)$, boundary effects have not yet reached the tagged particle. So we can take the limit of the system size L and the number of particles N to be infinite, such that $N/L=\rho$ is a constant. The individual particle propagators can be taken to be Gaussian now. $p_{-+}(x_0,x_t,t)$ etc. are obtained by performing the Gaussian integrals between appropriate bounds, first keeping L finite. Here we calculate $p_{-+}(x_0,x_t,t)$ for illustration. We need the probability that a particle starts on the left of x_0, and given that, that it ends up on the right of x_t. Since we start with a uniform distribution for every noninteracting particle,

$$p_{-+}(x_0,x_t,t)=\int_0^{x_0}(1/L)\int_{x_t}^{L}G^f(x_2,t;x_1,0)\,dx_1\,dx_2, \tag{2.6}$$

where $G^f(x_2,t;x_1,0)$ is the noninteracting particle propagator from $(x_1,t=0)$ to (x_2,t). For a Gaussian propagator,

$$p_{-+}(x_0,x_t,t) = \frac{\delta_-}{2L}(1+\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)) + \frac{1}{L}\sqrt{\frac{Dt^\alpha}{\pi}}e^{\frac{-\delta_-^2}{4Dt^\alpha}}, \tag{2.7}$$

where $\delta_- = x_0 - x_t$. Also, for example, $p_{-t}(x_0,x_t,t)$ is the probability density of starting on the left of x_0 and reaching x_t, and $p_{0-}(x_0,x_t,t)$ is the probability density of starting at x_0 and ending up on the left of x_t. Hence,

$$\begin{aligned} p_{-t}(x_0,x_t,t) &= \int_0^{x_0}(1/L)G^f(x_t,t;x_1,0)\,dx_1, \\ p_{0-}(x_0,x_t,t) &= \int_0^{x_t}(1/L)G^f(x_2,t;x_0,0)\,dx_2 \end{aligned} \tag{2.8}$$

Results for all the quantities of interest are asfollows:

$$\begin{aligned} p_{--}+p_{++} &= 1-(\delta_-/L)\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)-(2/L)\sqrt{\frac{Dt^\alpha}{\pi}}e^{\frac{-\delta_-^2}{4Dt^\alpha}} \\ p_{--}-p_{++} &= \delta_+/L \\ p_{-+}+p_{+-} &= (\delta_-/L)\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)+(2/L)\sqrt{\frac{Dt^\alpha}{\pi}}e^{\frac{-\delta_-^2}{4Dt^\alpha}} \\ p_{-+}-p_{+-} &= \delta_-/L \\ p_{0-}p_{-t} &= 1-(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right))^2/L^2 \\ p_{0+}p_{+t} &= 1-(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right))^2/L^2 \\ p_{0-}p_{+t} &= (1-\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right))^2/L^2 \\ p_{0+}p_{-t} &= (1+\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right))^2/L^2 \end{aligned} \tag{2.9}$$

where we have defined a new set of variables, $\delta_- = x_0 - x_t$ and $\delta_+ = x_0 + x_t - L$ for convenience. δ_- has the interpretation of displacement of the tagged particle in time t. From the above expressions, it is clear that only $p_{--}(x_0,x_t,t)+p_{++}(x_0,x_t,t)$ is $O(1)$ at short times, and hence, only ϕ integral can be done as a Gaussian integral. Here one needs to see that there are expansions about two points that contribute equally to the Gaussian integral[13]. We carry out these steps for $P_N^{(2)}(x_0,x_t,t)$ also. Now extra factors of $\exp(\pm i\phi)$ or $\exp(\pm i\theta)$ appear as prefactors to the summation and to the exponential term in the integral as the number of particles

crossing from left to right is one more or less than the ones from right to left. Taking the limit $L \to \infty, N \to \infty$ such that $N/L = \rho$ is a constant, we notice that the particle has a vanishing (equilibrium)distribution, and hence we integrate $P_N(x_0, x_t, t)$ over δ_+, to get the distribution of the displacement at short times as

$$P(\delta_-,t) = \frac{1}{\pi}\int_0^{2\pi} d\theta \left[\frac{e^{\frac{-\delta_-^2}{4Dt^\alpha}}}{2\sqrt{\pi Dt^\alpha}} + \frac{\rho}{2\pi}\left(\left(1 - \left(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\right)^2\right) + \left(1 + \left(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\right)^2\right)\cos\theta\right)\cos(\rho\delta_-\sin\theta) - \frac{\rho}{4\pi}\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\sin(\theta+\rho\delta_-\sin\theta)\right] \quad (2.10)$$

To get the MSD of the tagged particle, we further integrate δ_-^2 with the above weight over δ_- in the range $(-\infty, \infty)$.

$$\langle\delta_-^2(t)\rangle = \frac{1}{\pi}\int_0^{2\pi} d\theta \int_{-\infty}^{\infty} d\delta_-\delta_-^2 \left[\frac{e^{\frac{-\delta_-^2}{4Dt^\alpha}}}{2\sqrt{\pi Dt^\alpha}} + \frac{\rho}{2\pi}\left(\left(1 - \left(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\right)^2\right) + \left(1 + \left(\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\right)^2\right)\cos\theta\right)\cos(\rho\delta_-\sin\theta) - \frac{\rho}{4\pi}\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)\sin(\theta+\rho\delta_-\sin\theta)\right] \quad (2.11)$$

Here, integrals over δ_- and θ need to be evluated numerically.

2.4 Long time limit for a finite sized system

When $Dt^\alpha \sim L^2$, boundary effects are being felt, and we can no longer hold on to the Gaussian propagators. So we take the appropriate propagators for a box of size L with reflecting boundaries:

$$G^{f,R}(x_2,x_1,t) = \sum_n \cos(\frac{\pi n x_2}{L})\cos(\frac{\pi n x_1}{L})\exp(-n^2\pi^2 Dt^\alpha/L^2) \quad (2.12)$$

Now, from the knowledge that at equilibrium, the spread in position of the tagged particle, i.e., δ's will be $\sim O(L/N)$, in the large N limit we can expand the cos and sin terms to first order in δ/L -the deviation from $L/2$ for the middle particle. Hence,

$$p_{-+}(x_0, x_t, t) = (1/L^2)\left(x_0(L - x_t) - \sum_n \frac{L^2}{n^2\pi^2}\sin(\frac{\pi n x_0}{L})\sin(\frac{\pi n x_t}{L})\exp(-n^2\pi^2 D t^\alpha/L^2)\right) \quad (2.13)$$

For x_0 and x_t close to $L/2$, to first order in $= x_0 - L/2$ and $\delta_t = x_t - L/2$,

$$p_{-+}(x_0, x_t, t) = (1/L^2)\left(-L\delta_t/2 - \sum_{n-odd} \frac{L^2}{n^2\pi^2}\exp(-n^2\pi^2 D t^\alpha/L^2)\right). \quad (2.14)$$

Repeating the calculation for other quantities of interest, to first order in (δ/L)s,

$$\begin{aligned}
p_{--} + p_{++} &= 1/2 + 2a(t) \\
p_{-+} + p_{+-} &= 1/2 - 2a(t) \\
p_{--} - p_{++} &= \delta_+/L \\
p_{-+} - p_{+-} &= \delta_-/L \\
\text{where } a(t) &= \sum_{n\ odd} \frac{\exp(-n^2\pi^2 D t^\alpha/L^2)}{n^2\pi^2} \\
\text{Also, to same order, } p_{0-}p_{-t} &= (1/4 + \delta_+/2L)/L^2 \\
p_{0+}p_{+t} &= (1/4 - \delta_+/2L)/L^2 \\
p_{0-}p_{+t} &= (1/4 - \delta_-/2L)/L^2 \\
p_{0+}p_{-t} &= (1/4 + \delta_-/2L)/L^2
\end{aligned} \quad (2.15)$$

See that now for $N >> 1$ we can carry out the Gaussian integrals in both θ and ϕ, as both $p_{--} + p_{++}$ and $p_{-+} + p_{+-}$ are $O(1)$.The result is the probability to start at x_0 and reach x_t after time t. We don't write out this fairly long expression. Instead, we further calculate the MSD of the tagged particle by integrating this probability over both δ_- and δ_+. This results in

$$\langle \delta_-^2(t) \rangle = \frac{N}{\rho^2}\left(1/2 - 2\sum_{n\ odd} \frac{\exp(-n^2\pi^2 D t^\alpha/L^2)}{n^2\pi^2}\right) \quad (2.16)$$

2.5 Long-time, infinite size limit

What happens if there are no walls, i.e. when we have an infinite line with a density ρ of particles on it? See that at long times, both $p_{--}+p_{++}$ and $p_{-+}+p_{+-}$ will be $O(1)$ as can be seen from (2.9). This means that now we can carry out the Gaussian integrals in θ, ϕ, and δ_+. Also, at long times, i.e., when $\sqrt{Dt^\alpha} >> \rho^{-1}$, major contribution to $\langle\delta_-^2(t)\rangle$ comes from $\delta_- << \sqrt{Dt^\alpha}$. So we take the limit $\delta_-/\sqrt{Dt^\alpha} << 1$ in the expression(2.9), which allows us to calculate this long time limit exactly. Setting $\left(\frac{\delta_-}{\sqrt{4Dt^\alpha}}\right)=0$, $e^{\frac{-\delta_-^2}{4Dt^\alpha}}=1$, and also $1/(\rho\sqrt{Dt^\alpha})=0$, the integral becomes,

$$\begin{aligned}\langle\delta_-^2(t)\rangle &= \int_{-\infty}^{\infty}\int_0^{2\pi}\delta_-^2\rho\frac{2\cos(\rho\delta_-\sin\theta)(\cos\theta-1)}{8\pi} \\ &\times \exp[(\cos\theta-1)\rho 2\sqrt{Dt^\alpha/\pi}]\,d\delta_-\,d\theta \end{aligned} \tag{2.17}$$

Now, we see that in the exponent in the square brackets, $\rho 2\sqrt{Dt^\alpha/\pi}(>>1)$ multiplies $(\cos\theta-1)$, and hence we can once again expand $(\cos\theta-1)$ and $\sin\theta$ to quadratic order in θ around $\theta=0$, and expand the range of integration of θ to $(-\infty,\infty)$ to get

$$\begin{aligned}\langle\delta_-^2(t)\rangle &= \frac{\rho}{4\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\delta_-^2\exp[-\theta^2\rho 2\sqrt{Dt^\alpha/\pi}+i\rho\delta_-\theta] \\ &\quad (2+2\cos\theta)\,d\delta_-\,d\theta \end{aligned} \tag{2.18}$$

Now, carrying out the Gaussian integrals, we finally get

$$\langle\delta_-^2(t)\rangle = \frac{2}{\rho}\sqrt{\frac{Dt^\alpha}{\pi}} \tag{2.19}$$

When $\alpha=1$, i.e. for normal diffusion we get

$$\langle\delta_-^2(t)\rangle = \frac{2}{\rho}\sqrt{\frac{Dt}{\pi}} \tag{2.20}$$

which is exactly the form obtained by others before [9].

For the Newtonian ballistic particles with equal mass, when started from a Maxwell distribution of velocities with rms velocity v_m, and equilibrium position distribution, we have $\alpha=2$. MSD is

$$\langle\delta_-^2(t)\rangle = \frac{1}{\rho}\frac{v_m t}{\sqrt{\pi}} \tag{2.21}$$

so that the long time motion is diffusive with diffusion coefficient $D=\frac{v_m}{2\rho\sqrt{\pi}}$, which agrees with the expresssion obtained by Jepsen[7].

2.6 Comparison with simulations

We have performed Brownian dynamics simulations of the diffusive particle system and compared our analytic results with MSD obtained from simulations.

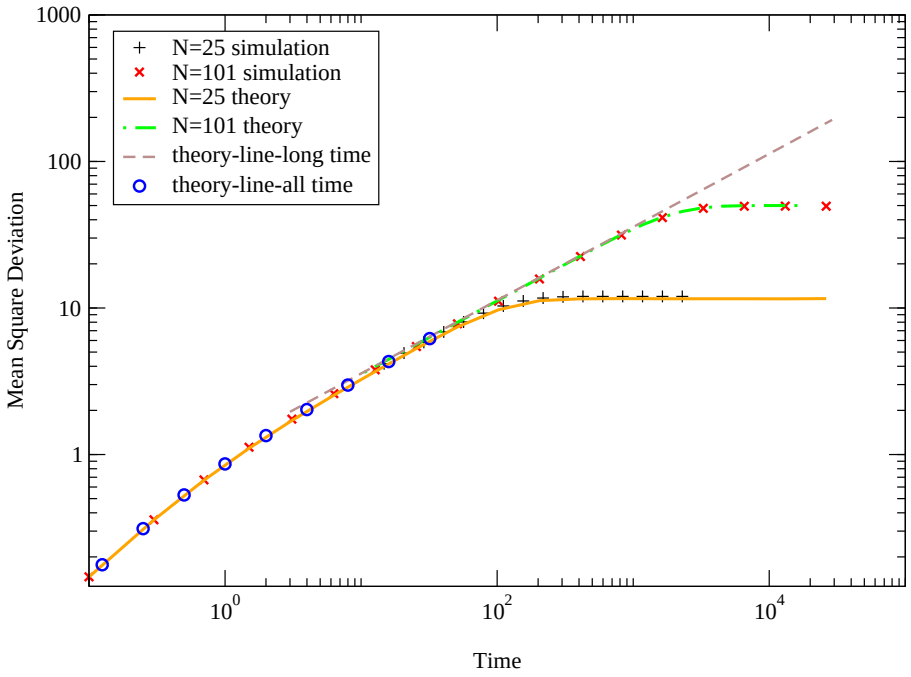

FIGURE 2.3: Brownian dynamics simulations, performed at $\rho = 1, D = 1$, for N particles, compared with analytic results. The dashed line (–) gives the long time $t^{1/2}$ behavior for infinite system size.

It is evident that our asymptotic solutions allow us to match the simulation results really well in all regimes.

2.7 Summary

For one dimensional systems with hard point particles each of which has a Gaussian propagator, we have come up with exact asymptotic expressions for mean square deviation of the tagged

particle as a function of time. We have also calculated the propagators and distribution of displacements for the tagged particle. We have compared our analytic results in the diffusive case with brownian dynamics simulations that we have performed. The results match very well for both numericlally integrated and analytically integrated expressions. The compact approximate result for the finite sized box captures the crossover from $t^{1/2}$ to t of MSD really well, even for particle numbers as small as 25. We have also rederived already known long time results for infinite systems with partcles of arbitrary powerlaw MSD. This result has subdiffusive and ballistic Newtonian equal mass particles as special cases. We also derive a general expression for tagged particle distribution in time in terms of noninteracting single particle propagators. This result is valid for systems with external time and space dependent potentials. One can foresee that the method will also work for systems of equal mass particles with arbitrary damping and external fields.

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3

Chapter 3

3.1 Introduction

Tagged particle correlations are important markers of underlying microscopic dynamics in interacting particle systems. As we have already noted, in one-dimensional systems, tagged particle diffusion and response is very different from that in higher dimensions. Although there are analytical results in many cases, physical understanding of these phenomena would be helped greatly by simpler methods, which may not reproduce numerical coefficients, but capture the scaling behavior correctly.

In this chapter, we notice that local equilibrium is a property of many systems that we are interested in. We also note that there is a characteristic timescale associated with equilibration of a system of certain size. From here we make a leap, and conclude that the time dependent properties of the system (like the tagged particle displacement) assume their locally equilibrated

values. Since size of the locally equilibrated region depends on time, this gives us the approximate values of the time-dependent variables, by which we mean the scaling answers sans the numerical factors. This also allows for various initial conditions to be taken into account.

We have seen that hard point particles in one dimension produce a diffusive tagged particle when following Hamiltonian dynamics. But in real one dimensional systems, the particles themselves are experiencing thermal noise due to the environment(and hence also damping) all the time, because of which the dynamics itself is stochastic. These particles could be gas molecules, which can be idealized as hard particles at low densities. In this limit, we can consider them as random walkers bouncing off each other. We give a scaling argument to explain the Gaussian features of tagged particle motion in this system. This argument is also found to hold in case of Hamiltonian identical hard particles starting from distribution of velocities.

At high densities, we will be forced to consider the short range interaction between the particles, and hard particle approximation would not hold. Also many systems that one can imagine need not be consisting of particles with hard or short-range interactions, but are chains of particles. To deal with these systems, we consider the locally equilibrated distribution of variables, which follows from the equilibrium free energy of the local system with a time dependent size. We use extensivity of free energy and a quadratic expansion of free energy to recover known results about MSD of tagged particle in force chains, both overdamped and Hamiltonian. This approach works as long as we can identify modes in the system which lead to local equilibration, no matter what the microscopic interaction between particles is.

We note that the quadratic expansion of free energy has been used in [4] to derive an effective spring constant for tagged particle in overdamped chains. Also, the local equilibration enters the arguments in [24], where it is used in combination with the known exact result for MSD in an infinite overdamped single file of hard particles. From this the authors derive scaling laws for MSD of tagged particle in overdamped hard particle single files with athermal but symmetric initial conditions. We will show that our approach can be used for asymmetric initial conditions as well, where it would predict the drift due to the asymmetry too. Also, we predict the drift and diffusion in case of N particles starting at the same point in presence of a reflecting boundary nearby.

Through simulations and heuristic arguments, we show that the way disturbances propagate

in certain nonlinear chains becomes similar to that in harmonic chains on thermalization. This allows us to derive the behavior of tagged particle MSD in these chains when there is noise in initial velocities or the systems have noise with damping. On a more rigorous level, we show that the effective damped sound wave model for Hamiltonian nonlinear chains from [6] allows for our equilibration arguments.

