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In continuum mechanics, the conservation laws for mass, momentum and energy coupled with the constitutive relations of the stress and heat flux could be a powerful solution method for continuum systems. However, it is required that the equations form a closed system, i.e. that the stress and heat flux are formulated as functions of the conserved variables.

This thesis studies the constitutive relations of the stress and heat flux in the Fermi-Pasta-Ulam-Tsingou model with Langevin dynamics, by the means of molecular dynamics simulations. In essence, the model consists of a many particle system in the presence of a heat bath, where each particle is chained to its two neighbors by a nonlinear quadratic spring force.

A numerical method is implemented to propagate the particle dynamics. Following Hardy [7], formulas relating the macroscopic entities to the particle dynamics are employed in order to study the behavior of the stress and heat flux in relation to the mass, momentum and energy. In fact, the numerical result show that the stress appears as a linear function of the energy.

En värdefull lösningsmetod för kontinuumsystem är att lösa det system av partiella differentialekvationer som utgörs av konserveringslagarna för massa, rörelsemängd och energi tillsammans med två konstitutiva relationer för spänning och värmeflöde. För detta krävs det att ekvationerna bildar ett slutet system, dvs. att spänningen och värmeflödet är funktioner av de konserverade storheterna.

Detta examensarbete studerar de konstitutiva relationerna för spänningen och värmeflödet i Fermi-Pasta-Ulam-Tsingou modellen med Langevindynamik, som bestäms genom simulering av molekyldynamiken. Modellen består väsentligen av många partiklar som är kopplade till ett värmebad, där varje partikel är länkad till sina två grannar genom en ickelinjär fjäderkraft.

En numerisk metod implementeras för att propagera partikeldynamiken. Baserat på Hardys arbete [7] bestäms först spänningen och värmeflödet, sedan studeras deras beroende av konserveringsvariablerna. De numeriska resultaten visar att spänningen är en linjär funktion av energin.

1   Introduction

Conservation of mass, momentum and energy are fundamental to continuum mechanics. The conservation laws states that the rate of change of a quantity in a specific volume is equal to the flow through the encapsulating surface. The conservation of mass, momentum and energy, together with two constitutive relations for stress and heat flux, form a system of differential equations. The constitutive relations are required for the system to be solvable, and they can be approximately determined from measurements or from molecular dynamics simulations. For the second option a way to express the macroscopic variables in terms of the molecular dynamics is required. In 1950 Irving and Kirkwood [4] derived and formulated expressions for the mass, momentum, energy, stress and heat flux in terms of the molecular dynamics. These formulas are widely used in studies of continuum phenomena and have later been improved, for example in 1982 by Hardy in his study of shock waves [7].

Although the expressions for density, momentum, energy, stress and heat flux in terms of the molecular dynamics are known, it has not to our knowledge been studied if these expressions form a closed system; i.e. whether it is possible to express the stress and heat flux as some functions of the density, momentum, energy and their derivatives. Seeking such constitutive relations will be the focus of this thesis for a specific model, namely the Fermi-Pasta-Ulam-Tsingou (FPUT) model with Langevin dynamics (LD). We are interested in whether it is at all possible to formulate a closed system when the macroscopic variables are derived from particle dynamics. FPUT with LD is simple enough that it is possible to understand the behaviour of the system on a particle to particle level, while at the same time being sophisticated enough for the endeavour to become non-trivial.

The FPUT model was first introduced in 1953. The model consists of identical particles chained together by non-linear spring forces. The aim of the original study [3] was to investigate statistical properties of the chain, in particular how fast a many particle system reaches thermal equilibrium. It has since then been thoroughly studied, recently in the field of metastability [1] and thermalization [6].

In this thesis, we use the FPUT model as the microscopic description of the system, which keeps track of the position and momentum of every particle. Then, the Irving-Kirkwood expressions are used to acquire the macroscopic description from the microscopic description of the system. With the macroscopic description of the system, we are interested in whether it is possible to express the stress and heat flux as functions of the conserved variables and thus forming a closed system. If one finds that the system is closed, then the system of equations formed by the conservation laws and constitutive relations is ready to be used as a solution method for the continuum model. The focus of this thesis is to determine the constitutive relations of the stress and heat flux for the FPUT model with LD.

In section 2 the reader is introduced to the model and some material needed to understand it. The inter-particle forces are discussed, as well as the addition of LD on top of the FPUT model. Furthermore, the conservation laws of mass, momentum and energy are presented and derived. In the process we acquire the formulas for the density, momentum, energy, stress and heat flux in terms of the molecular dynamics.

Section 3 discusses the numerical method for propagating the particle dynamics, from which we then acquire the macroscopic variables. Moreover, it discusses the validation of the numerical method.

The results are presented in section 4. The main – and surprising – result is that the stress is a linear function of the energy for the FPUT model with LD. No such relation was found for the heat flux, however, the existence of such a relation is far from excluded.

Section 5 present some thoughts on the results and future work.

2 Theory

The theory is divided in two main parts. In the first the molecular dynamics model is described (section 2.1-2.3) and in the second part the macroscopic conservation laws are formulated and derived in terms of the molecular dynamics (section 2.4).

2.1 The model

The Fermi-Pasta-Ulam-Tsingou (FPUT) model with Langevin dynamics (LD) is chosen for this study mainly for its simplicity yet interesting properties. The FPUT model is one-dimensional, imagine identical particles distributed on a line, where each particle is connected to its two neighbors by a spring force. Consider two adjacent particles: if they move too far away from each other, they are pulled back towards their center. If they are too close together, then they push away from each other. This is illustrated in figure 1, showing the force on particle j exerted by its neighbours i and k. Of course, all particles exert forces on their neighbors simultaneously. The LD is an extension to the system, where many small particles are in contact with the established system, forming a heat bath. The FPUT model consists of N identical particles with periodic boundary conditions. Described as a system of equations, the full model looks like this:

$$dq(t) = m^{-1}p(t)dt$$
$$dp(t) = F(q)dt - \gamma p(t)dt + \sqrt{(2\gamma k_B T m)}dW(t) \tag{1}$$

where $q : [0, \infty) \to \mathbb{R}^N$ is the position and $p : [0, \infty) \to \mathbb{R}^N$ the momentum of the particles, m the mass and $F : \mathbb{R}^N \to \mathbb{R}^N$ the force by which the particles interact. The time dependence of the position q and momentum p is left implicit in what follows. The force is explained in detail in section 2.2. The two terms containing γ originates from the LD and are investigated in section 2.3.