Later we extend our scaling argument to lattice systems, viz. exclusion process, including the driven asymmetric case to recover known results about the tagged particle MSD. Then we move on to a 2D square lattice of identical particles connected by harmonic springs, and use the results to understand tagged particle motion in overdamped hard disks in 2D. We estimate MSD of a tagged particle connected to multiple chains, using extensivity of free energy. Since local equilibration holds true even when an external force is applied to the tagged particle, we study the response of the tagged particle in a chain to an external constant force. We show that a generalized fluctuation-dissipation relation holds for these systems under our approximations.

Then we examine simulations of tagged particle MSD in Hamiltonian and overdamped combs, which are chains composed of further chains. We once again see that the tagged particle MSD scaling is same for harmonic and quartic chains. Seeing that they obey Percus relation, we propose that this could be a general feature of iterated structures, which would allow one to produce a series of powerlaws for the MSD of a tagged particle, starting with either damped or Hamiltonian chains. We note that the response of the tagged particle to a constant external force in branched overdamped harmonic structures has been found analytically in [23]. A fluctuation dissipation relation in this case would recover our results and our proposal for the harmonic overdamped case.

To our knowledge this is the only study which recovers tagged particle scaling behavior in such wide ranging systems. Further, our arguments are based only on local equilibrium and existence of equilibrating modes. This makes it the simplest and shortest way of deriving these scaling relations. This also gives a unifying view of tagged particle behavior in systems with fixed topology.

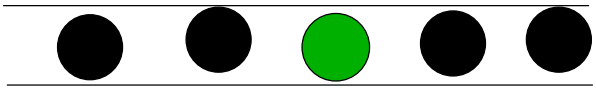

FIGURE 3.1: Particles in a narrow tube. Tagged particle is shown in green.

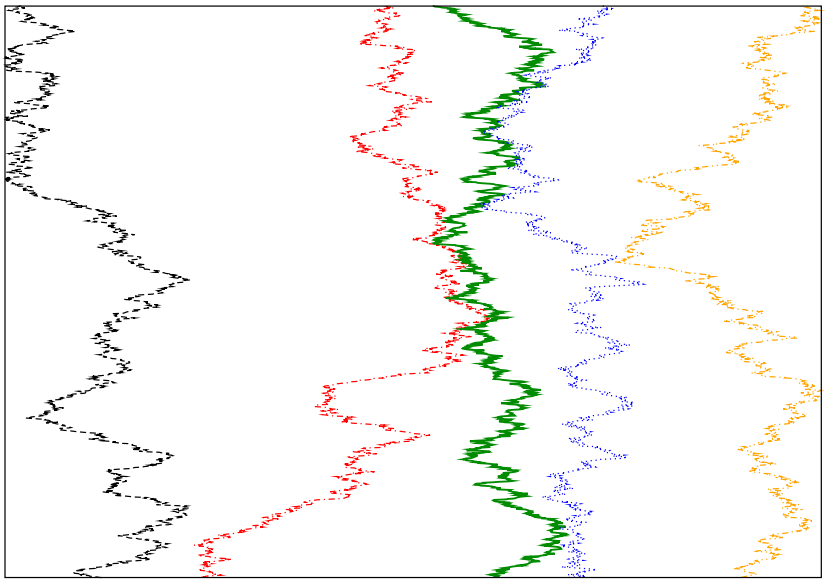

FIGURE 3.2: Identical point particles diffusing and reflecting off each other. One realization of motion is shown.

3.2 Scaling Argument

In almost all the cases described above, it is found (either through simulation or theory) that the tagged particle propagator is a Gaussian within its variance, and has tails that are non-Gaussian. Is there a way we can explain the central Gaussian in a simple manner? To start with, let us look at the *equilibrium* probability density for a tagged particle in a box with hard walls. Let the box be of length $2L$, containing $2N$ particles. A good way of coming up with the equilibrium distribution is to sprinkle the particles independntly, each with a uniform probability density $(2L)^{-1}$ all over the box. Now, during a single trial, after all particles have been placed somewhere, the mth particle from left boundary is the tagged particle. This gives us the mth interacting, non-crossing particle every time.

Now we ask the question: with what probability do we get our particle at a point x? View this as a biased coin toss. What is the probability of getting m points to the left of x, and $2N-m$ to the right of x? Of course the answer is

$$P(x) = \frac{(2N)!}{m!(2N-m)!}\left(\frac{L+x}{2L}\right)^{m}\left(\frac{L-x}{2L}\right)^{2N-m}. \tag{3.1}$$

When $m = N$, the answer reduces to a large deviation form

$$P(x) \sim e^{\rho L\left[\ln\left(1+\frac{x}{L}\right)+\ln\left(1-\frac{x}{L}\right)\right]}. \tag{3.2}$$

When $N >> 1$ and $x << L$, the answer reduces to a Gaussian around the mean, with a variance $\sim L^2/N$.

$$P(x) \sim e^{\frac{-x^2}{L^2/N}} \tag{3.3}$$

Now let us allow the particles to move around with time. Starting with some configuration, can we get the probability of the tagged particle reaching x in time t? See that when we talked of equilibrium densities in the box, if we started with some configuration, we would have to allow as much time as the dynamics needs to reach equilibrium, i.e. all the configurations allowed for the full system with equal probability. How much time is required for this to happen? In general, this is a function of the system size, and also depends on the dynamics. For example, diffusive dynamics implies a timescale going as L^2/D. This opens a small window. If we see that a region

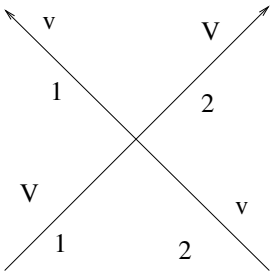

FIGURE 3.3: Two identical Newtonian ballistic particles collide to intarchange their velocities, and hence their trajectories.

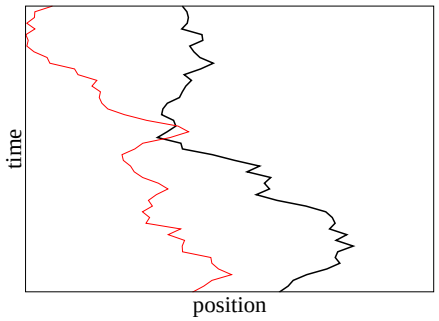

FIGURE 3.4: Trajectories of two Brownian particles.

of size $L(t)$ around the tagged particles equilibrates in itself (including the tagged particle) in time t, by treating the tagged particle as a member of this equilibrated smaller box of size $L(t)$, we should be able to get approximate answers to our questions about time dependent behavior of the tagged particle.

In order find $L(t)$, we need to find modes that equilibrate the system. How do we do that? In general, there could be sound modes- as in certain Hamiltonian systems, or there could be diffusive modes, like in damped, dissipative systems. In systems that we are considering- particles with hard core interactions, or in case of low density systems with short range repulsive interactions with a hard core, particles are reflecting off each other on collision. We know the law of motion or propagator for non-interacting particles, we need to use that information to figure out their motion when they reflect off each other. Look at a two particle collision. A good thing happens

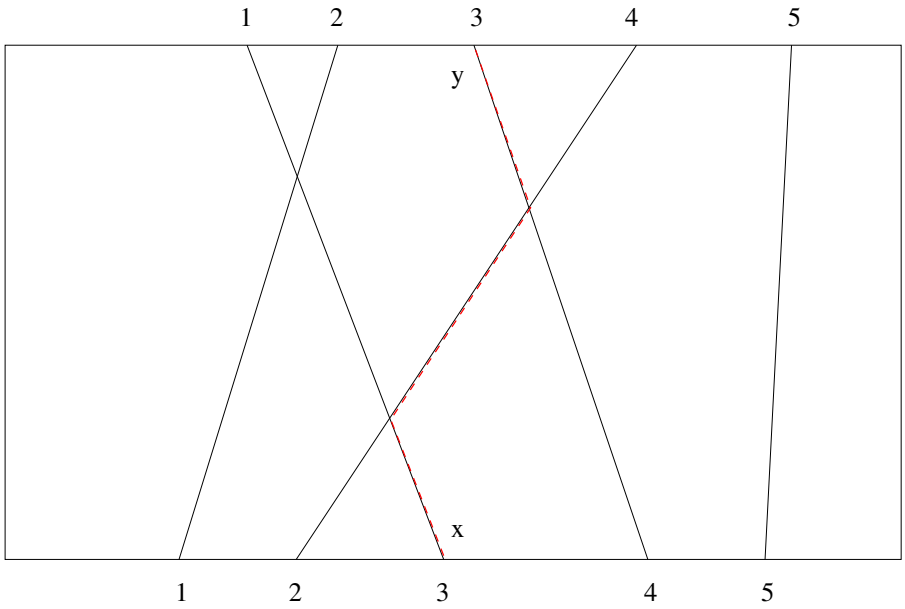

Figure 3.5: 5 identical Newtonian ballistic point particles reflecting off each other.

if our particles are identical and have only one step memory (i.e. motion is Markovian), or are identical Newtonian elastic particles: the motion after collision is as if they have gone through each other, only their labels have been exchanged, as we pointed out earlier (Fig. 3.3). For two particles that are diffusing, the particle trajectories just diffuse through each other (Fig. 3.4), (Fig. 3.2). So the Newtonian system we considered has particle like modes- ballistic (Fig. 3.5) if the region is force free, and diffusive system has diffusive modes. An additional short range repulsive interaction might just make the effective particle size bigger, if the densities are low enough that the average particle separations are large compared to the range of the potential.

This gives us a recipe to calculate $L(t)$. In systems with sound modes with speed v, $L(t) \sim vt$. But do these waves equilibrate the system? See that that need not happen, would not if the system is linear, and even when it is nonlinear, equilibration could take a long time depending upon the initial state and interactions in the system. Hence, one sure way of reaching equilibrium is to start with an equilibrium distribution in intial conditions. In diffusive systems, $L(t) \sim (Dt)^{1/2}$, as this is the length over which probability density of a noninteracting trajectory spreads in time t. In ballistic systems with rms velocity v, $L(t) \sim vt$. If these systems have a uniform spatial density of particles on average, then $N(t)$, the number of particles contained in $L(t)$ scales as

$\rho L(t)$. Following the equilibrium MSD for a tagged particle in a box, the tagged particle MSD would scale as $L(t)^2/N(t) \sim L(t)/\rho$. This provides us with a nice scaling form for the tagged particle MSD. The results compare well with the known theoretical and simulation results, which in general predict $t^{\alpha/2}$ tagged particle MSD for a noninteracting particle MSD of t^{α}, and a $\sim t$ MSD for Hamiltonian systems [14] [2]. This would also explain the results for harmonic systems-overdamped [4] or otherwise. Also, one would expect our scaling argument to hold for systems with non-identical particles, provided one can find modes that equilibrate the system in position space.

The above scaling argument also gives one an approximate way of differentiating between initial conditions- since all the particles $N(t)$ within $L(t)$ equilibrate in time t, but one would have to work harder to take into account the fluctuations in $N(t)$. Fluctuations in $N(t=0)$ could arise from initial position distributions. $N(t)$ would also fluctuate due to stochastic motion of particles or velocity distribution of Newtonian particles. These would not only give rise to fluctuations in $N(t)$, but also a fluctuating rank for the tagged particle in $L(t)$. One can of course calculate these corrections, but at the end of the day we never have a true box of length $L(t)$ with hard walls. Of course the simplest cases are where the initial positions are fixed. Two particular examples - one where each particle starts from a distinct lattice site with equal spacing, and another where all particles start from the same point (Fig. 3.6), have been treated in literature. When the noninteracting particles are diffusive, the first case gives rise to $MSD \sim t^{1/2}$, but the prefactor is $\sqrt{2}$ smaller than that with equilibrium initial condition [10] [7]. The prefactor is not given by our argument, but the $t^{1/2}$ scaling follows easily. In the second case, when N particles start from the same point, one sees that $L(t) \sim (Dt)^{1/2}$, but N is fixed and doesn't change with time. Hence $MSD \sim Dt/N$, which matches the previously obtained results [9] [8]. One can easily think of other systems and initial conditions. Summarizing,

$$\langle x^2(t) \rangle \sim \langle x^2(L(t), N(t)) \rangle_{eq}, \tag{3.4}$$

where $L(t)$ is the size of the system that the particle sees in time t, and $N(t)$ is the number of particles within $L(t)$.

Another way to think about the above is in terms of different modes relaxing at different rates.

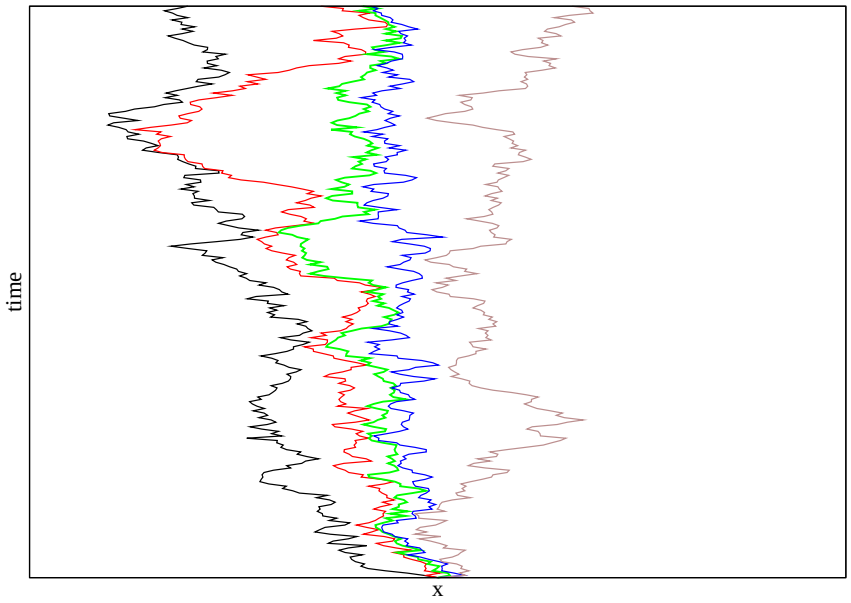

Figure 3.6: All diffusive particles starting at the same point. One realization of motion is shown.

The dominant contribution to the MSD at long times comes from the longest wavelength modes -of size $L(t)$, and they relax with a timescale $\sim (k^2 D)^{-1} \sim L^2/D$.

We note that local equilibrium has been used to calculate a local particle density $\rho(x = 0, t)$ at the origin in [24]. Then the authors put this value of ρ into the relation for tagged particle MSD in a uniform density single file $\langle x^2(t) \rangle \sim \sqrt{Dt}/\rho$. This yields the MSD for a variety of athermal but symmetric initial conditions in their case.

3.3 Beyond hard particles

Now we aim to go beyond the hard particle systems. Since local equilibrium is a feature found in many systems, this should be possible. Further, since equilibrium properties of a system, including the tagged particle properties are given by the thermodynamic free energy in the limit of large system size, we hope to derive some time dependent features(at not too small times)

using quadratic expansions of free energy. For a system of size V with free energy F_V, equilibrium probability distribution of a fluctuating variable ϕ is given by

$$P_V^{eq}(\phi) \sim e^{-\beta F_V(\phi)}, \tag{3.5}$$

where $\beta = (k_B T)^{-1}$. Now, when local equilibrium holds, for a system S of size $V' >> V$, when we start from an initial state ψ of S, local probability distribution of ϕ at a point $\bar{r}$ at time t is approximately given by

$$P_{\bar{r},\psi}(\phi, t) \sim e^{-\beta(\psi,\bar{r}) F_{\psi,\bar{r},V(\psi,\bar{r},t),\beta(\psi,\bar{r})}(\phi)}, \tag{3.6}$$

where $F_{\psi,\bar{r},V(\psi,\bar{r},t),\beta(\psi,\bar{r})}(\phi)$ is the free energy of the locally equilibrated volume $V(\psi, \bar{r}, t)$ around $\bar{r}$. See that β, V and F have an explicit ψ dependence as ψ dictates the local temperature, local speed of the equilibrating modes, and also possibly other parameters such as local density and interaction strength that determine the free energy.

For small deviations of ϕ from its equlibrium average $\langle\phi\rangle_{\psi,\bar{r},V(\psi,\bar{r},t),\beta(\psi,\bar{r})}$, the free energy can be expanded to quadratic order. Suppressing all subscripts and local dependencies,

$$P_{\bar{r},\psi}(\phi, t) \sim e^{-\beta\left[F(\langle\phi\rangle) + F''(\langle\phi\rangle)(\phi - \langle\phi\rangle)^2/2\right]}. \tag{3.7}$$

Here we have dropped the first order term as equilibrium corresponds to minimum of free energy. This is a Gaussian distribution in ϕ, centred at $\langle\phi\rangle$, and a variance proportional to $(F''(\langle\phi\rangle))^{-1}$.

The local dependences on temperature etc. can be maintained only in case where the equilibration of all the local parameters happens at the same rate, or in other words, all the modes that equilibrate these various fields propagate with same speed. One can easily imagine system of damped particles, where the smaller particles of the medium would equilibrate, for example, the temperature field far more quickly than the configurations of the larger particles. In that case, the faster field has to be a constant all over the system from the beginning.

See that it could also be that the system does not equilibrate, like a harmonic chain or identical mass hard particle gas. In this situation, we could start with an ensemble with equilibrium

distribution which is preserved under time evolution, or in general any stationary distribution. In case of equilibrium ensembles the above relation still holds.

Also, for overdamped systems, one can start with any initial condition since local equilibration is guaranteed. Not only that, we could use this formulation for systems with a bulk drive, provided a local steady state is established through the modes. In that case, transient time dependent properties can be calculated from the knowledge of steadystate distributions for the same in finite sized systems.