2.2 The force

In this section we take a closer look on the interaction between the particles. In fact, as we change the complexity of the model, it will be the expression for the force that will be altered. We begin with the simplest case, the harmonic oscillator, and then move on to the anharmonic spring force consisting of the FPUT model. Section 2.3 will consider the LD and does not describe how the particles of the system interact with each other – which is the concern of this section – but how the system interacts with many much lighter particles to model a heat bath.
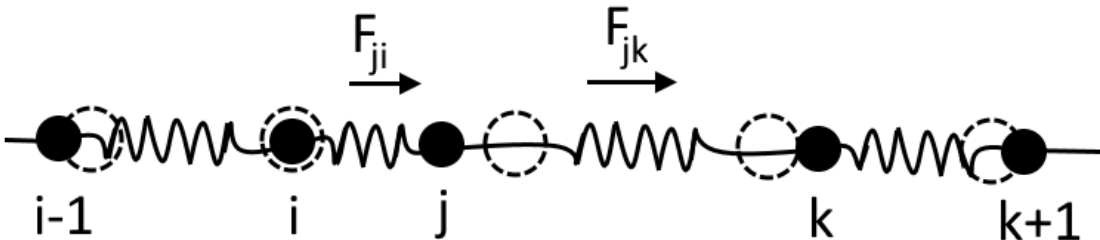

Figure 1: Schematic figure of the model. The dashed circles indicate the closest particle's equilibrium position. By F_{ji} we mean the force exerted on particle j by particle i.

2.2.1 Harmonic oscillator

The harmonic oscillator is a classical model much used in both classical and quantum mechanics. Consider a particle, when displaced by Δx from its equilibrium position it experiences a restoring force

$$F = -k\Delta x \tag{2}$$

where k is a positive constant. This is analogous to a mass on a spring. We will consider a one dimensional multiple particle system illustrated in figure 1, where each particle is connected to its two neighbors by a spring force. The spring force is in the harmonic oscillator case described by equation (2).

2.2.2 Fermi Pasta Ulam Tsingou model

We quickly move on from the harmonic oscillator and consider the potential ϕ expressed as a power series of the deformation Δx:

$$\phi(\Delta x) = -\frac{k}{2}\Delta x^2 + \frac{\alpha}{3}\Delta x^3 + \frac{\beta}{4}\Delta x^4 + \ldots \tag{3}$$

The FPUT model consists of N identical particles in one dimension, where each particle is connected to its neighbors by a non-linear spring force. The α-FPUT chain, which is studied here, is a special case where $\alpha \neq 0$ and $\beta = 0$; moreover, the higher order terms denoted by "..." are also set to zero. Consider particle j, theforce has the following form:

$$F(q_j) = (q_{j+1} + q_{j-1} - 2q_j)[k + \alpha(q_{j+1} - q_{j-1})]. \tag{4}$$

In figure 1, the force on particle j – denoted by $F(q_j)$ – would correspond to $F_{ji} + F_{jk}$, where we by F_{ji} mean the force on particle j exerted by particle i.

2.3 Langevin dynamics

A molecular system in the real world is unlikely to be present in vacuum. Jostling of solvent or air molecules causes friction, and the occasional high velocity collision will perturb the system. This could be modeled with many much lighter particles surrounding the system of larger particles. Let the system particles be denoted by $q = (q_1, \ldots, q_N)$ and $p = (p_1, \ldots, p_N)$ with mass $m = (m_1, \ldots, m_N)$, the heat bath is a collection of harmonic oscillators and denoted by $\hat{q} = (\hat{q}_1, \ldots, \hat{q}_K)$ and $\hat{p} = (\hat{p}_1, \ldots, \hat{p}_K)$ with mass $\hat{m} = (\hat{m}_1, \ldots, \hat{m}_K)$. Each system particle is given its own set of heat bath particles, hence we should write $k = k(n)$, however, this dependence is dropped for ease of notation. $U(q)$ is an arbitrary potential, in the derivation of the conservation laws in section 2.4.1 it will be restricted to a pair potential. The Hamiltonian of this coupled system is then:

$$H(q, p, \hat{q}, \hat{p}) = \frac{p^2}{2m} + U(q) + \frac{\hat{p}^2}{2\hat{m}} + \frac{1}{2}\sum_n \sum_k \omega_k^2 \left(\hat{q}_k - \frac{c_k q_n}{\omega_k^2} \right)^2. \tag{5}$$

However, such a description quickly becomes cumbersome and computationally expensive. Zwanzig [8] showed that a special heat bath coupled to an arbitrary nonlinear system can be approximately described by (1), where the dynamics of the heat bath is reduced to a stochastic differential equation and only one free parameter as opposed to $2K$.

To understand more about the Langevin equations which Zwanzig obtains from his choice of heat bath, we first need to introduce some concepts. The Weiner process will be briefly presented followed by the Ornstein-Uhlenbeck stochastic differential equation. The Ornstein-Uhlenbeck equation is

then interpreted and it is in fact present in the second row of equation (1). For a comprehensive introduction to stochastic differential equations we recommend a book on the subject, for example [2] or chapter 6 of [5].

The Weiner process $W(t)$ is a stochastic process which has the following properties:
Definition 1.

1. $W(0) = 0$

2. the sample path $t \mapsto W(t)$ is almost surely continuous

3. $W(t_2) - W(t_1) \in N(0, t_2 - t_1)$ for $t_2 > t_1$

4. for any partition $0 < t_1 < \cdots < t_n$, all increments $W_{t_1}, W_{t_2} - W_{t_1}, \ldots, W_{t_k} - W_{t_{k-1}}$ are independent.