We note that the use of expansion to quadratic order of the free energy in case of tagged particle displacement in single file diffusion of overdamped systems has been done and the local equilibrium noted as the reason for its validity in [4]. There the use of quadratic expansion was made only to derive the effective spring constant of an equivalent overdamped harmonic chain, and then the time dependent tagged particle MSD in this harmonic chain was calculated.

3.4 Extensivity

Since free energy is extensive, $F_L = LF_{L=1}$, when all other parameters like density are constant. Consider a 1-D chain of identical particles. If the middle particle is displaced by a distance x, free energy of the chain is

$$F_{2L}(x) = F_{L+x} + F_{L-x} = L\left(F_{1+x/L} + F_{1-x/L}\right). \tag{3.8}$$

On replacing L by $L(t)$, this gives us

$$P(x,t) \sim e^{-L(t)\left(F_{1+x/L}+F_{1-x/L}\right)}, \tag{3.9}$$

which can be seen as a kind of large deviation form of the probability distribution function. However, one needs to keep in mind that our arguments are not rigorous, and would break down at the tails of the tagged particle position distribution, where the large deviation form would be important. Now, expanding F to quadratic order in x, we get the Gaussian approximation to the PDF:

$$P(x,t) \sim e^{-2L(t)\left(F_1+ax^2\right)}, \tag{3.10}$$

from which we see that

$$\langle x^2(t)\rangle \sim L(t). \tag{3.11}$$

Also, with no need to invoke local equilibrium, since $N = \rho L$ we see that

$$\langle x^2\rangle_{eqm} \sim N. \tag{3.12}$$

Or, putting back the temperature and $a \sim F''_{L=1}(x=0)$ in Eq. (3.10),

$$\langle x^2\rangle_{eqm} \sim N\frac{k_BT}{F''_{L=1}(x=0)}. \tag{3.13}$$

3.5 Harmonic chain

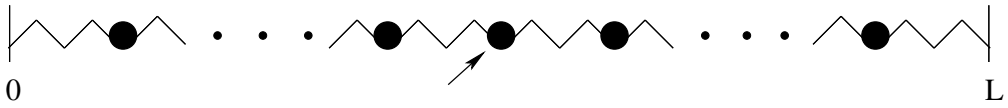

FIGURE 3.7: A chain of N particles with fixed boundaries length L apart. Tagged particle is indicated with an arrow.

Essentially our argument involves two parts: (i) Establishing that there are propagating modes for the relevant variable in the system. (ii)Establishing local equilibrium for the variable of interest (like density). We start with the simplest interacting chain that one can think of, the harmonic chain. Neighbouring particles here interact via a potential given by $V(x) = kx^2/2$. In continuum limit, displacement field u of the Hamiltonian chain obeys

$$\rho\frac{\partial^2 u}{\partial t^2} = Y\frac{\partial^2 u}{\partial y^2}, \tag{3.14}$$

which is a wave equation with sound speed $c = \sqrt{Y/\rho}$. See that here y is actually the particle index, converted to a continuum variable. Here Y is the Young's modulus and ρ is mass density

of the chain. For an impulse at $x, t = 0$, the solution is a rectangular pulse whose front and back ends speed away from origin at a speed c. So a Hamiltonian harmonic chain conveys to any of its particles the information that is at a distance ct from the particle at time t.

Let us also look at the overdamped chain, where each particle obeys an equation of motion $\gamma\dot{x} = f(x)$. In continuum limit

$$\Gamma\frac{\partial u}{\partial t} = Y\frac{\partial^2 u}{\partial y^2}, \tag{3.15}$$

where Γ is the damping coefficient. We see that this is simply the heat equation, and for a displacement at $x, t = 0$, has Gaussian solution with diffusive spread in time, with $D = Y/\Gamma$.

What remains to be done is determining the equilibrium position distribution for the tagged middle particle in a chain of $2N$ particles. A very easy way of getting an estimate is the following. In equilibrium, each spring has an average extension of $\zeta = \pm\sqrt{k_B T/k}$. Since N such stochastic displacements add to give the tagged particle displacement $x = \sum \zeta_i$, for $N >> 1$, we can use the central limit theorem to get

$$P(x) \sim e^{\frac{-x^2}{Nk_B T/k}}. \tag{3.16}$$

Essentially same result is got by a more rigorous analysis [6] which applies equipartition to harmonic modes of the system. Here we see that $\langle x^2\rangle \sim N$, which is consistent with our earlier result of Eq. (3.12).

3.6 Noise Picture

Now we resort to noise summation based methods to establish the results obtained above, since these calculations would hold when equilibration can't be established, and also would throw more light on the dynamics even when the above methods work. We have already done this in case of ballistic hard particle gas, where every kick took the tagged particle a distance ζ, which was a stochastic variable. We do it now for Harmonic chains.

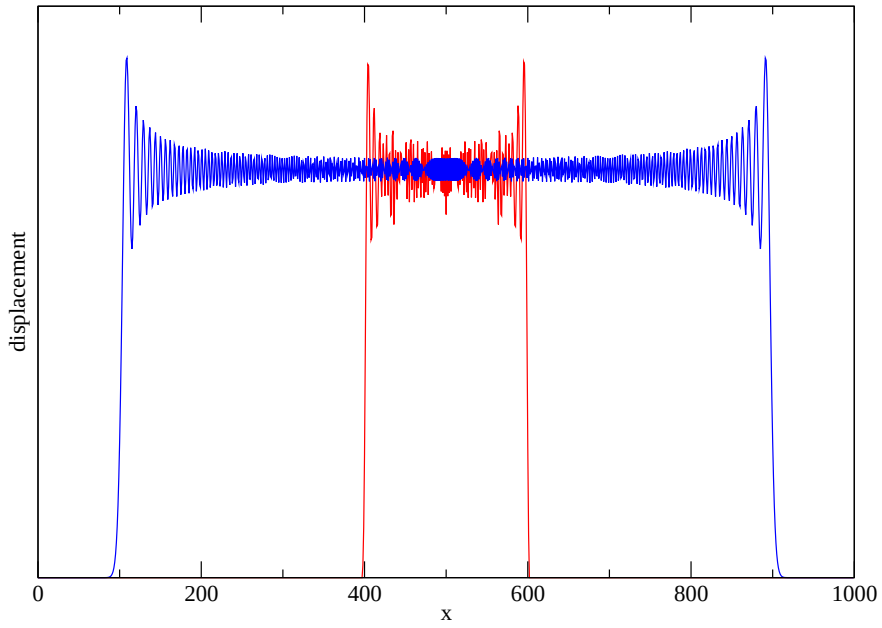

FIGURE 3.8: Pulse propagation in a harmonic Hamiltonian chain. $t = 100$(red) and $t = 400$(blue).

3.6.1 Hamiltonian Harmonic Chain

In case of a Hamiltonian chain, a pulse is propagated from every particle that is kicked at $t = 0$. The pulse profile, as we have already discussed, is an expanding rectangle in case of a harmonic system. In this case, we see that all the particles within a distance ct of the impulse are displaced by a constant amount (see Fig. 3.10). If we start with a harmonic chain whose every particle is given a kick at $t = 0$, resulting in a displacement ζ_i of every particle within ct of the ith particle, for the tagged 0th particle starting at $x, t = 0$, we have

$$x(t) = \sum_{i=-ct}^{ct} \zeta_i. \tag{3.17}$$

From this, applying central limit theorem,

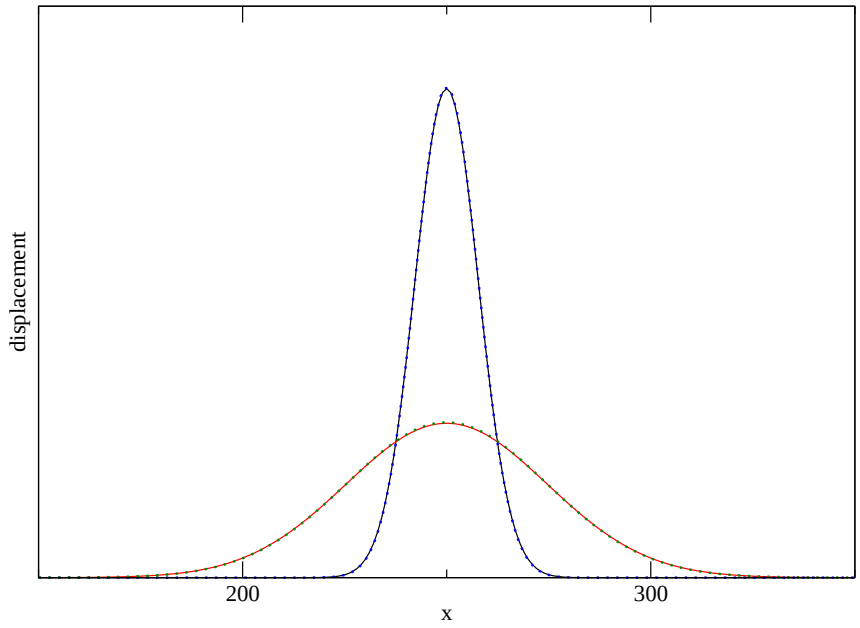

Figure 3.9: Pulse propagation in an overdamped harmonic chain. t=30(black) and t=300(red). Analytic predictions of a diffusive spread are plotted in dotted lines.

$$P(x,t) \sim e^{\frac{-x^2}{ct\langle\zeta^2\rangle}}, \tag{3.18}$$

where we have assumed $\langle\zeta(i',t')\zeta(i'',t'')\rangle = \delta_{i'i''}\delta_{t't''}$. We can read off tagged particle MSD as

$$\langle x^2(t)\rangle \sim ct\langle\zeta^2\rangle. \tag{3.19}$$

This essentially is the answer we got from other methods above.

3.6.2 Overdamped Harmonic Chain

When we look at an overdamped harmonic chain, the displacement $x(t)$ of the tagged 0th particle due to a displacement $\zeta(i, t=0)$ of the ith particle goes as

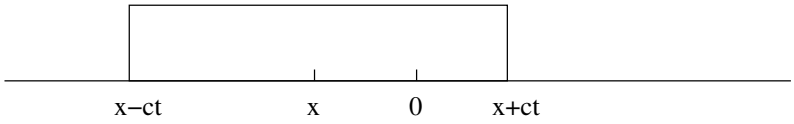

FIGURE 3.10: Schematic displacement profile of a harmonic Hamiltonian chain at time t due to a disturbance originating at $(x, t = 0)$.

$$x(t) \sim \zeta(i, t = 0) \frac{1}{\sqrt{Dt}} e^{\frac{-i^2}{Dt}}. \tag{3.20}$$

Given that the tagged particle experiences disturbances originating at all the particles at all times in the past starting from $t = 0$,

$$x(t) \sim \sum_{t'=0}^{t} \frac{1}{\sqrt{t'}} \sum_{x'=0}^{\infty} \zeta(x', t') e^{-x'^2/t'}. \tag{3.21}$$

Taking average over histories,

$$\langle x^2(t) \rangle \sim \left\langle \left(\sum_{t'=0}^{t} \frac{1}{\sqrt{t'}} \sum_{x'=-\infty}^{\infty} \zeta(x', t') e^{-x'^2/t'} \right) \left(\sum_{t''=0}^{t} \frac{1}{\sqrt{t''}} \sum_{x''=-\infty}^{\infty} \zeta(x'', t'') e^{-x''^2/t''} \right) \right\rangle. \tag{3.22}$$

Since $\langle \zeta(x', t') \zeta(x'', t'') \rangle = \delta_{x'x''} \delta_{t't''}$, only the terms with $x' = x'', t' = t''$ survive. Collecting them together,

$$\langle x^2(t) \rangle \sim \sum_{t'=0}^{t} \frac{1}{t'} \sum_{x'=-\infty}^{\infty} e^{-2x'^2/t'}. \tag{3.23}$$

Converting the second sum to integral, the sum of exponentials becomes a Gaussian integral and is $\sim \sqrt{t'}$.

$$\langle x^2(t) \rangle \sim \sum_{t'=0}^{t} \frac{1}{t'} \sqrt{t'}. \tag{3.24}$$

Converting the remaining sum to an integral,

$$\langle x^2(t) \rangle \sim \sqrt{t}. \tag{3.25}$$

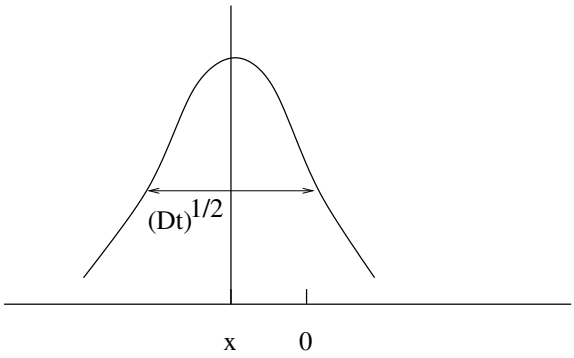

FIGURE 3.11: Schematic displacement profile(Gaussian) of an overdamped harmonic chain at time t due to a disturbance originating at $(x, t = 0)$.

3.7 Nonlinear chains

We now go over to chains which are not harmonic. When we look at a weakly nonlinear chain with $V(x) = kx^2/2 + kx^4/4$, we find that behavior of tagged particle MSD doesn't change, and propagation of disturbances in both Hamiltonian (Fig. 3.13) and overdamped(Fig. 3.14) chains is similar to that in their harmonic counterparts. But when we make the chain purely nonlinear by taking $V(x) = kx^4/4$, we see that the unstretched chains show different pulse propagations as compared to a linear chain. The Hamiltonian pulse has many fronts (Fig. 3.15), whereas the overdamped pulse is strongly subdiffusive (Fig. 3.19). This is not limited to the quartic chain, as is evident from simulation results for the octic chain(Fig. 3.17).

To remedy this situation, we stretch the chains. Reason being, when a nonlinear chain is stretched, i.e., $L \neq 0$, the effective potential becomes weakly nonlinear. Potential between two particles at a distance of $a + x$ is

$$V(a + x) = a^4/4 + a^3x + 3a^2x^2/2 + ax^3 + ax^4/2. \tag{3.26}$$

If we consider the neighbours to left and right of the particle, potential felt by it is

$$V(a + x) = a^4/2 + 3a^2x^2 + ax^4/2, \tag{3.27}$$

which is again a weakly nonlinear potential for small values of x. Now we look at the corresponding simulation results. The pulse in the Hamiltonian case doesn't have as many fluctuations,

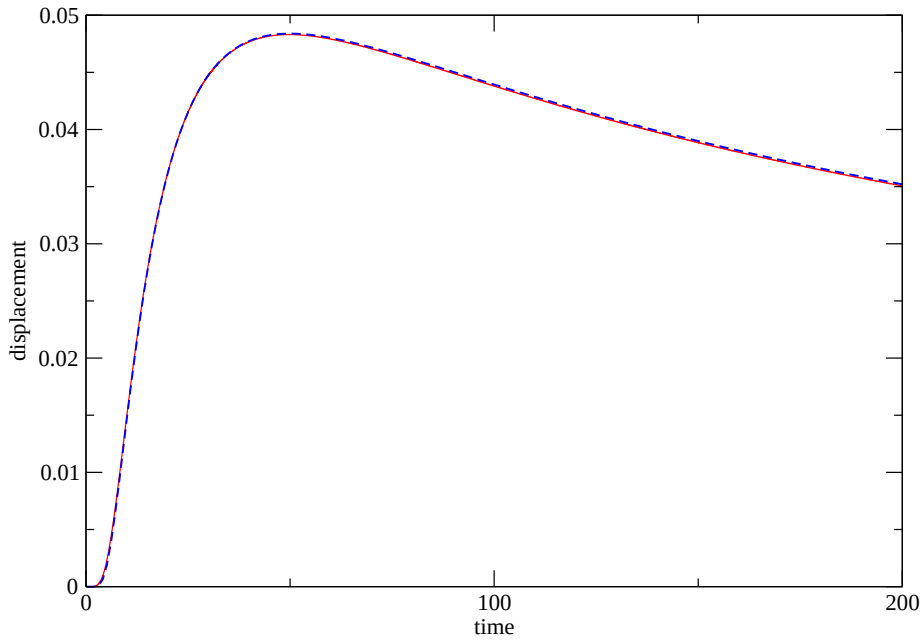

FIGURE 3.12: Displacement of 10th particle from the middle as a function of time in an overdamped harmonic chain due to displacement of the middle particle at $t = 0$. Analytic prediction (Eq. (3.12)) is plotted as a dashed blue curve.

but it is asymmetric about the origin(Fig. 3.16). This is true of the octic chain too(Fig. 3.17). The overdamped chain though does become diffusive (Fig. 3.20). What do we do now? Notice that in a diffusion simulation, the chains are thermalized, through initial velocities in case of Hamiltonian chains, and through noise in case of overdamped chains. So we take chains with no pre-stretch, and average over velocities and noise to see the pulse propagation in both cases. The results seem prettier. Hamiltonian pulse is now symmetric and its fluctuations die with time (Fig. 3.18). The overdamped pulse is also Gaussian, although it does deviate a little from the harmonic evolution (Fig. 3.21). The symmetry of the harmonic chain on thermalization can be explained as follows. When there is prestretch, the expansion and contraction of an anharmonic spring experience different effective harmonic stiffnesses. Because of this, the left moving expansion front and the right moving compression front move at different velocities. For a potential

stiffer than the harmonic one, like quartic or octic, one expects the compression front to move slower, and this is what we see. But when the chain is thermalized at zero prestretch, an effective stretching of springs does occur, but now the stretches of individual springs are effectively uncorrelated, hence the sense of compression and stretching is not conserved for a given front. Or we could argue that the response of the system on thermalization is governed by free energy, whose quadratic expansion once again leads to a harmonic-like behavior.