In the following we will find the need of integrating stochastic processes. Just as for deterministic variables, an integral can be constructed as the limit of the Riemann sum:

$$\int_0^\tau g(t)dW(t) = \sum_{k=0}^{\nu-1} g(t_k)[W((k+1)\delta t) - W(k\delta t)], \quad \lim \nu \to \infty. \tag{6}$$

Unlike deterministic functions, this limit yields different answers depending on where t_k is chosen in the δt interval. The choice of $t_k = k\delta t$ (left endpoint) is referred to as Itô integration and the choice $t_k = (k + \frac{1}{2})\delta t$ as Stratonovich integration. We will be using Itô integration. We refrain from delving deeper into the theory of stochastic integration and finish this section with a useful property of Itô integrals:

Proposition 1. *Let g be a smooth deterministic function and $W(t)$ a Weiner process, the stochastic integral $Y(t) = \int_0^t g(s)dW(s)$ is normally distributed with mean zero and variance $\int_0^t g^2(s)ds$.*

The Ornstein-Uhlenbeck stochastic differential equation is defined as:
Definition 2.

$$dX = -\gamma X dt + \theta dW, \tag{7}$$

where $\gamma > 0$ and θ are constants. The exact distributional solution of the Ornstein-Uhlenbeck stochastic differential equation will be presented along with an interpretation, from which the LD formulation will appear.

In the derivation we follow the steps of [5], chapter 6.3.2. Multiply both sides of equation (7) by the integrating factor $e^{\gamma t}$ and observe that :

$$d\left(e^{\gamma t}X\right) = e^{\gamma t}(dX + \gamma X dt),$$

thus (7) becomes

$$d\left(e^{\gamma t}X\right) = \theta e^{\gamma t}dW.$$

We then integrate both sides and obtain

$$e^{\gamma t}X(t) = X(0) + \int_0^t \theta e^{\gamma s}dW(s).$$

Multiplying by $e^{-\gamma t}$ gives

$$X(t) = e^{-\gamma t}X(0) + e^{-\gamma t}\int_0^t \theta e^{\gamma s}dW(s).$$

Using proposition 1 we know that $Y(t) = \int_0^t e^{\gamma s}dW(s)$ is a normally distributed random variable with mean zero and variance

$$Var(Y(t)) = \int_0^t e^{2\gamma s}ds = \frac{e^{2\gamma t} - 1}{2\gamma}, \tag{8}$$

the solution is therefore:

$$X(t) = e^{-\gamma t} X(0) + \theta \sqrt{\frac{1 - e^{-2\gamma t}}{2\gamma}} \hat{Y}(t), \quad \hat{Y}(t) \sim \mathcal{N}(0, 1). \tag{9}$$

This is the exact solution of the Ornstein-Uhlenbeck stochastic differential equation and its existence is exploited in the numerical method, see section 3.1. For large t the exponential $e^{-\gamma t}$ tends to zero, and if we let $\theta = \sqrt{2\gamma k_B T m}$ then

$$X(t) \approx \sqrt{k_B T m} \hat{Y}(t),$$

which means that in the long term, $X(t)$ samples from a normal distribution. In fact we can think of X as the momentum, in which case the Ornstein-Uhlenbeck equation samples the Gibbs-Boltzmann distribution associated with a particle in a thermal heat bath at temperature T. This is exploited in Langevin's model, where the differential equation for momentum is refined with the Ornstein-Uhlenbeck equation. Compare equation (7), where $X = p$ and $\theta = \sqrt{2\gamma k_B T m}$, with the second row of the full model (1).

2.4 Conservation laws

In continuum mechanics the mass, momentum and energy must be conserved, commonly referred to as conservation laws. Thus, if we can formulate the conservation laws in terms of our molecular dynamics, we can verify if the system behaves as a continuum or not. Since we are dealing with a one dimensional model, where $q_i \in \mathbb{R}$ and $p_i \in \mathbb{R}$, the one dimensional conservation laws suffice; but the reader should be assured that the three dimensional analogy still holds true. We now present the conservation laws of mass, momentum and energy:

$$\partial_t \rho + \nabla_y[\rho u] = 0,$$
$$\partial_t[\rho u] + \nabla_y[\rho u^2 - \sigma] = 0, \tag{10}$$
$$\partial_t[E + \frac{1}{2}\rho u^2] + \nabla_y[Eu + \frac{1}{2}\rho u^3 - \sigma u + Q] = 0,$$

where $\rho = \rho(y, t)$ is the mass density, $\rho u = \rho u(y, t)$ the momentum, $E = E(y, t)$ the energy, $\sigma = \sigma(y, t)$ and $Q = Q(y, t)$ the stress and heat flux respectively. The dependence on position y and time t is left implicit for ease of notation.

In the process of formulating the conservation laws in terms on the molecular dynamics, we will also formulate the macroscopic variables in terms of the molecular dynamics. These are collected in section 2.4.2 and enable the study of the macroscopic behaviour of the system – whether or not a closed system can be found.

Note that the conservation laws are exact for the FPUT-model, i.e. when $\gamma = 0$. However, with the LD ($\gamma > 0$) the system is coupled to a heat bath from which energy can be transferred. Since only the system particles, and not both system and heat bath, are considered in our derivations of the conservation laws, we cannot require conservation when considering the coupling to the heat bath, i.e. when $\gamma > 0$. It would be possible to take the Hamiltonian of Zwanzig (5) and formulate a general pair potential including both system and heat bath particles, which is then put into the derivations below. However, that is not studied here, we are content with expressions of the system particles only, which are exact for $\gamma = 0$.

2.4.1 Derivations of the conservation laws

In this section we will derive the above conservation laws (10) from classical particle dynamics. Conservation laws are a special case of continuity equations, which in their general differential form

look like this:

$$\partial_t \varphi + \nabla \cdot j = s, \tag{11}$$

where φ is the density of the quantity, j the flux and s the source or sink term. If $s = 0$ then the quantity is said to be conserved and the differential equation is called a conservation law. In words, the conservation laws states that the change of a quantity in a specific volume is equal to the flow out through the encapsuling area. We will seek to express our equations in this form, where φ is replaced by the mass density, the momentum density or the energy density. However, we first need a way of expressing the macroscopic density, momentum and energy as functions of the particle dynamics.