From these results, we could revert back to our treatment of harmonic chains and infer that since the pulse propagation is not too different between the harmonic and thermalized quartic or weakly nonlinear chains, the tagged particle MSD is also not different. A more rigorous analytical way is to model the nonlinear Hamiltonian chains as having damped sound modes [6]. In this method, the long wavelength modes are assumed to be damped by the short wavelength ones, which also act as a source of noise in the evolution of the former. The condition that the momentum be conserved during evolution leads to a damping of the form

$$\Gamma_n \sim \frac{\gamma}{m}\left(1 - cos\left(\frac{n\pi}{N+1}\right)\right), \tag{3.28}$$

where Γ_n is inverse damping timescale for the amplitude of the wave with wavenumber $n\pi/L$, and N is the number of particles of mass m and damping γ in this chain of size L. Since we are concerned with dominant contributions to equilibration at long time scales, we look at small wave number modes in the limit of large N. In this limit, we can expand the cos term to quadratic order in n/N. Now,

$$\Gamma_n \sim \frac{\gamma}{m}\left(\frac{n\pi}{N}\right)^2, \tag{3.29}$$

which implies that the timescale over which the mode decays is

$$\tau_n \sim \frac{m}{\gamma}\left(\frac{N}{n\pi}\right)^2. \tag{3.30}$$

This implies that the timescale over which the long wavelength modes decay is $\sim N^2$, which is $\sim L^2(t)$ in our model. Since equilibration time for Hamiltonian chains is $\sim L(t)$, we infer that the decay times for the relevant long wavelength modes are much longer than the equilibration

time, and hence our scaling argument still holds for the nonlinear Hamiltonian chains where the damped sound mode model works.

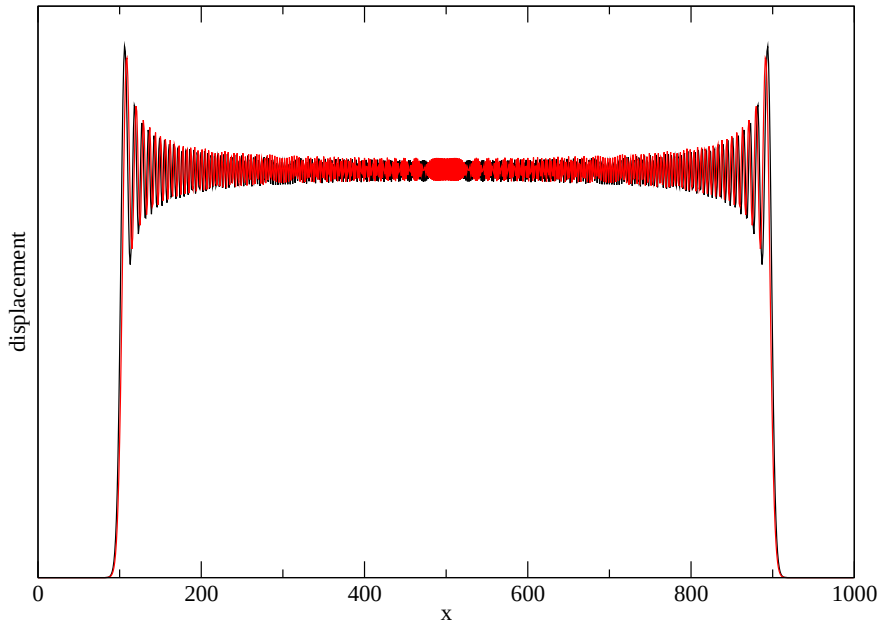

FIGURE 3.13: Comparison of pulse propagation in a harmonic(black) and a weakly nonlinear(red) Hamiltonian chain. Nonlinear potential is $x^2/2 + x^4/4$.

3.8 Symmetric exclusion process

There is no reason why we can't extend this treatment to motion of particles on discrete lattices. So we will do it for the simple exclusion process(see Fig. 3.22), where particles move on a lattice, subject to the constraint that a site can't be doubly occupied. The hopping rate is p.

Now, for a system with $2L$ sites and $2N+1$ particles, number of ways in which you can place the particles such that the middle particle is at the xth site is

$$W(x) = \frac{(L+x)!}{N!(L+x-N)!}\frac{(L-x)!}{N!(L-x-N)!}. \tag{3.31}$$

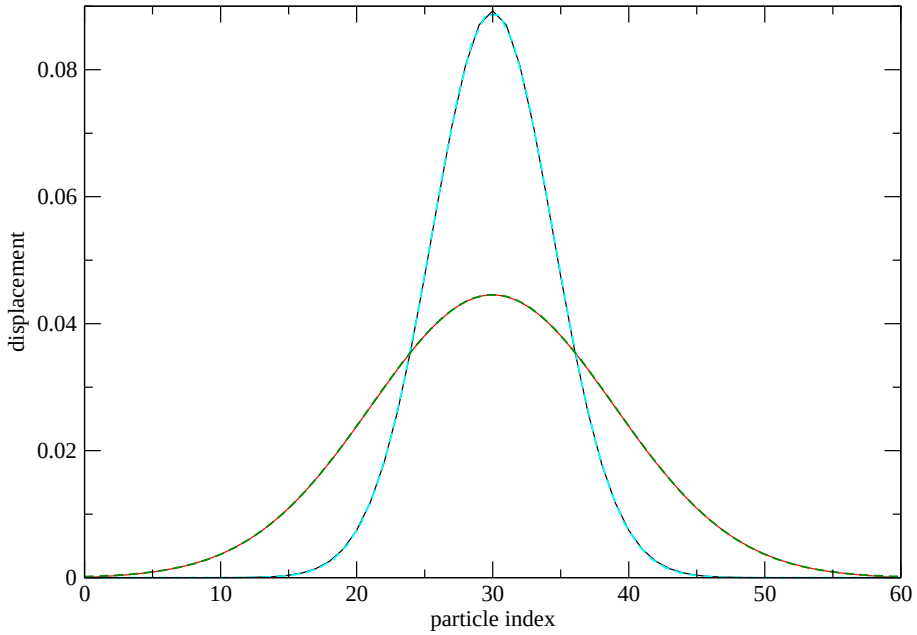

Figure 3.14: Pulse propagation in a weakly nonlinear overdamped chain. $t = 10$(black) and $t = 40$(red). Corresponding Gaussians are drawn in dashed lines. Nonlinear potential is $x^2/2 + x^4/4$.

Now, for $L, N, L - N, L - N - x >> 1$,

$$P(x) \sim e^{\frac{-2Nx^2}{L(L-N)}}. \tag{3.32}$$

Setting $N/L = \rho$,

$$P(x) \sim e^{\frac{-2\rho}{1-\rho}\frac{x^2}{L}}. \tag{3.33}$$

Since density relaxes diffusively [13], $L \sim \sqrt{pt}$, and hence

$$P(x) \sim e^{\frac{-2\rho}{1-\rho}\frac{x^2}{\sqrt{pt}}}. \tag{3.34}$$

We can read off the MSD as

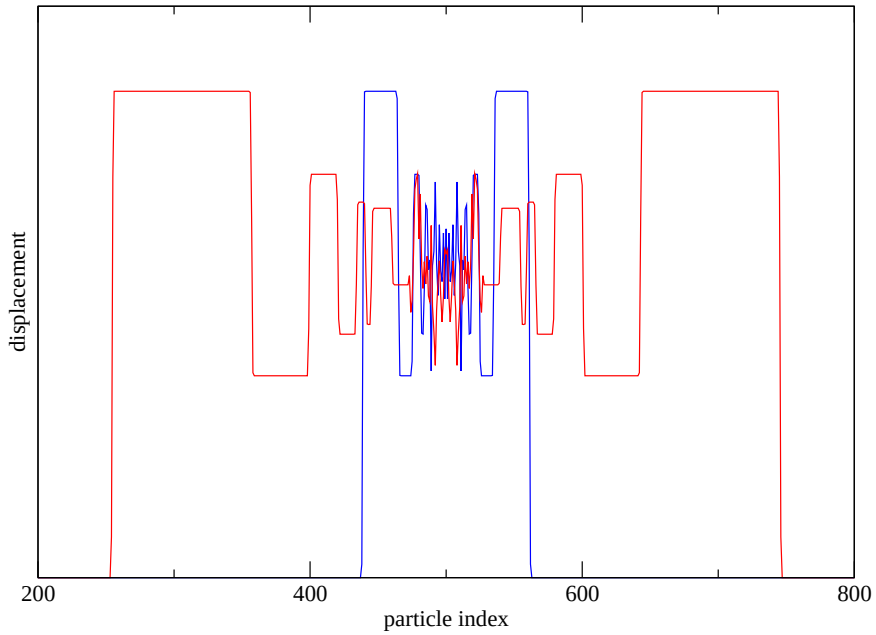

FIGURE 3.15: Pulse propagation in a quartic Hamiltonian chain with no pre-stretching. t=100(blue) and t=400(red). The pulse is symmetric about its origin. The pulse fronts are traveling at a constant speed. Also the amplitude of the leading edge remains same over time.

$$\langle x^2(t)\rangle \sim \frac{(1-\rho)\sqrt{pt}}{\rho}, \tag{3.35}$$

which indeed matches the exact result [1] upto a numerical factor of the order of unity.

3.9 Beyond Equilibrium: Asymmetric exclusion process

Note that one can easily imagine extending the above argument to driven systems, provided there is a local steady state in place of local equilibrium. We look at the example of asymmetric exclusion process(ASEP)(see Fig. 3.23). Here the hopping rates are q and p for the left hop and right hop resp.

See that the local steady state requirement implies that the drive be in the bulk and not just

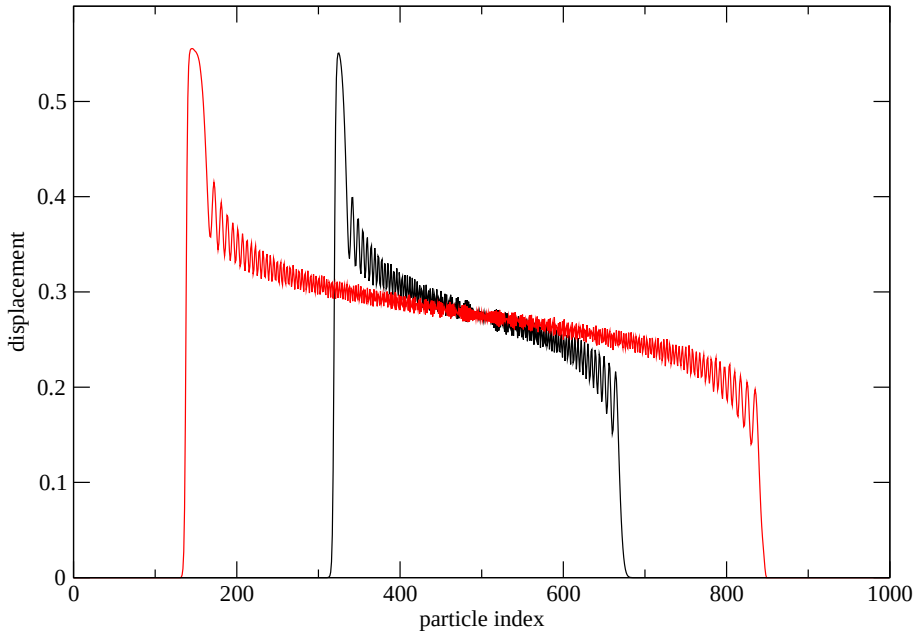

Figure 3.16: Pulse propagation in a quartic Hamiltonian chain with pre-stretching($L/N = 1$). t=100(blue) and t=200(red). Both displacement and speed are different for the forward and backward moving fronts. But they do maintain their speeds over time. Also the amplitude of the leading edge remains same over time.

at the boundaries, and this is how it is in this case. In ASEP, it is known that there exist kinetic density waves propagating with a velocity given by $v_K \sim (p-q)(1-2\rho)$ [1]. Given that these are the fastest density modes, we take them to be the dominant equilibration modes. However, one needs to note that the density is transported bodily, and hence starting from an ensemble with stationary distribution is necessary for the following argument to hold. Now, we need to go to a frame moving with the avg. velocity of the tagged particle $v_P \sim (p-q)(1-\rho)$, which is different from the velocity of kinetic density waves. In this frame, speed of the modes is $v \sim (p-q)\rho$. Putting $L \sim (p-q)\rho t$,

$$P(x) \sim e^{\frac{-2\rho}{1-\rho}\frac{x^2}{(p-q)\rho t}}. \tag{3.36}$$

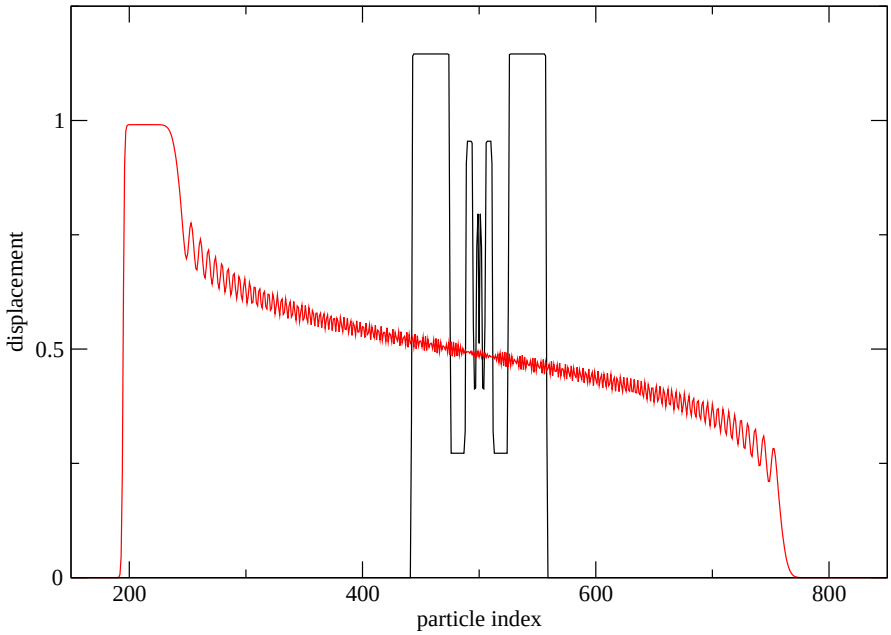

FIGURE 3.17: Pulse propagation in an octic Hamiltonian chain with(red) and without(black) pre-stretching($L/N = 1$) at t=100(blue). Again the behavior is similar to the quartic chain.

from which we can read off the MSD as

$$\langle x^2(t)\rangle \sim (1-\rho)(p-q)t, \tag{3.37}$$

which again matches the known results [1].

3.10 Asymmetric initial conditions

Now we will move on to a situation where a non-zero drift can be found in absence of bulk drive. Consider a single file of hard particles, but with an asymmetry in the initial conditions. A local equilibration can now result in a drift of the tagged particle. In general, if $\rho(x', t = 0)$ is the density of particles at $t = 0$, then

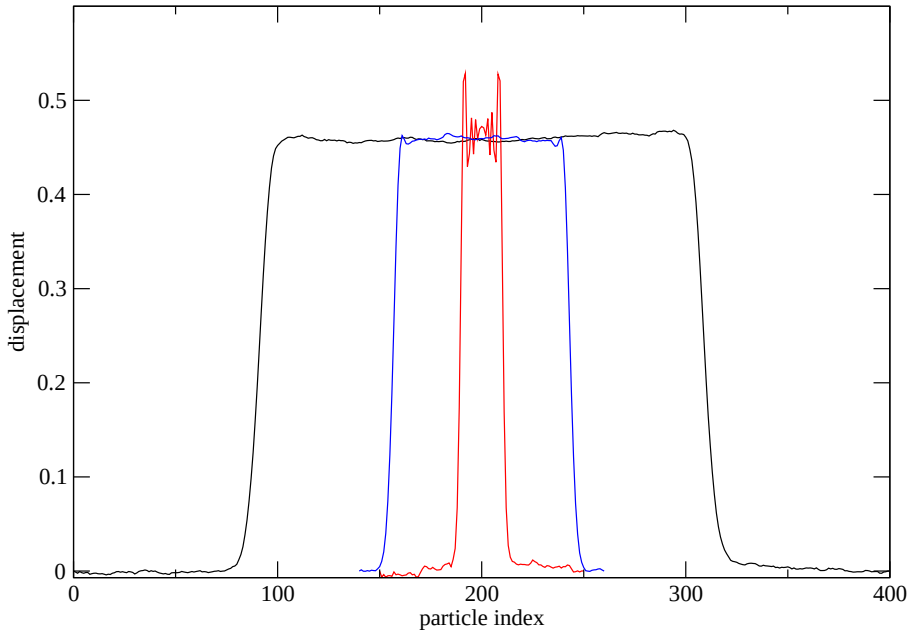

Figure 3.18: Pulse propagation in a quartic Hamiltonian chain with no pre-stretching, but averaged over initial velocities of particles. t=10(red), t=40(blue) and t=100(black). The pulse is symmetric about its origin. The pulse fronts are traveling at a constant speed, although they do tend to spread out with time. Also fluctuations die out over time and the amplitude of the pulse remains same.

$$\langle x(t)\rangle \sim L(t)\left(1-\frac{2\int_0^{L(t)}\rho(x',t=0)dx'}{\int_{-L(t)}^{L(t)}\rho(x',t=0)dx'}\right). \tag{3.38}$$