For a deterministic Hamiltonian system, i.e. equation (1) with $\gamma = 0$, the time dependence of the position and momentum of each individual particle (q_i, $p_i = m_i \dot{q}_i$) are determined by the initial conditions and Newton's second law:

$$m_i \ddot{q}_i = \sum_j F_{ij}, \tag{12}$$

where m_i is the mass of particle i – in this derivation we will allow this weaker restriction, however, remember that the model requires identical particles. Furthermore, F_{ij} is the force on particle i from particle j and $\ddot{q}_i$ the acceleration of particle i. The dot notation is used to indicate the time derivative. In this derivation, it is assumed that the force is derivable from a general pair potential ϕ_{ij}:

$$F_{ij} = -\nabla_i \phi_{ij}(|q_i - q_j|) = -\phi'_{ij}(|q_i - q_j|) \frac{q_i - q_j}{|q_i - q_j|}. \tag{13}$$

In what follows, the argument of ϕ_{ij} is left implicit. Since particles do not exert forces on themselves, it is assumed that $\phi_{ii} = 0$, hence $F_{ii} = 0$. In general, ϕ_{ij} is different for different pairs of subscripts, but independent of the order of the subscripts. It is also clear that equation (13) satisfies Newton's third law:

$$F_{ij} = -F_{ji}. \tag{14}$$

To define the macroscopic variables density, momentum and energy and their dependence on the space coordinate y, we construct a locality function $\eta(y)$ which satisfies the conditions for a positive symmetric mollifier. There is freedom in the choice of this mollifier $\eta(y)$, Hardy [7] states in his conclusion that the conservation laws are independent of the mollifier and suggests that the most convenient localization function should be chosen. Thus, we choose the Gaussian:

$$\eta(y - q_i) = (\sqrt{2\pi}\varepsilon)^{-1} \exp\left\{-\frac{(y - q_i)^2}{2\varepsilon^2}\right\}, \tag{15}$$

where $(\sqrt{2\pi}\varepsilon)^{-1}$ is the normalizing constant and ε a tweaking parameter which decides the width of the Gaussian. If ε tends to zero we approach the Dirac delta function.

We are now ready to define the macroscopic density, momentum and energy as functions of the particle dynamics:

$$\rho(y, t) = \sum_i m_i \eta(y - q_i), \tag{16}$$

$$\rho u(y, t) = \sum_i m_i \dot{q}_i \eta(y - q_i), \tag{17}$$

$$E^0(y, t) = \sum_i \left[\frac{1}{2} m_i |\dot{q}_i|^2 + \frac{1}{2} \sum_j \phi_{ij}\right] \eta(y - q_i). \tag{18}$$

Superscript zeros, as on E^0, indicate properties with the local velocity $u = 0$. The local velocity is defined by equation (17).

The conservation of mass falls out by differentiating the density (16):

$$\partial_t \rho = \partial_t \sum_i m_i \eta(y - q_i)$$

$$= -\sum_i m_i \dot{q}_i \nabla_y \eta(y - q_i)$$

$$= -\nabla_y \sum_i m_i \dot{q}_i \eta(y - q_i).$$

we obtain the conservation law of mass by the definition of momentum (17) and rearranging of terms:

$$\partial_t \rho + \nabla_y [\rho u] = 0. \tag{19}$$

We follow the work of Hardy [7] when deriving the continuity equations for momentum and energy, and thus our expressions for stress and heat flow. Beginning by differentiating the momentum (17):

$$\partial_t \sum_i m_i \dot{q}_i \eta(y - q_i) = \sum_i m_i \ddot{q}_i \eta(y - q_i) - \sum_i m_i \dot{q}_i^2 \nabla_y \eta(y - q_i)$$

$$= \sum_{ij} F_{ij} \eta(y - q_i) - \nabla_y \sum_i m_i \dot{q}_i^2 \eta(y - q_i), \tag{20}$$

where we have used Newtons second law (12) to rewrite the first term. The second term is already on differential form, however, the coordinate is relative a fixed frame of reference and we would like the expression to be relative a frame of reference moving at velocity u. The velocity of particle i is thus $\dot{q}_i - u$. In general, different frames of reference are needed at different positions y and different times t. The relative velocity can be introduced with the identities:

$$\dot{q}_i = (\dot{q}_i - u) + u \tag{21}$$

$$\dot{q}_i^2 = (\dot{q}_i - u)^2 + 2(\dot{q}_i - u) \cdot u + u^2. \tag{22}$$

One could write $u = u(y, t)$, however, the dependence on position y and time t is left implicit. By substituting (22) into the second term of equation (20) we obtain:

$$-\nabla_y \sum_i m_i \dot{q}_i^2 \eta(y - q_i) = -\nabla_y \sum_i \left[m_i(\dot{q}_i - u)^2 - 2m_i(\dot{q}_i - u)u + m_i u^2 \right] \eta(y - q_i)$$

$$= -\nabla_y \sum_i \left[m_i(\dot{q}_i - u)^2 + 2m_i \dot{q}_i u - 2m_i u^2 + m_i u^2 \right] \eta(y - q_i)$$

$$= -\nabla_y \left(\sum_i m_i(\dot{q}_i - u)^2 \eta(y - q_i) + 2 \sum_i m_i \dot{q}_i \eta(y - q_i) \cdot u - \sum_i m_i \eta(y - q_i) \cdot u^2 \right)$$

$$= -\nabla_y \left(-\sigma_K + 2\rho u^2 - \rho u^2 \right)$$

$$= -\nabla_y \left(-\sigma_K + \rho u^2 \right),$$

where

$$\sigma_K = \sum_i m_i(\dot{q}_i - u)^2 \eta(y - q_i) \tag{23}$$

is the kinetic contribution to the stress in the moving frame of reference. Furthermore, the definitions of density (16) and momentum (17) has been used to identify the ρu^2-terms. We will now

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continue by re-expressing the first term of equation (20) in order to have the whole expression on differential form:

$$\sum_{ij} F_{ij}\eta(y - q_i) = \sum_{ij}\left(\frac{1}{2}F_{ij}\eta(y - q_i) + \frac{1}{2}F_{ij}\eta(y - q_i)\right)$$

$$= \sum_{ij}\left(\frac{1}{2}F_{ij}\eta(y - q_i) + \frac{1}{2}F_{ji}\eta(y - q_j)\right)$$

$$= \sum_{ij}\frac{1}{2}F_{ij}\left(\eta(y - q_i) - \eta(y - q_j)\right)$$

$$= \nabla_y\left(-\frac{1}{2}\sum_{ij}F_{ij}\cdot(q_i - q_j)B(q_i, q_j, y)\right)$$

$$= \nabla_y\left(\sigma_V\right).$$

We call σ_V the potential contribution to the stress. In the second equality, the indices of the second term are renamed. Followed by a use of Newton's third law (14) in the third equality. In the last step, we converted the difference at the corresponding points to a gradient term and introduced the bond function $B(q_i, q_j, y)$:

$$\eta(y - q_i) - \eta(y - q_j) = \int_0^1 \frac{d}{ds}\eta(y - sq_i - (1 - s)q_j)ds$$

$$= \int_0^1 (q_j - q_i)\cdot\nabla_y\eta(y - sq_i - (1 - s)q_j)ds$$

$$= -\nabla_y\int_0^1 \eta(y - sq_i - (1 - s)q_j)(q_i - q_j)ds$$

$$= -\nabla_y(q_i - q_j)B(q_i, q_j, y). \tag{24}$$

Finally, both terms are on the appropriate form, and we are thus able to formulate the conservation law for momentum and identify the stress within a moving frame of reference:

$$\partial_t\sum_i m_i\dot{q}_i\eta(y - q_i) = \sum_{ij} F_{ij}\eta(y - q_i) - \nabla_y\sum_i m_i\dot{q}_i^2\eta(y - q_i)$$

$$= \nabla_y\left(-\frac{1}{2}\sum_{ij}F_{ij}\cdot(q_i - q_j)B(q_i, q_j, y)\right)$$

$$+ \nabla_y\left(-\sum_i m_i(\dot{q}_i - u)^2\eta(y - q_i) - \sum_i m_i\dot{q}_i\eta(y - q_i)\cdot u\right),$$

which yields

$$\partial_t(\rho u) + \nabla_y(\rho u^2 - \sigma) = 0,$$

where

$$\sigma = \sigma_V + \sigma_K \tag{25}$$

$$\sigma_V = -\frac{1}{2}\sum_{ij}F_{ij}\cdot(q_i - q_j)B(q_i, q_j, y)$$

$$\sigma_K = -\sum_i m_i(\dot{q}_i - u)^2\eta(y - q_i).$$

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Moving on to energy and the heat flux, consider the energy E^0 (equation (18)). The derivative of the first factor can be rewritten to a divergence term in the following fashion:

$$\sum_i \partial_t \left(\frac{1}{2} m_i |\dot{q}_i|^2 + \sum_j \frac{1}{2} \phi_{ij} \right) \cdot \eta(y - q_i) = \sum_i \left(m_i \ddot{q}_i \cdot \dot{q}_i + \frac{1}{2} \sum_j \phi'_{ij} \cdot (q_i - q_j) \frac{\dot{q}_i - \dot{q}_j}{|q_i - q_j|} \right) \eta(y - q_i)$$

$$= \sum_i \frac{1}{2} \sum_j F_{ij} (\dot{q}_i + \dot{q}_j) \eta(y - q_i)$$

$$= \sum_{ij} \frac{1}{2} F_{ij} \dot{q}_i (\eta(y - q_i) - \eta(y - q_j))$$

$$= -\sum_{ij} \frac{1}{2} F_{ij} \dot{q}_i (q_i - q_j) \nabla_y B(q_i, q_j, y),$$

where equation (13) is used in the second step, and in the last step the bond function defined in (24) is used. Using this result, we can readily take the derivative of E^0 (equation (18)):

$$\partial_t E^0 = -\nabla_y \sum_{ij} \frac{1}{2} F_{ij} \dot{q}_i (q_i - q_j) B(q_i, q_j, y) - \sum_i \left[\left(\frac{1}{2} m_i |\dot{q}_i|^2 + \frac{1}{2} \sum_j \phi_{ij} \right) \dot{q}_i \nabla_y \eta(y - q_i) \right]$$

$$= -\nabla_y \left[Q_V^0 + Q_K^0 \right], \tag{26}$$

where

$$Q^0 = Q_V^0 + Q_K^0$$

$$Q_V^0 = \frac{1}{2} \sum_{ij} F_{ij} \cdot \dot{q}_i (q_i - q_j) B(q_i, q_j, y)$$

$$Q_K^0 = \sum_i \left(\frac{1}{2} |\dot{q}_i|^2 + \frac{1}{2} \sum_j \phi_{ij} \right) \dot{q}_i \eta(y - q_i).$$

The above equations hold for a fixed frame of reference, by substituting (22) into equation (18) we obtain an expression for the energy within a moving frame of reference:

$$E^0 = \sum_i \left(\frac{1}{2} m_i |\dot{q}_i|^2 + \frac{1}{2} \sum_j \phi_{ij} \right) \eta(y - q_i)$$

$$= \frac{1}{2} \sum_i \left(m_i |\dot{q}_i - u|^2 + 2 m_i (\dot{q}_i - u) u + m_i |u|^2 + \sum_j \phi_{ij} \right) \eta(y - q_i)$$

$$= \frac{1}{2} \sum_i \left(m_i |\dot{q}_i - u|^2 + 2 m_i \dot{q}_i u - 2 m_i u^2 + m_i |u|^2 + \sum_j \phi_{ij} \right) \eta(y - q_i)$$

$$= \sum_i \left(\frac{1}{2} m_i |\dot{q}_i - u|^2 + \sum_j \phi_{ij} \right) \eta(y - q_i) + \sum_i m_i \dot{q}_i u \eta(y - q_i) - \sum_i m_i u^2 \eta(y - q_i) + \frac{1}{2} \sum_i m_i |u|^2 \eta(y - q_i)$$

$$= \sum_i \left(\frac{1}{2} m_i |\dot{q}_i - u|^2 + \sum_j \phi_{ij} \right) \eta(y - q_i) + \rho u^2 - \rho u^2 + \frac{1}{2} \rho |u|^2$$

$$= E + \frac{1}{2} \rho u^2. \tag{27}$$

In the same fashion, we acquire expressions for heat flux within a moving frame of reference:

$$Q_V^0 = Q_V - u\sigma_V \tag{28}$$

$$Q_K^0 = Q_K - u\sigma_K + u\left(E + \frac{1}{2}\rho|u|^2\right) \tag{29}$$

$$Q = Q_V + Q_K. \tag{30}$$

Finally, the conservation law for energy in a moving frame of reference is obtained by substituting equations (27)-(30) into equation (26):

$$\partial_t[E + \frac{1}{2}\rho u^2] = -\nabla_y[Eu + \frac{1}{2}\rho u^3 - \sigma u + Q].$$