MSD is as usual given by the equilibrium MSD of the tagged particle within a box of size $L(t)$ with the average density dictated by the initial density, but now the centre of the box is $\langle x(t)\rangle$. Hence

$$\langle x^2(t)\rangle - \langle x(t)\rangle^2 \sim \frac{L^2(t)}{\int_{\langle x(t)\rangle-L(t)}^{\langle x(t)\rangle+L(t)}\rho(x',t=0)dx'}. \tag{3.39}$$

Let us apply this method to two particular cases. First consider an infinite line with a density ρ_1 of particles in the left half and $\rho_2 < \rho_1$ in the right half (Fig. 3.24). Let the tagged particle be at $x = 0$. With time, there will be a nett flow of particles from left to right, and the tagged

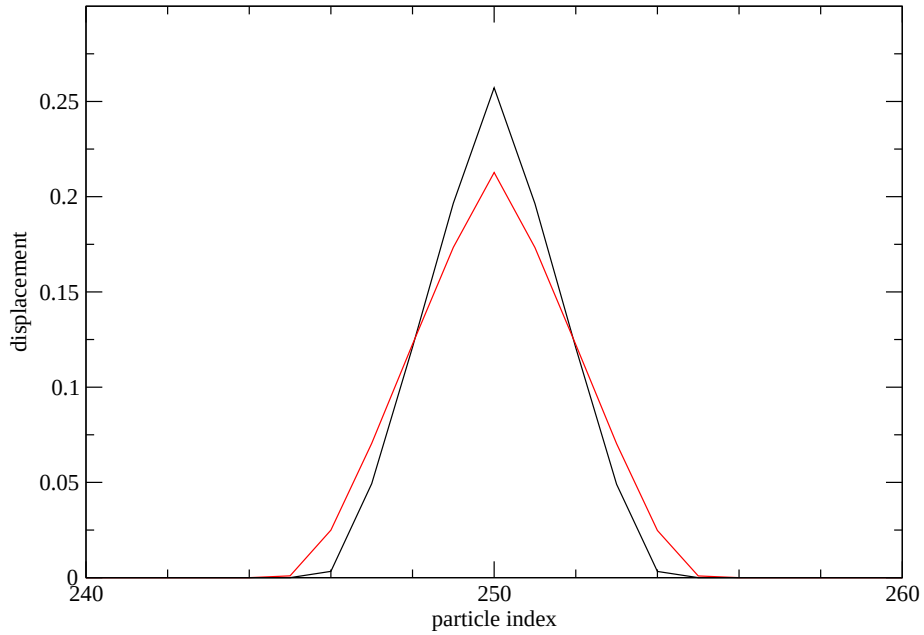

FIGURE 3.19: Pulse propagation in an overdamped quartic chain at zero temperature and no prestretching($L = 0$). t=100(black) and t=300(red). See that the pulse propagation is extremely slow and subdiffusive.

particle will be pushed to right on an average. Now, from above,

$$\langle x(t) \rangle \sim \frac{\rho_1 - \rho_2}{\rho_1 + \rho_2} L(t). \tag{3.40}$$

MSD would be given by

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 \sim \frac{L(t)(\rho_1 + \rho_2)}{4\rho_1 \rho_2}. \tag{3.41}$$

A slightly better picture would be to assume a uniform gradient of density in $L(t)$. This would change the pre-factor for the MSD, but the time-scaling would still be the same.

We simulate the overdamped hard particles with this kind of initial conditions, and find that the time scaling is correctly captured by our expressions, and that the density dependence is almost correct. For a given ρ_1/ρ_2, all the curves do collapse to a single curve with our scaling.

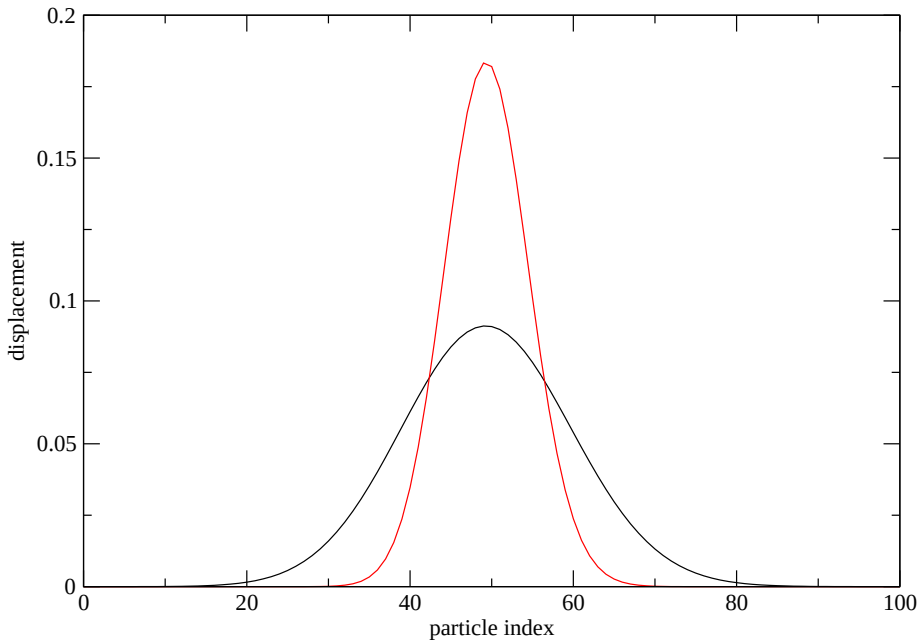

Figure 3.20: Pulse propagation in a prestretched($L/N = 2$) overdamped quartic chain at zero temperature. t=1(red) and t=4(black).

But there is an additional weak ρ_1/ρ_2 dependence for both MSD and drift. This is expected since the exact location of $\langle x(t)\rangle$ in the equilibrated region depends on the average density profile in this region. While we get it right for the flat profile, the deviation of the true profile, and hence tagged particle position, from this would be a function of ρ_1/ρ_2, as the shape of the profile is a function of ρ_1/ρ_2 only, when rescaled by $L(t)$, in the long time limit. To account for this, we see that a scaling term linear in ρ_1/ρ_2 is sufficient. We see that for $\langle x(t)\rangle$, we need to scale by $\beta = (\rho_1 - \rho_2)(\rho_1 + \rho_2)$ as dictated byEq. (3.40) and then multiply by $1 + \kappa$ where $\kappa = .05\delta(\rho_1/\rho_2)$, where $\delta(\rho_1/\rho_2) = (\rho_1^0/\rho_2^0) - (\rho_1/\rho_2)$ is the difference between the density ratios between the reference system, $\rho_1 = 4, \rho_2 = 1$ in this case, and the present system. In long time limit, all curves collapse to the reference curve (Fig. 3.26). For MSD, we see that we need to scale by $\alpha = (\rho_1 + \rho_2)(\rho_1\rho_2)$ as dictated byEq. (3.41) and then multiply by $1 + \epsilon$ where $\epsilon = .07\delta(\rho_1/\rho_2)$, where $\delta(\rho_1/\rho_2) = (\rho_1/\rho_2) - (\rho_1^0/\rho_2^0)$ is the difference between the density ratios

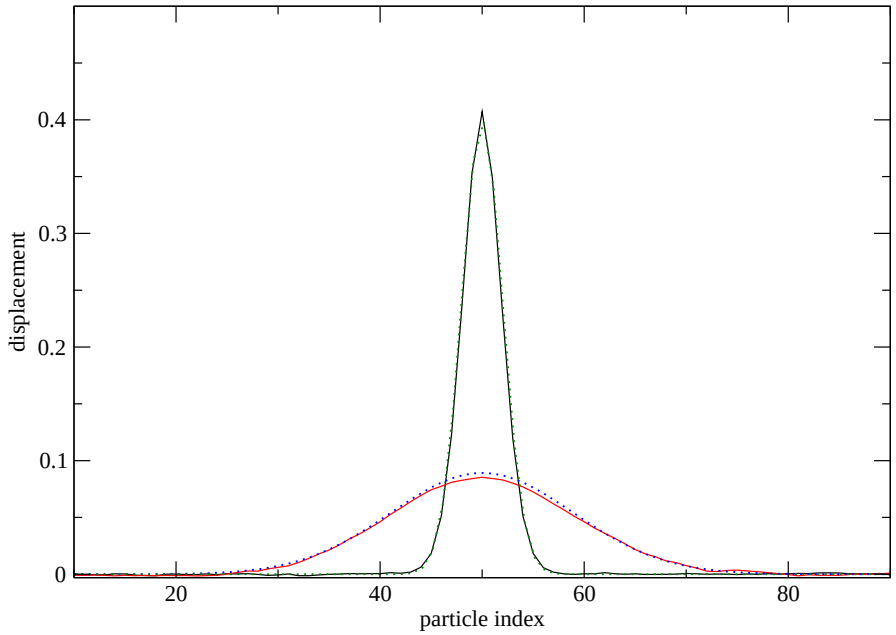

FIGURE 3.21: Pulse propagation in an overdamped quartic chain at a non-zero temperature. t=2(black) and t=40(red). Gaussians for corresponding times are plotted in dotted lines. Amplitude and diffusivity are the two parameters that have been fitted.

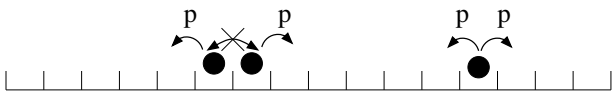

FIGURE 3.22: Symmetric exclusion process. Double occupancy of a site is not allowed. Hence the tranisitions that are not allowed are crossed out.

between the reference system, $\rho_1 = 3, \rho_2 = 2$ in this case, and the present system. In long time limit, all curves collapse to the reference curve (Fig. 3.25).

Now let us look at another situation- N particles, all starting at $x = 0^+, t = 0$. Further, we will put a reflecting boundary at $x = 0$. This will again give rise to a drift for the tagged middle particle. Using Eq. (3.38) and Eq. (3.39),

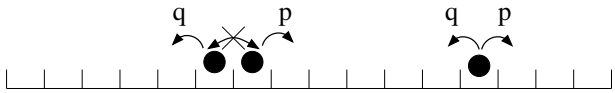

Figure 3.23: Asymmetric exclusion process.

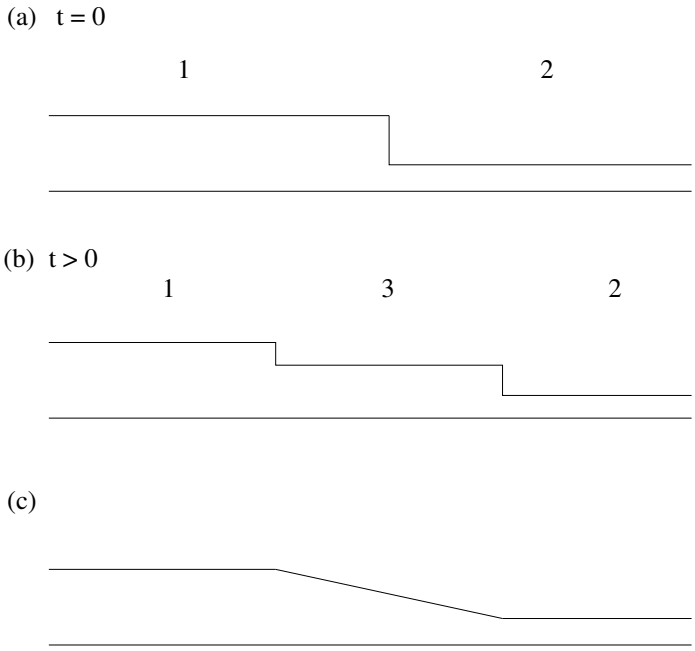

Figure 3.24: (a)An asymmetric initial condition with density of particles ρ_1 and ρ_2 in region 1 and 2 resp. (b) At a time $t > 0$, a 3rd region of size $L(t)$ with an equilibrated density $(\rho_1 + \rho_2)/2$ arises in the middle. (c) A better approximation would be to assume a uniform gradient in the region 3.

$$\langle x(t) \rangle \sim L(t), \tag{3.42}$$

and

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 \sim \frac{L^2(t)}{N}. \tag{3.43}$$

We verify the above results through simulation in case of overdamped hard diffusive particles (Fig. 3.27) for $N = 100$ and $N = 1000$. MSD in case of $N = 100$ is found to be 10 times that of $N = 1000$, and drifts are same in both cases, as predicted above.

See that the hard particle condition in asymmetric initial condition problems is in general

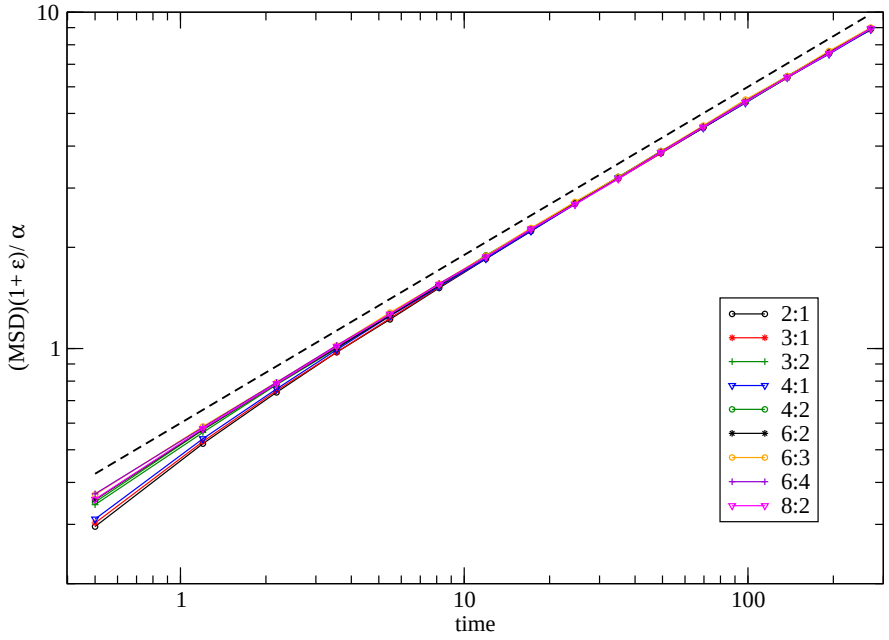

FIGURE 3.25: MSD of the tagged particle in an overdamped single file when starting with different densities on two sides of the tagged particle. The densities are indicated in the legend box, and the MSD is scaled by density dependent factors as explained in the text. A dashed black line $\sim t^{1/2}$ is drawn for comparison.

unnecessary, and we could start with any other interaction, and the general reasoning followed in the examples above will go through.

3.11 Higher dimensions

We get a little more adventurous, and extend our domain to higher dimensions. Let us consider a square lattice of identical particles connected by harmonic springs (Fig. 3.28).

As before, $L(t)$ and $N(t)$ both scale as $\sqrt{D_c t}$ and ct in case of dissipative and Hamiltonian cases respectively. But as is well known in solid state physics, equilibrium MSD of a tagged particle now diverges logarithmically with system size L, i.e.$\langle x^2(L)\rangle_{eq} \sim \ln L$ [22]. Hence,

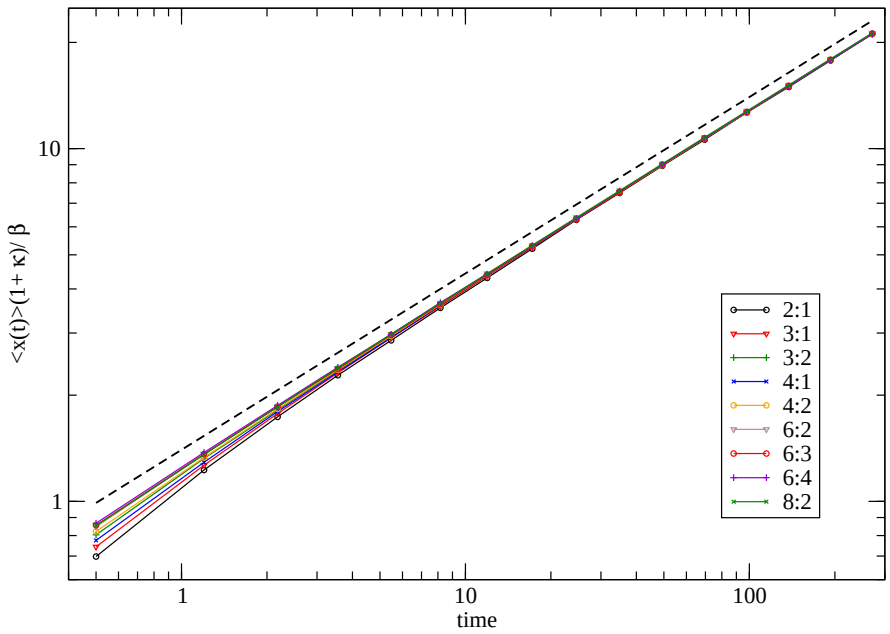

FIGURE 3.26: Mean position $\langle x(t)\rangle$ of the tagged particle as a function of time in an overdamped single file when starting from different particle densities on left and right of the tagged particle. The densities on the left and right are given in the legend box. The mean displacement is scaled by density dependent factors as explained in the text. A dashed black line $\sim t^{1/2}$ is drawn for comparison.

$$\langle x^2(t)\rangle \sim \ln t, \tag{3.44}$$

in both dissipative and Hamiltonian cases. We verify it in the overdamped harmonic case through simulations (Fig. 3.29).