2.4.2 Formulas for macroscopic properties

In this section, we collect the expressions for the macroscopic variables as functions of the particle dynamics in the moving frame of reference. These will be used to study the macroscopic behaviour of the system, with the ultimate goal of finding whether or not a closed system can be formulated for the FPUT model with LD. Beginning with the three conserved variables density ρ, momentum ρu, and energy E:

$$\rho(y,t) = \sum_i m_i \eta(y - q_i) \tag{16 revisited}$$

$$\rho u(y,t) = \sum_i m_i \dot{q}_i \eta(y - q_i) \tag{17 revisited}$$

$$E(y,t) = \sum_i \left[\frac{1}{2}m_i|\dot{q}_i - u|^2 + \frac{1}{2}\sum_j \phi_{ij}\right]\eta(y - q_i). \tag{31}$$

There are two additional macroscopic variables which appear in the conservation laws for momentum and energy, see equation (10), namely the stress σ and heat flux Q. If it is possible to express the stress and heat flux as functions of the conserved variables, then the system is closed. A possible function could for example be a linear function, as opposed to a point cloud. The expressions for stress σ and heat flux Q in a moving frame of reference are:

$$\sigma(y,t) = \sigma_V + \sigma_K \tag{25 revisited}$$

$$\sigma_K(y,t) = -\sum_i m_i(\dot{q}_i - u)^2 \eta(y - q_i)$$

$$\sigma_V(y,t) = -\frac{1}{2}\sum_i F_{ij} \cdot (q_i - q_j)B(q_i, q_j, y)$$

$$Q(y,t) = Q_V + Q_K \tag{30 revisited}$$

$$Q_K(y,t) = \frac{1}{2}\sum_i \left(m_i|\dot{q}_i - u|^2 + \sum_j \phi_{ij}\right)(\dot{q}_i - u)\eta(y - q_i)$$

$$Q_V(y,t) = \frac{1}{2}\sum_{ij} \left(F_{ij} \cdot (\dot{q}_i - u)\right)(q_i - q_j)B(q_i, q_j, y).$$

Remember that the conservation is only exact when the system is independent of the heat bath, i.e. with $\gamma = 0$. The macroscopic expressions only consider interactions between the system

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particles. Thus, when the system is coupled to the heat bath the macroscopic expressions are missing correction terms. However, they are by no means useless, one must simply be aware of the fact that they describe the interactions of the system particles perturbed by the heat bath.

3 Implementation

In this section we first present a numerical method for propagating the particle dynamics and then perform some validation of the method.

3.1 Numerical method

In section 2.4 we not only derived the conservation laws, but also formulated the macroscopic variables in terms of the molecular dynamics, which are collected in section 2.4.2. These formulas give us the tools needed to study the macroscopic behaviour of the system at every given time and position. However, in order to study the system at different times, we must develop a tool to propagate the molecular dynamics, which is achieved in the current section.

For convenience we restate the full model comprising our molecular dynamics:

$$dq = m^{-1}pdt$$
$$dp = F(q)dt - \gamma pdt + \sqrt{(2\gamma k_B Tm)}dW, \tag{1 revisited}$$

where m is the mass, q the position, p the momentum and dW is a Wiener increment. Note that q, p, F and dW are vectors where each element corresponds to a particle's coordinate, force and stochastic increment. Furthermore, γ is the friction parameter, k_B the Boltzmann constant, T the temperature and $F(q_i)$ the force on particle i given by the FPUT-model:

$$F(q_i) = (q_{i+1} + q_{i-1} - 2q_i)[k + \alpha(q_{i+1} - q_{i-1})]. \tag{4 revisited}$$

We consider a numerical method to solve the FPUT system with LD. By setting either one or both parameters α and γ to zero, the special cases of interest are obtained. We will implement a splitting method suggested by [5] in chapter 7.3.1, namely BAOAB, the acronym is explained in the next paragraph.

Consider equation (1), we seek to decompose the system in such a way that each individual piece can be solved exactly. The method is then built from a sequence of updates corresponding to an exact solve of each piece. There are a great number of plausible splitting strategies for LD. Different strategies are investigated in [5], and the best method is presented here. Since the Ornstein-Uhlenbeck process can be solved exactly, this feels like a natural choice for solving the stochastic part of the system of differential equations – we call this step O. It happens to be favourable to split the method which solves the deterministic part in two, called A and B. In addition, the method must be symplectic in the case $\gamma = 0$.

$$dq = m^{-1}pdt \tag{A}$$
$$dp = F(q)dt \tag{B}$$
$$dp = -\gamma pdt + \sqrt{(2\gamma k_B Tm)}dW \tag{O}$$

We could for example use a symplectic Euler scheme to solve the deterministic part followed by an exact Ornstein-Uhlenbeck solve. This would, with our newly introduced notation, be called [ABO]. As it happens, a velocity Verlet method with an Ornstein-Uhlenbeck solve in the middle, [BAOAB], has favorable properties; including allowance of a large time step while keeping the error small, without any extra expenses in complexity. The algorithm is formulated below, where p and

q are updated from the time step n to $n + 1$:

$$p_{n+1/2} = p_n + \frac{h}{2}F(q_n); \qquad\qquad (B)$$

$$q_{n+1/2} = q_n + \frac{h}{2m}p_{n+1/2}; \qquad\qquad (A)$$

$$\hat{p}_{n+1/2} = e^{-h\gamma}p_{n+1/2} + \sqrt{k_B T(1 - e^{-2\gamma h})m}W_n; \qquad\qquad (O)$$

$$q_{n+1} = q_{n+1/2} + \frac{h}{2m}\hat{p}_{n+1/2}; \qquad\qquad (A)$$

$$p_{n+1} = \hat{p}_{n+1/2} + \frac{h}{2}F(q_{n+1}); \qquad\qquad (B)$$

where h is the step size and $W_n \sim \mathcal{N}(0, 1)$ a vector of normally distributed stochastic variables, one for each particle. The quantities q, p and F should also be thought of as vectors, where each element is related to a particle. Note that the force only has to be calculated once per iteration, since it can be reused from the previous iteration. The force on particle i is given by the FPUT-model:

$$F(q_i) = (q_{i+1} + q_{i-1} - 2q_i)[k + \alpha(q_{i+1} - q_{i-1})]. \qquad\qquad \text{(4 revisited)}$$

With $\alpha = 0$ the expression of the force reduces to that of the harmonic oscillator. With $\gamma = 0$ the O-step does nothing and the method reduces to the normal velocity Verlet, although the A-step could have been written on one line. Exploiting this, it is easy to vary the parameter in the model for different simulations.

3.2 Validity

Before performing any real experiments, we must convince ourselves that the simulation is behaving correctly. In continuum mechanics, the conservation laws of mass, momentum and energy must hold. Thus, we can test if all of the macroscopic variables are correctly formulated – and if the numerical method approximate a continuum closely enough – by verifying that the conservation laws holds. This is performed with $\gamma = 0$ since the energy of the system is not conserved when it is coupled to a heat bath ($\gamma > 0$).

It is clear from figure 2 (left) that the mass is conserved, and the expressions for conservation of momentum and energy both stay promisingly close to zero. If we increase the number of particles by a factor 10 and adjust the width of the locality function $\eta(y)$ proportionally, figure 2 (right), the energy- and momentum conservation is reduced by a factor of $\frac{1}{10}$. Thus deducing that the expressions for the conservation laws tends to zero as the number of particles are increased. Our system seems to behave well. In favour of a shorter and more focused report we have omitted plots of, for example, stress as a function of density and comparing the system with 100 particles to that of 1000 particles; however, be assured that they are indistinguishable. As a side effect, more particles increases the total mass of the system, which due to inertia forces longer simulation time in order to observe the same number of periods.
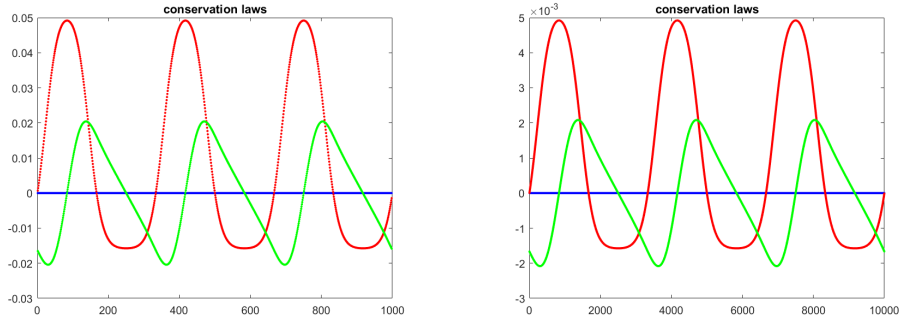
Figure 2: Conservation of energy (green), momentum (red) and mass (blue). The model is the simplest, i.e. the harmonic oscillator ($\alpha = \gamma = 0$). The spatial coordinate is fixed around $y = \frac{3N}{5}$; the time is spanning the simulation and correspond to the value of the x-axis multiplied by the step size $h = 0.2$. The number of particles are $N = 100$ to the left and $N = 1000$ to the right.

4   Results

In this section we are investigating whether it is possible to formulate a closed system for the FPUT model with LD. A closed system is found if the stress and heat flux can be expressed as functions of the mass, momentum, energy and possibly their derivatives. Thus, we will systematically seek such relations, starting with what we can see in the most basic special case.

Throughout the simulations we set:

$$m = k = k_B = T = 1,$$

and – unless specified otherwise – fix the spatial locality parameter y as two fifth's of the system length.

The system is not only dependent on the dynamics, but also very much so on the initial conditions. Initialization is performed with the particles in equilibrium positions and a velocity determined by a sinusoidal function, which period is the spatial length of the system. Many different possible initial conditions are imaginable, such as zero velocity and positions randomly perturbed around the equilibrium of each particle. However, for the model to behave as a continuum, the particles close to each other must behave similarly, hence the choice of initial state.

We begin by presenting the results for the stress in the most basic special case, namely the harmonic oscillator. We the continue with FPUT, then the harmonic oscillator with LD and finally FPUT with LD. The results section is concluded with what could be gathered about the heat flux.

4.1   Harmonic oscillator

Here we model the particle interactions as harmonic oscillators, i.e. with the parameters $\alpha = \gamma = 0$. The effects of the initial velocity is tested in figure 3, we see that the system with higher initial velocity indeed have a larger kinetic contribution to the stress and there is a higher variation in the density.

In figure 4 we seek to find the stress as a function of either the density, momentum, energy and possibly their derivatives. The stress plotted against the momentum $\sigma(\rho u)$ is not a function, nonetheless we cannot exclude the possibility that the stress can be a function of the momentum and another variable. However, both the density and energy look like much more promising candidates.
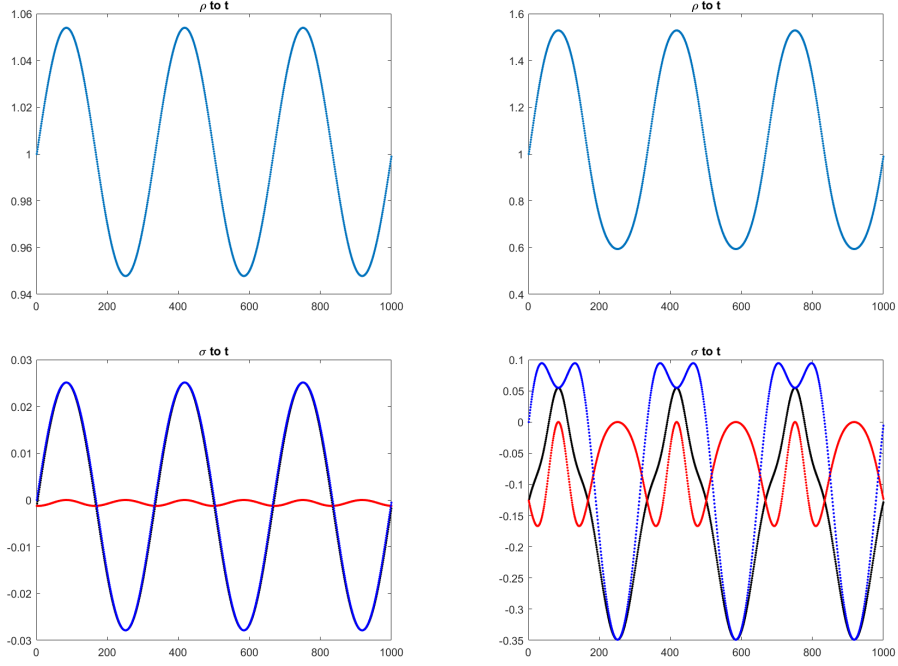
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Figure 3: Harmonic oscillator: $\alpha = \gamma = 0$. Low amplitude to the left and high amplitude to the right, the density in the top row and the stress in the bottom. Black is the total stress, blue the potential contribution and red the kinetic contribution.