Now that we have the result for a harmonic lattice in 2D, why not go from point particles in 1D to hard disks in 2D? Although there is no 'no-crossing condition' like in 1D, at short times a tagged particle (see Fig. 3.30) is trapped by its crowding neighbours, somewhat like the tagged particle in the 1D case. Hence, we propose/expect that a harmonization of this system should hold at short times- before a tagged particle escapes from its cage, and hops to the next cage, or the cage rearranges/relaxes. If this is true, then the MSD of this particle should go as $\log t$ as long as the particle is confined to within this cage. Of course, at very short times, i.e. before

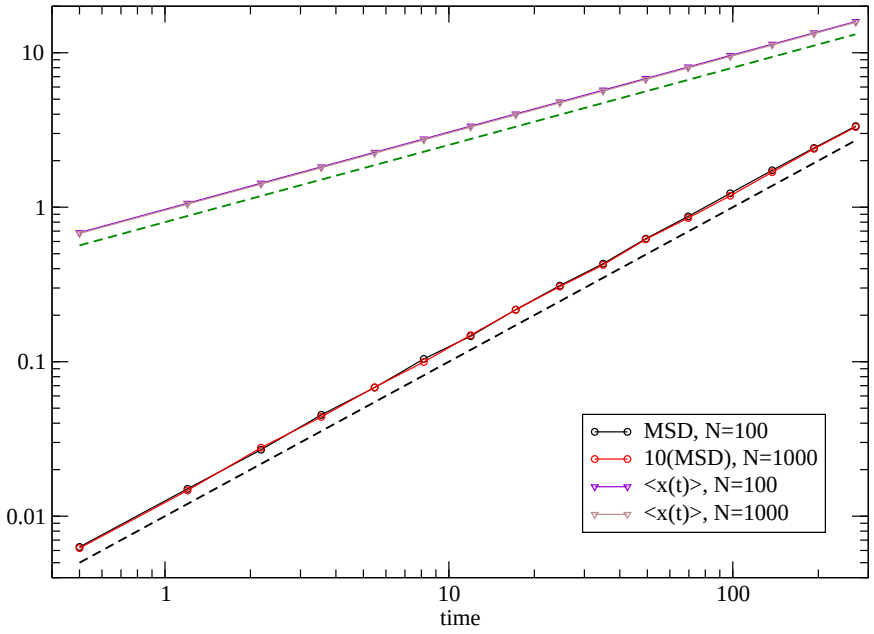

FIGURE 3.27: Scaled MSD (circles) and $\langle x(t) \rangle$ (triangles) for a tagged middle particle in a system of N overdamped point hard particles, all starting at $x = 0^+$, with a reflecting boundary at $x = 0$. Dashed lines $\sim t$ (black) and $t^{1/2}$ (green) are drawn for comparison.

it sees its neighbors, it diffuses freely. And at long times, i.e. after it escapes from the cage, it effectively diffuses, although with a smaller diffusivity than the noninteracting particle. Looking at previous studies, we find this behavior as having been confirmed by experiments on colloidal sphere monolayers [18] [19] [20], ellipsoids [21] and by theory [16] [17].

3.12 Response and fluctuation-dissipation relation

We ask another question now: how does a given system respond to an applied force? To this end, we apply a constant force f^{ext} to the tagged particle and see the response of the system. Again, we see that the part of system that sees the force is dictated by the extent to which the applied force has been propagated in the system.

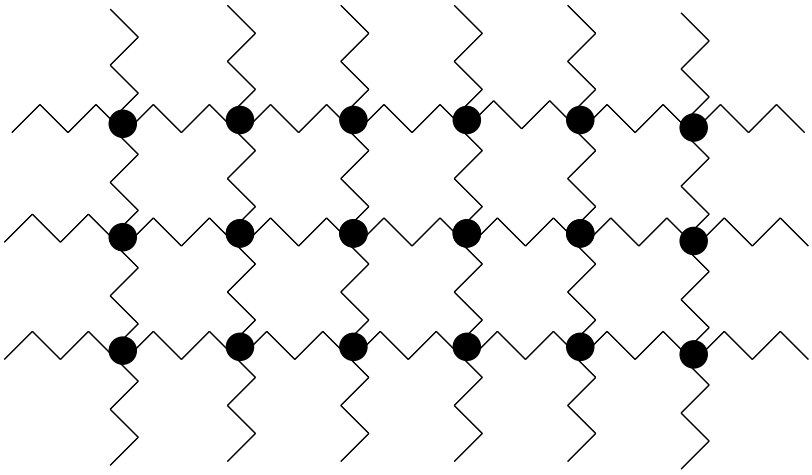

Figure 3.28: A harmonic square lattice of identical particles.

In an overdamped chain, we propose that a portion $\sqrt{D_c t}$ of particles would be in equilibrium with the tagged particle, where D_c is the collective diffusion coefficient. Or in other words, this is simply mechanical equilibrium of a chain of this length on application of this force to the middle particle. This would mean that $\sqrt{kt/\gamma}$ springs around the tagged particle are extended to a length of f^{ext}/k each. Hence, in time t,for a chain at zero temperature, force balance gives us

$$x(t) \sim \frac{f^{ext}}{k}\sqrt{\frac{kt}{\gamma}}, \tag{3.45}$$

from which we get

$$v(t) \sim \frac{f^{ext}}{\sqrt{\gamma k t}}. \tag{3.46}$$

For anharmonic chains

$$x(t) \sim a(f^{ext})\sqrt{D_c t}, \tag{3.47}$$

where $a(f^{ext})$ is the length of a spring on application of a force f^{ext}.

Alternatively, $L(t)$ springs around the tagged particle are moving with a velocity v. Once again force balance gives us

$$\gamma v L(t) \sim f^{ext}, \tag{3.48}$$

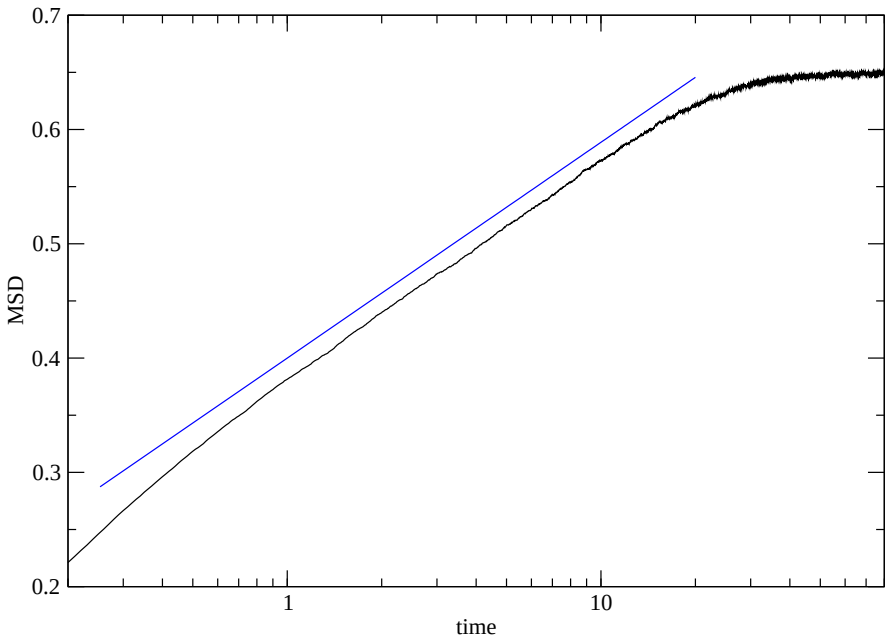

FIGURE 3.29: MSD of the tagged middle particle in an overdamped harmonic square lattice of $L = 20$. Blue straight line is drawn proportional to $\ln(t)$.

by substituting $L(t) \sim \sqrt{D_c t}$, we get

$$\gamma v \sim \frac{f^{ext}}{\sqrt{D_c t}}. \tag{3.49}$$

We verify our assumptions about the displacement profile of particles (Fig. 3.32) and the velocity of the tagged particle (Fig. 3.31) for harmonic and quartic chains.

For Hamiltonian systems, we have seen that any impulse on a particle results in a constant displacement of all the particles within a distnace ct. Seeing the applied constant force as a series of infinitesimal impulses, it is obvious that the tagged particle moves with a constant velocity, and all the particles within a distance ct of it also do the same. Momentum conservation tells us that

$$f^{ext} t = \rho c t v. \tag{3.50}$$

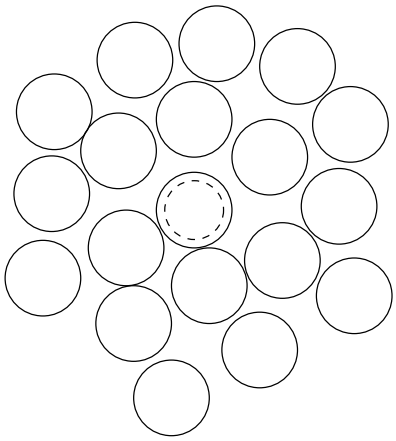

Figure 3.30: Identical hard spheres in 2d. Tagged particle is indicated with a dashed circle inside.

From above,

$$v \sim \frac{f^{ext}}{c\rho}. \tag{3.51}$$

We verify our assumptions about the displacement profile of particles (Fig. 3.34) and coclusions about the velocity of the tagged particle (Fig. 3.33) for harmonic and quartic chains. Once again we do encounter the asymmetry of the profile about the origin in case of the quartic chain.

This local equlibration behavior again does show up at nonzero temperature, provided we do not apply too great a force, which would result in a big displacement of the tagged particle, because of which the quadratic approximation to the free energy change might cease to hold, i.e., higher order terms would start contributing significantly.

In presence of a constant external force f and a finite temperature T,

$$F^{f}_{L(t)}(x) = F^{f=0}_{L(t)}(x) - fx. \tag{3.52}$$

As long as quadratic approximation holds,

$$F^{f=0}_{L(t)}(x) = F^{f=0}_{L(t)}(x=0) + \frac{x^2}{bL(t)}. \tag{3.53}$$

Hence probability density of x at t is

$$P^f(x,t) \sim e^{fx + \frac{1}{k_B T}\frac{-x^2}{bL(t)}}. \tag{3.54}$$

Completing the square in the exponent, we can read off

$$\langle x(t) \rangle \sim bL(t)f \tag{3.55}$$

and

$$\langle x^2(t) \rangle \sim k_B T b L(t) \tag{3.56}$$

This verifies a generalized fluctuation dissipation relation:

$$\frac{\langle x^2(t) \rangle}{\langle x(t) \rangle_f} \sim \frac{k_B T}{f}. \tag{3.57}$$

Such a generalized fluctuation dissipation relation has been established in various contexts, including the case of overdamped harmonic chains, and for overdamped chains where the harmonic approximation works, in [4]. In [15], such a relation is established for a single random walker on a comb and antenna-like lattices.

Also, see that the above derivation did not rely upon the dimensionality of the system, and hence should go through unchanged in case of, for example, the 2D harmonic lattice that we talked of, and its nonlinear versions, and overdamped 2D hard disks at intermediate times. There Eq. (3.55) would imply $x(t) \sim f \ln(t)$.

We again verify our assumptions about the average displacement profile of particles (Fig. 3.38, Fig. 3.36) and conclusions about the tagged particle average displacement or velocity (Fig. 3.39, Fig. 3.37) by performing simulations with noisy initial velocities for Hamiltonian chains and with noisy evolution for overdamped chains. The asymmetry of the Hamiltonian quartic profile again does go away when noise is present.

3.13 Parallel chains and stars

Now we can think of building other structures with chains. First we connect many chains to the tagged particle, instead of making it the middle particle of just one chain (see Fig. **??**). Now, the

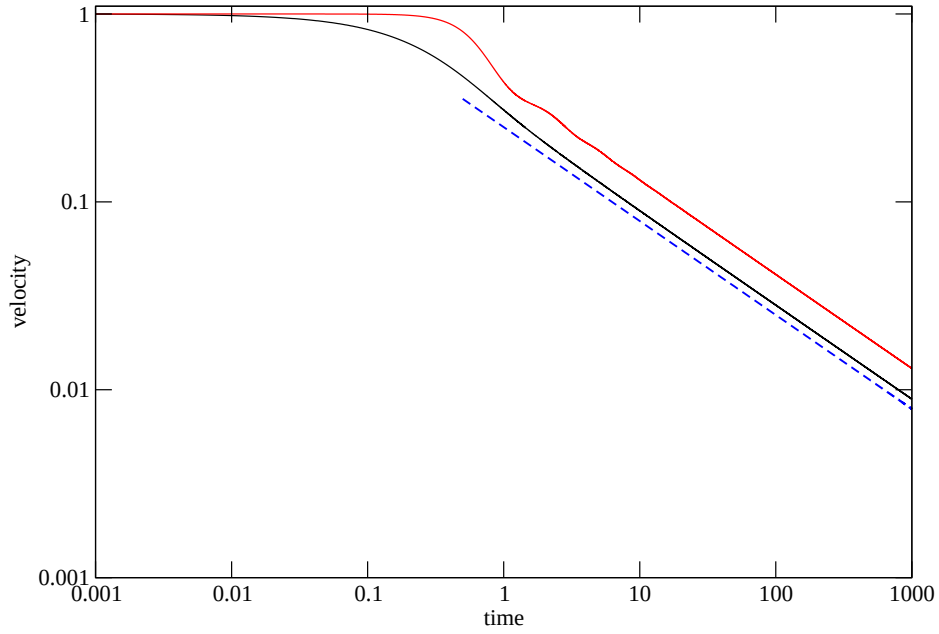

Figure 3.31: Velocity of a tagged particle in an overdamped harmonic (black) and a quartic (red) chain as a function of time, in response to a constant applied force of unit magnitude. Long time behavior is compared with $1/\sqrt{t}$(blue dashed line).

free energy of a length L of the system with n chains scales as nF_L where F_L is the free energy of one chain of length L. Modes of the individual chains are unaffected by the number of chains in the system.

$$F_{L,n}(x) = nF_L(x). \tag{3.58}$$

Hence,

$$\langle x^2(t)\rangle_n \sim \frac{\langle x^2(t)\rangle_1}{n}. \tag{3.59}$$

We verify the above relation with numerical simulations for overdamped harmonic chains (Fig. **??**).

One could ask, is it necessary for the chains to be parallel, i.e., do they have to live in one

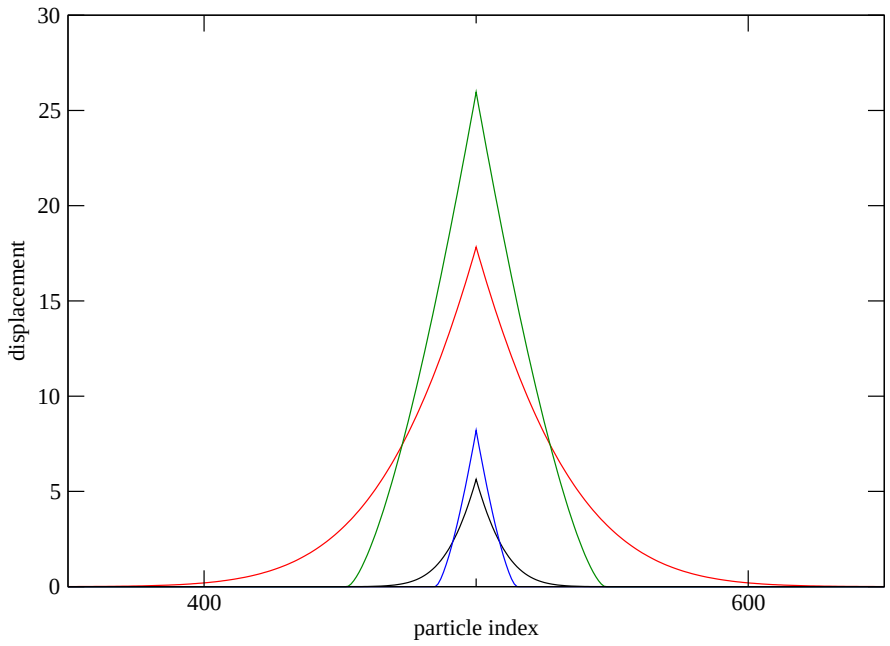

FIGURE 3.32: Displacement profiles of particles in an overdamped harmonic and quartic chain in response to a constant force of unit magnitude applied to the middle particle. $t = 100$ (black and blue resp.), and $t = 1000$ (red and green resp.). Width of the profiles at half maximum and their amplitudes are found to be proportional to $\sqrt{t}$. Notice that the tails are much spread out in case of harmonic chain.

dimension? As long as the harmonic approxiamation holds, they need not(see Fig. **??**). Hence we have stars living in higher dimensions, and the results would still hold.

It is also easy to recover the response of the tagged particle to an external constant force. Using Eq. (3.58) in Eq. (3.53) and putting it in Eq. (3.54), we see that b in Eq. (3.55) is replaced by b/n. Hence we have

$$\langle x(t)\rangle_n \sim \frac{bL(t)}{n} f, \tag{3.60}$$

which once again verifies fluctuation-dissipation relation. See that all these results for stars should hold good for generic interactions in both overdamped and Hamiltonian cases.

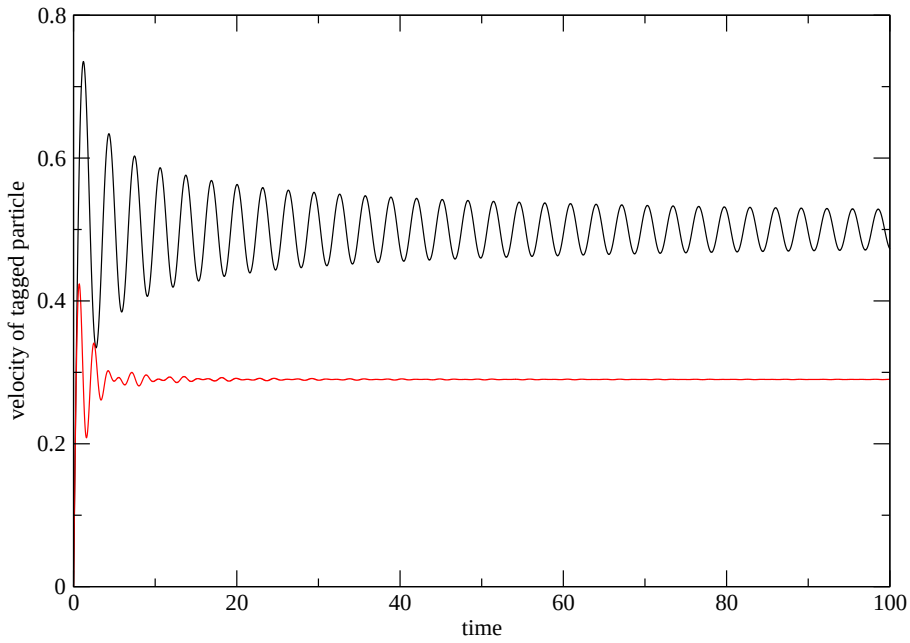

Figure 3.33: Velocity of a tagged particle in a Hamiltonian harmonic(black) and a quartic(red) chain as a function of time, in response to a constant applied force of unit magnitude.

3.14 Percus law beyond the 1D chain topology: what exponent do you want? (but not any!)

A question naturally arises. What if the individual particles in a chain themselves were middle particles of of other chains?(see Fig. 3.43) Would the Percus law still hold? If it does, we could do this over and over again(see Fig. 3.51), halving the exponent at each step, ad infinitum!

Given that the tagged particles in Hamiltonian chains behave like damped diffusive particles with no long-time memory, we expect a chain consisting of tagged particles of individual Hamiltonian chains to behave like an overdamped chain at long times. This implies that a tagged particle sitting in the middle of the main chain will be subdiffusive with MSD $\sim t^{1/2}$. To verify this, We simulate harmonic (Fig. 3.49) and quartic (Fig. 3.50) Hamiltonian chain of chains, or a comb. In both harmonic and quartic chains, a tagged particle sitting on the main chain (or backbone)

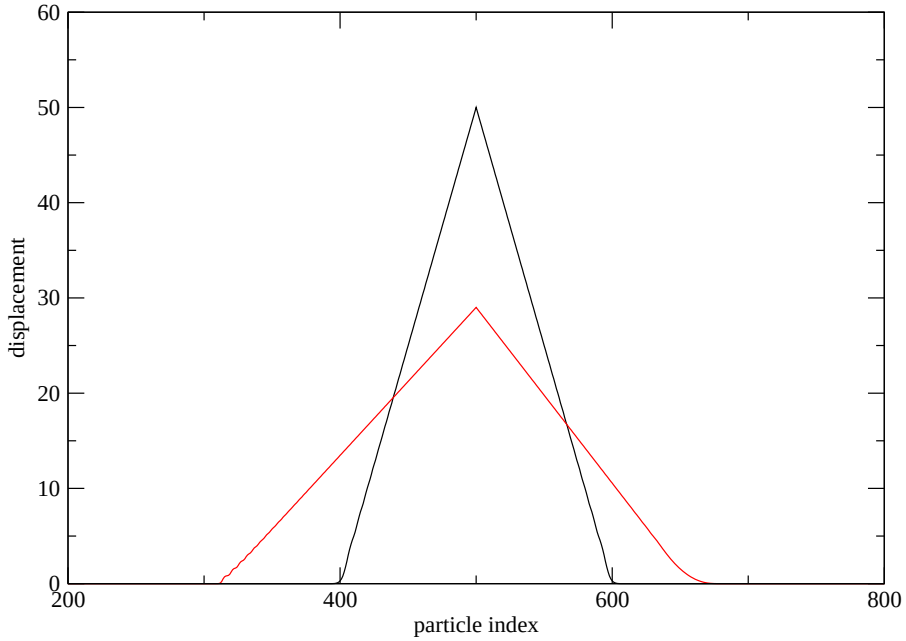

FIGURE 3.34: Displacement profiles of particles in a Hamiltonian harmonic(black) and a quartic(red) chain in response to a constant force of unit magnitude applied to the middle particle. Notice the asymmetry of the quartic profile about the origin.

is found to have MSD $\sim t^{1/2}$, as expected. So we have managed to produce an one dimensional Hamiltonian chain (of course having other chains attached to it, but they also lie in the same one dimensional space) which is subdiffusive. Also, this extends the validity of Percus law to such Hamiltonian chains.

Now, we move on to overdamped chains. We encounter a roadblock in our reasoning here. See that the members of the main chain- the tagged particles on the individual memebr overdamped chains themselves have long time memory. So we do not know what to expect from simulations. From preliminary simulations with systems of chain size $N = 39$, we find that the harmonic overdamped comb produces a tagged particle MSD $\sim t^{.28}$ (Fig. 3.46), and hence, doesn't obey the Percus relation. Then we simulate the quartic overdamped comb (Fig. 3.48), and find that this indeed does obey Percus law, producing an MSD $\sim t^{1/4}$. This forces us to check the response

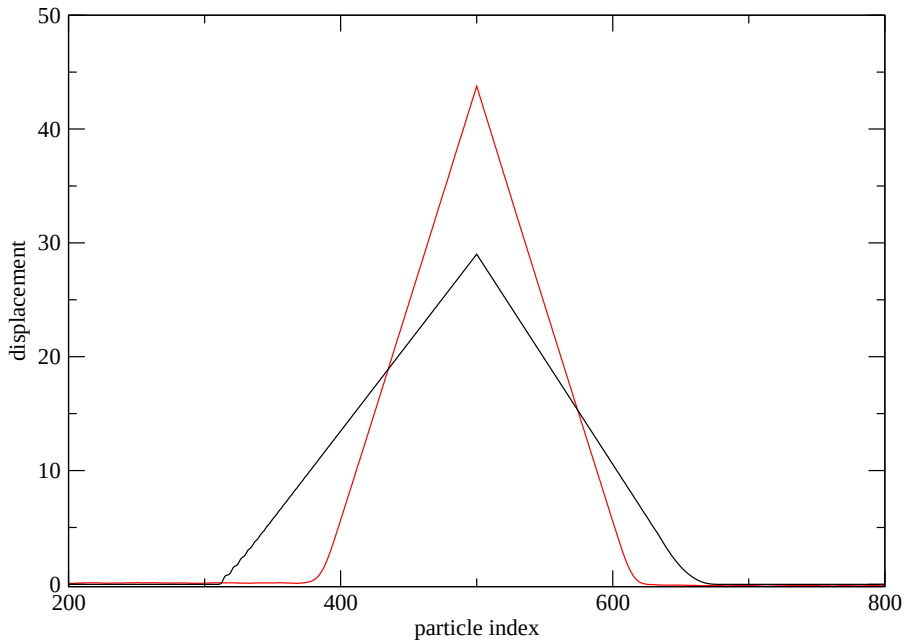

Figure 3.35: Displacement profiles of particles in a Hamiltonian quartic chain in response to a constant force of unit magnitude applied to the middle particle, with(red) and without(black) initial noise in velocities of all the particles. Notice that the asymmetry of the profile about the origin disappears when averaged over initial velocities.

of the tagged particle in a zero temperature harmonic comb to a constant force (since this is a very cheap simulation in terms of run-time), and find that the resulting displacement goes over to $\sim t^{1/4}$ after $t \sim 50$. So now we check the MSD with larger system sizes, and verify that MSD indeed crosses over to $\sim t^{1/4}$ (Fig. 3.47). This shows that these overdamped combs do obey Percus law.

Realizing that the tagged particles in stars behave like the ones in chains, we simulate an overdamped harmonic chain of 4-stars , or a "bottle brush" (Fig. 3.45). We once again see that the tagged particle MSD $\sim t^{.28}$ for intermediate times (Fig. 3.46), same as the harmonic comb. And then we do see it to go over to the Percus law behavior as one goes to larger times(Fig. 3.47). See that Fig. 3.45 is of a 2D bottle brush, but our simulations are for a 1D case.

These results naturally make one think what would happen if we went beyond combs, like the

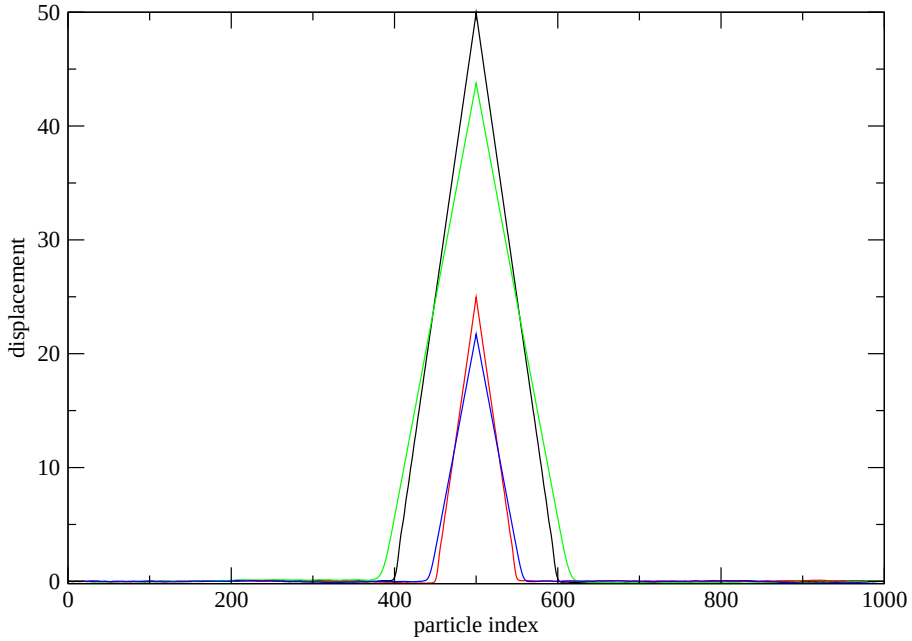

FIGURE 3.36: Displacement profiles of particles averaged over initial velocities in Hamiltonian harmonic and quartic chains in response to a constant force of unit magnitude applied to the middle particle, $t = 50$(red,blue resp.) and $t = 100$(black,green resp.). FWHMs are proportional to time.

antenna pictured in Fig. 3.51. If Percus law holds at all levels, we would have

$$\langle x^2(t)\rangle_n \sim \langle x^2(t)\rangle_1^{1/2^{n-1}}, \tag{3.61}$$

where $\langle x^2(t)\rangle_n$ is the MSD of the tagged particle in the structure of nth order. This would be applicable to both Hamiltonian and Overdamped systems which are hierarchical structures made up of chains or chains of stars.

We expect the relation to hold for these objects embedded in 2 or 3 dimensions as well, as the behavior of tagged particles on single chains embedded in 2 or 3 dimensions is similar to that of those in 1 dimension. At this point we see that in polymer literature, for overdamped harmonic regualr fractals with Langevin dynamics, displacement of the tagged particle in response to an applied constant force has been shown to be [23]

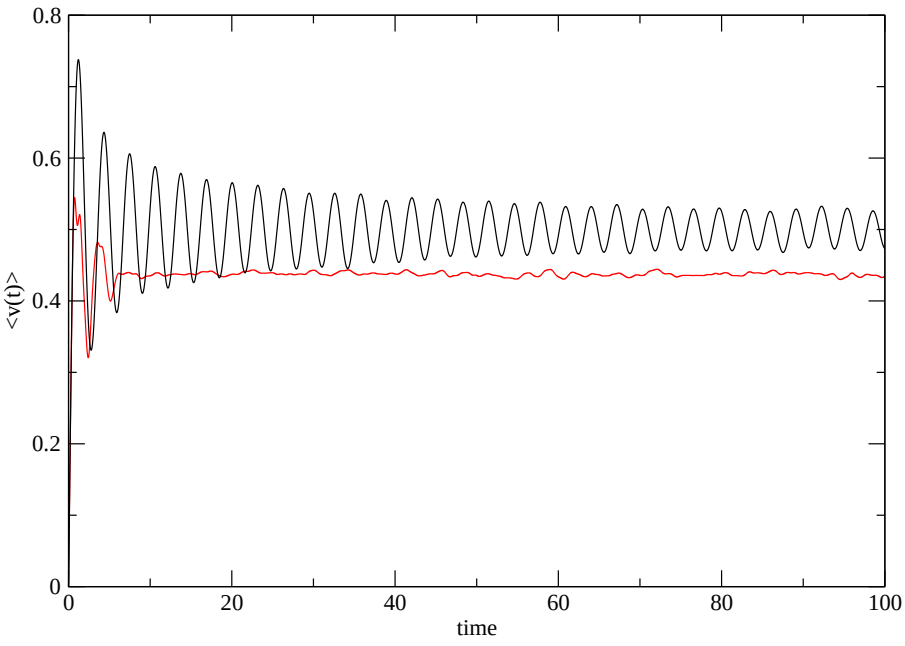

Figure 3.37: Velocity of a tagged particle averaged over initial velocities of particles in a Hamiltonian harmonic(black) and a quartic(red) chain as a function of time, in response to a constant applied force of unit magnitude.

$$\langle x(t) \rangle \sim t^{1-d_s/2}, \tag{3.62}$$

for spectral dimension $d_s < 2$. Spectral dimension of a structure is related to the return probability of a diffusive particle (see [15] for a definition). Given that an nth order"chain" of ours has a spectral dimension $d_s \sim 2(1 - 1/2^n)$ [15], Eq. (3.61) and Eq. (3.62) together imply a fluctuation dissipation relation for these overdamped structures. Also, since Eq. (3.55) is applicable in these cases, Eq. (3.61) and Eq. (3.62) actually imply each other. We note that in [15], a fluctuation dissipation relation has been proved for a particle diffusing on similar hierarchical lattices. Also, the tagged particle MSD follows similar scaling laws there. We suspect that the similarity of these results has to do with similarity of diffusion equation (which is same as continuum version of evolution equation for overdamped harmonic chains) and equation of

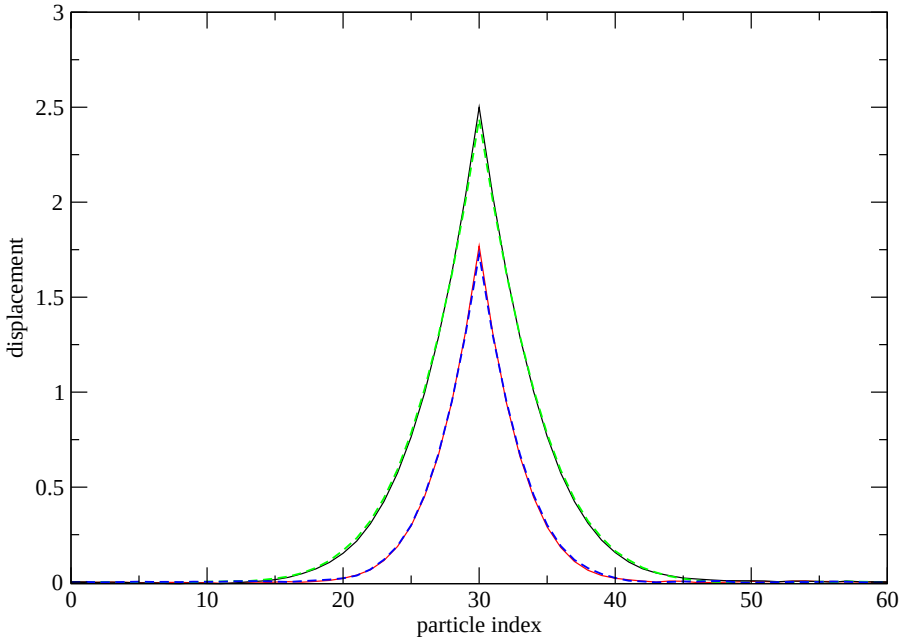

FIGURE 3.38: Displacement profiles of particles averaged over noise in overdamped harmonic and quartic chains in response to a constant force of unit magnitude applied to the middle particle, $t = 10$(red,blue resp.) and $t = 20$(black,green resp.). FWHMs are proportional to $\sqrt{t}$. Also, see that the nonzero temperature has made the responses of the two chains identical.

motion of mechanical vibrations identified in [25]. Looking at the way probability density spreads on a lattice, we see that the governing master equation is same as the evolution equation for displacement of a bead in an overdamped harmonic chain. This would be true even for branched structures. Hence, spread of a pulse in the overdamped structures would be same as spread of the probability density of a single particle. In [15], a particle diffusing on a lattice nth order has an MSD $\sim t^{1/2^{(n-1)}}$. Hence, this should also be the squared width of the pulse spreading on the backbone of the nth order overdamped chain. We can conclude that this suggests a tagged particle MSD of $t^{1/2^n}$ on the chain backbone, as we did in case of the linear overdamped chain. This is in agreement with Eq. (3.61).

Looking at these results, we suspect that a chain of tagged particles belonging to square lattices would show an MSD and force response going as $\sqrt{\ln t}$. Looking at the behavior of

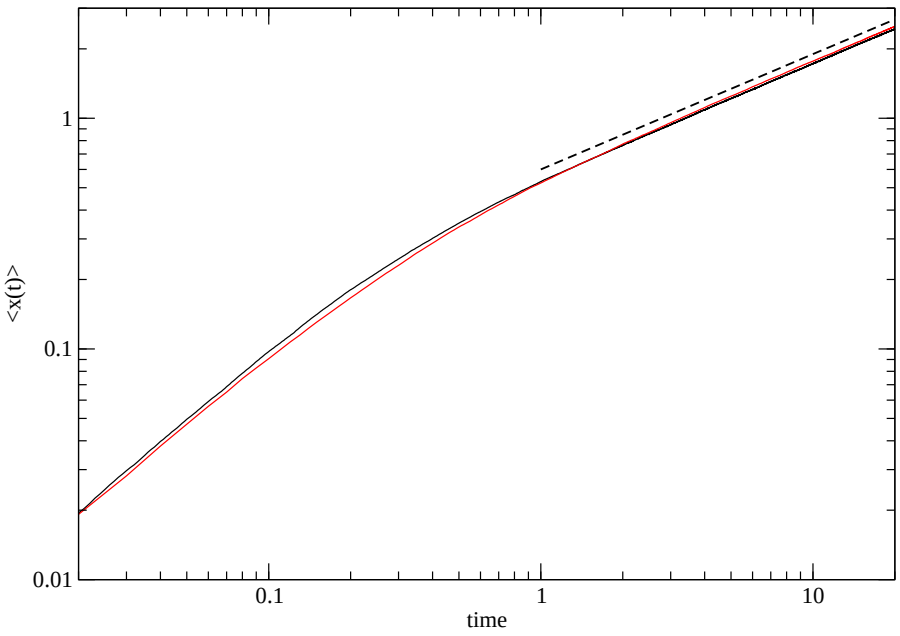

Figure 3.39: Displacement of a tagged particle averaged over noise in an overdamped harmonic(black) and a quartic(red) chain as a function of time, in response to a constant applied force of unit magnitude. A dashed line is drawn $\sim t^{1/2}$ for comparison.

a single particle diffusing on a set of 2D sheets connected in the middle by a backbone, it has been found that its MSD goes as $\ln t$ [15]. Hence it is natural to suppose as before that the corresponding overdamped chain system would show this behavior. Once again, an nth order structure composed of chains of these sheets is expected to show $(\ln t)^{1/2^n}$ tagged particle response and MSD. One could also come up with a square lattice of tagged particles belonging to different square lattices. Then a tagged particle on this superlattice is expected to show a $\ln(\ln t)$ behavior. And an nth order super lattice would give rise to n nested logarithms.

All this behavior is expected to show up for both Hamiltonian and overdamped chains, in both harmonic and anharmonic cases. One should remember that these simulations though would be quite costly.

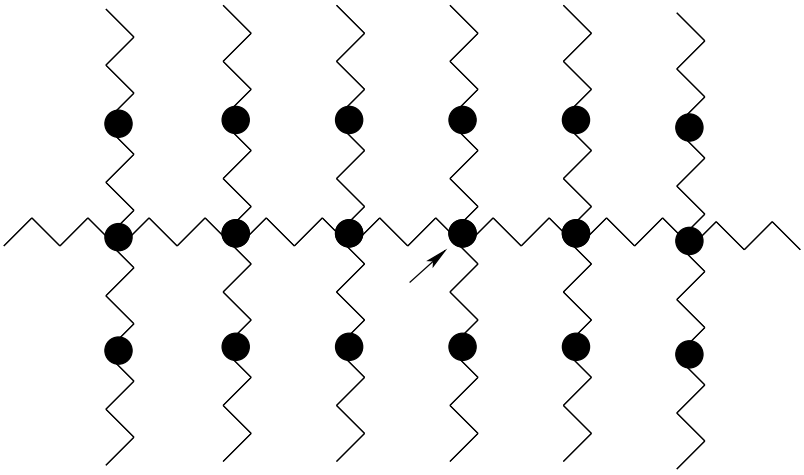

FIGURE 3.43: A comb. Tagged particle lies on the backbone, indicated here with an arrow. The comb lives in one dimension, and actual sidechains(teeth of the comb) lie along the backbone, but here have been drawn perpendicular to it for depiction.

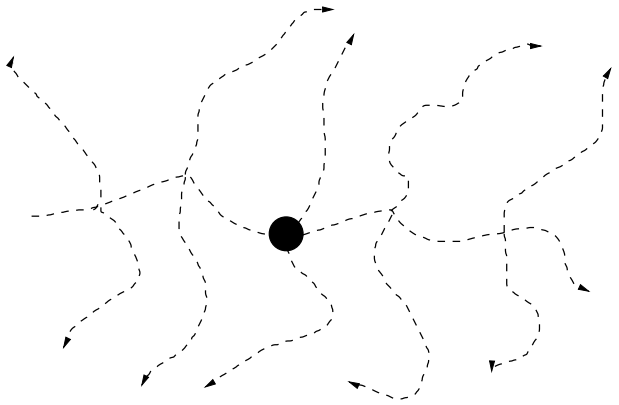

FIGURE 3.44: A comb, but now in 2d. Dashed lines have been drawn to indicate chains.

3.15 Summary

We have investigated the tagged particle behavior in a wide range of systems with fixed interaction topology. It is seen that harmonic approximation is able to reproduce all the results seen in simulations, for nonlinear and linear systems, for both overdamped and Hamiltonian cases. We conclude that local equilibrium, quadratic expansion of free energy, and existence of equilibrating modes together give rise to all these observed tagged particle correlations, including response to a constant external force.

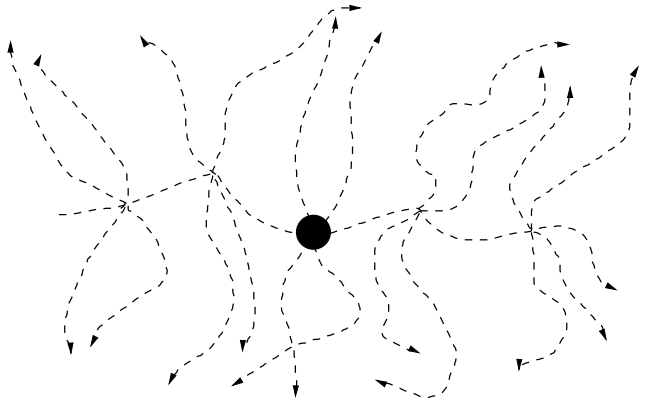

FIGURE 3.45: A bottle-brush or chain of 4-stars in 2d. Dashed lines have been drawn to indicate chains.

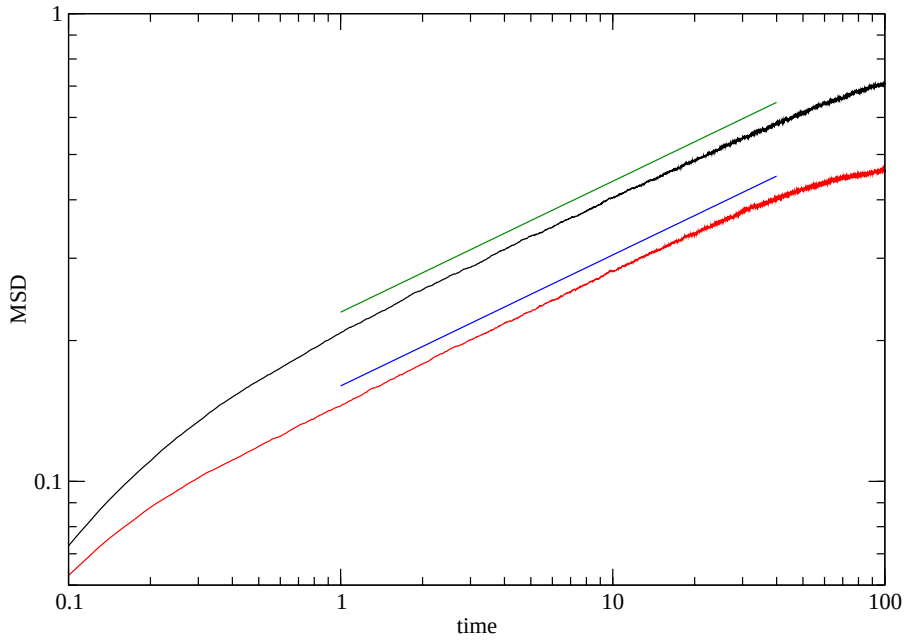

FIGURE 3.46: MSD of a tagged particle in an overdamped harmonic comb(black) and a chain of 4-stars(red) in 1D, and of chain size $N = 39$. Straight lines of $t^{.28}$ fit the curves well.

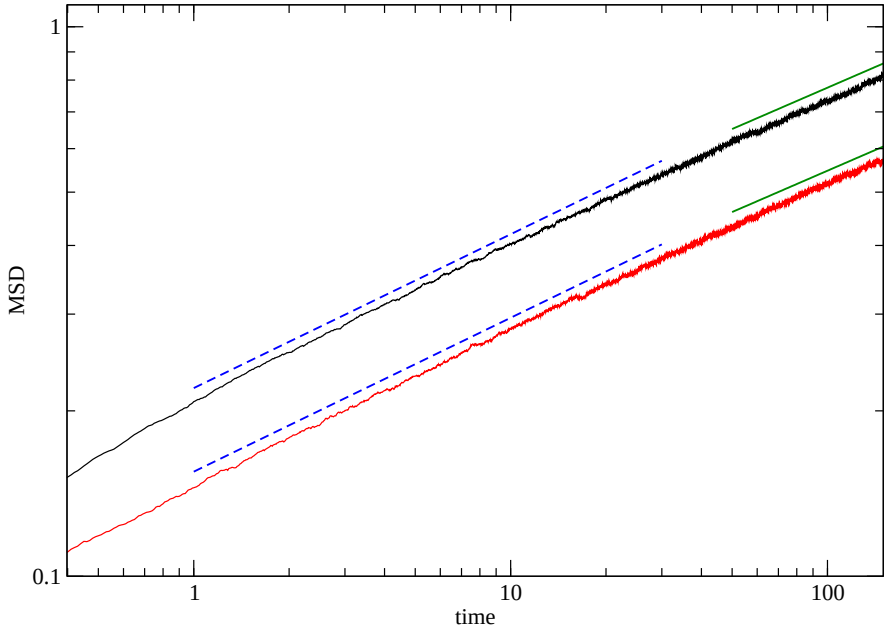

FIGURE 3.47: MSD of a tagged particle in an overdamped harmonic comb(black) and chain of 4-stars(red) of chain size $N = 69$ in 1D. Dashed lines of $t^{.28}$(blue) and solid lines of $t^{.25}$(green) fit the curves at intermediate and long times resp.

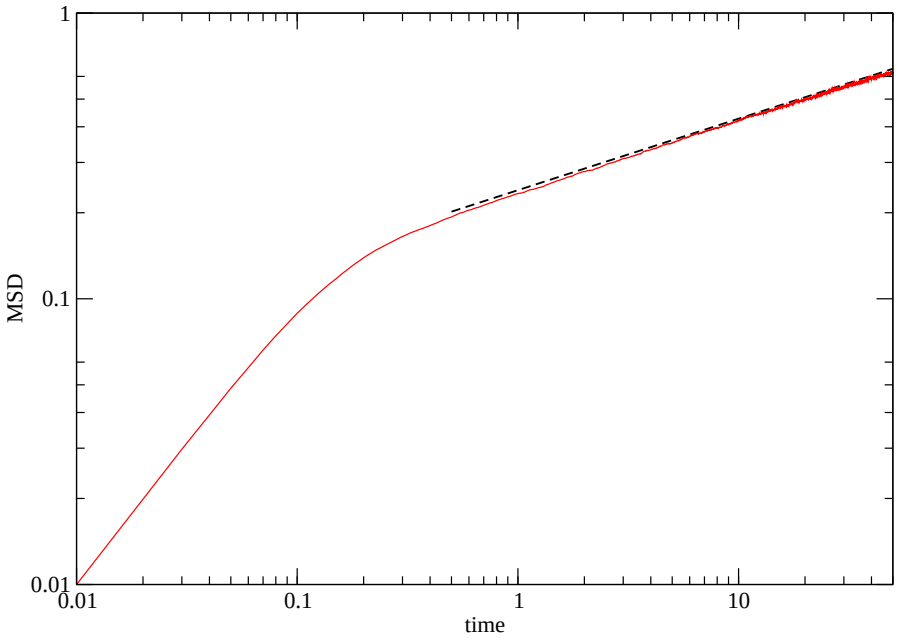

FIGURE 3.48: MSD of a tagged particle in an overdamped quartic comb of chain size $N = 39$ in 1D (red). Dashed straight line of $t^{.25}$ fits the curve well.

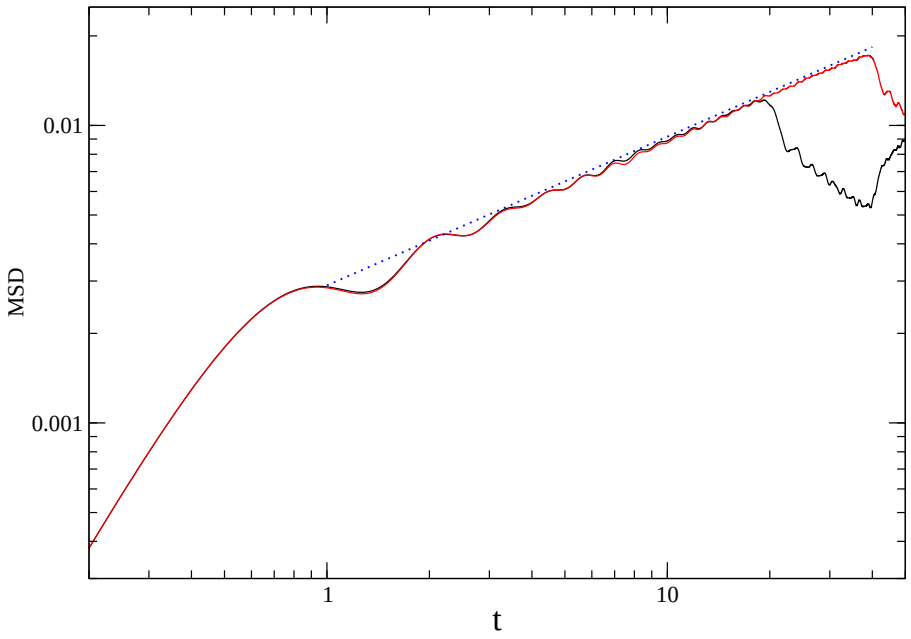

FIGURE 3.49: MSD of a tagged particle in Hamiltonian harmonic combs of chain size $N = 39$(black) and $N = 79$(red) in 1D. A dotted straight line of $t^{1/2}$ fits the curve well.

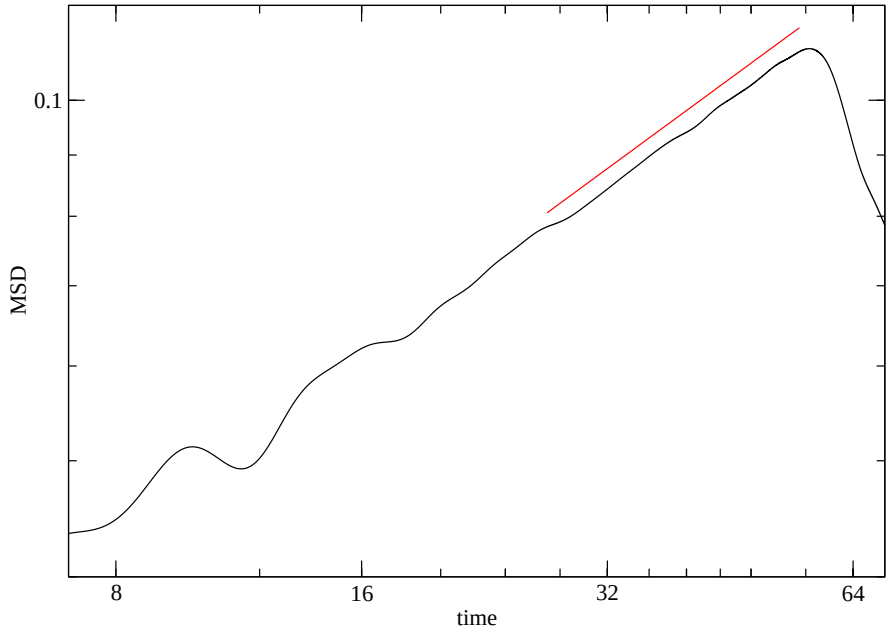

FIGURE 3.50: MSD of a tagged particle in Hamiltonian quartic comb of chain size $N = 39$(red) in 1D. A straight line of $t^{1/2}$ is drawn for comparison.

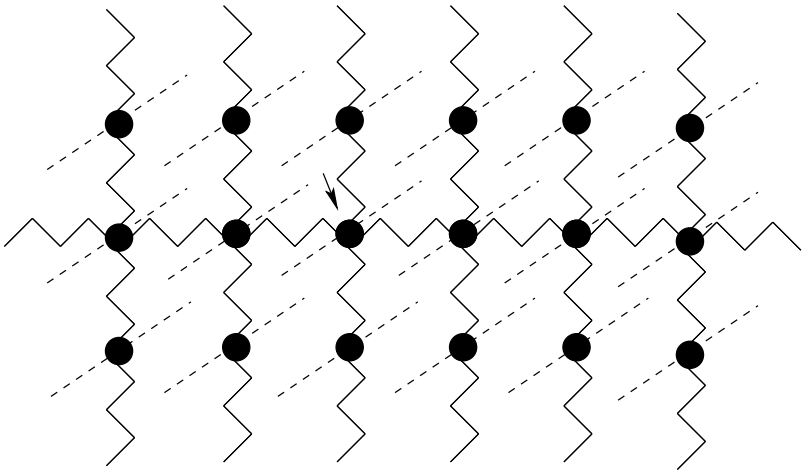

FIGURE 3.51: An "antenna" (we adopt this name from [15], where the chains are replaced by lattices). Dashed lines have been drawn to indicate further chains attached at the particles of the comb. Tagged particle lies on the backbone, indicated here with an arrow.

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