4.2 FPUT

We continue our investigation with the FPUT-model. In the experiments, we found that the lower amplitude allowed for a larger α. When varying both parameters the system showed the same behaviour, thus we choose to present the high velocity initial condition case. In figure 5 we see that for a small α-value the system is very close to the harmonic oscillator, and for a large α it turns chaotic. However, for the intermediate size of the anharmonic spring constant the $\sigma(\rho)$ plot is quite disturbed compared to its harmonic oscillator counterpart, while $\sigma(E)$ is surprisingly intact.

4.3 LD

Before showing the results of the full model, we test the LD separately i.e. $\alpha = 0$ and $\gamma \neq 0$. Figure 6 show that $\sigma(E)$ is robust against the perturbations of the LD, while $\sigma(\rho)$ does not fare so well.
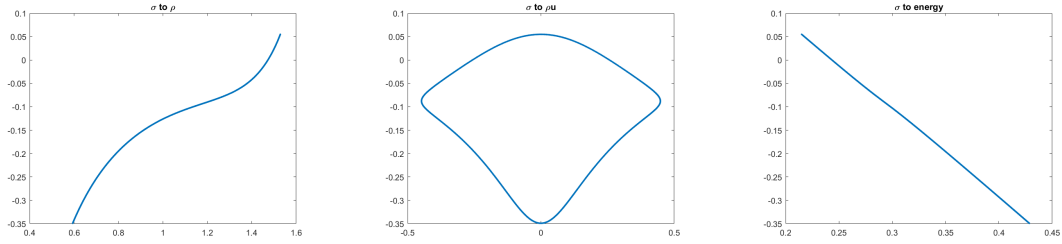
Figure 4: Harmonic oscillator: $\alpha = \gamma = 0$. From left to right: plots of the stress as a function of the density, momentum and energy.
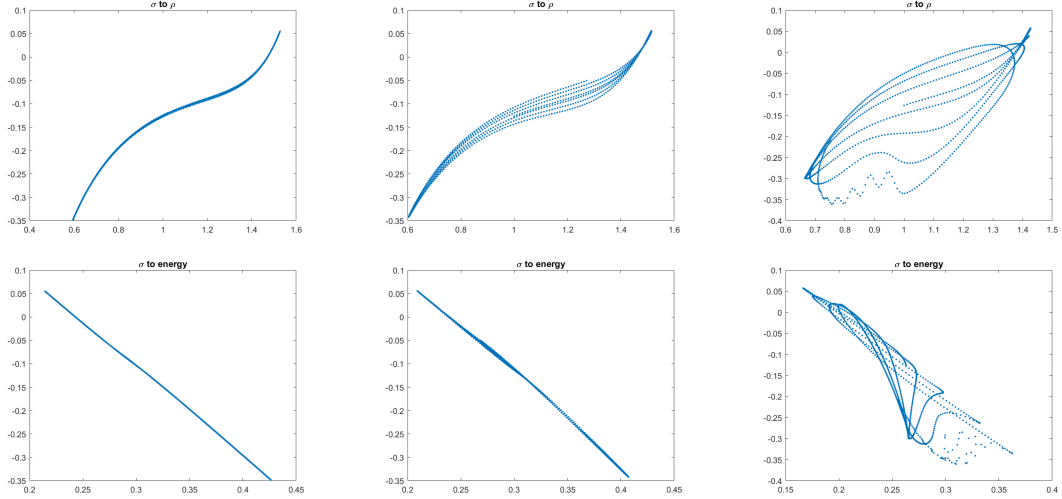

Figure 5: FPUT: $\gamma = 0$. From left to right: $\alpha = 0.003$, $\alpha = 0.03$, $\alpha = 0.3$. Top row depicts $\sigma(\rho)$ and bottom row $\sigma(E)$.
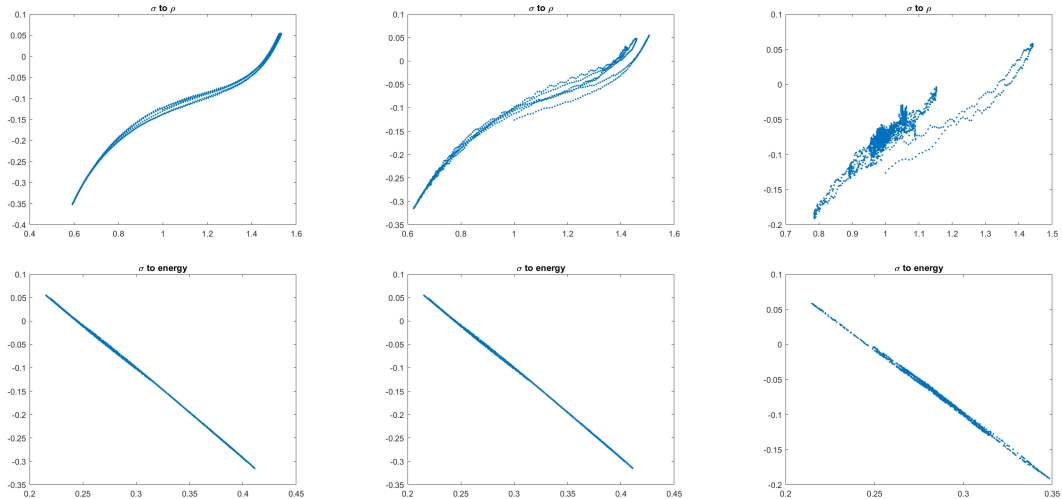

Figure 6: Harmonic oscillator with LD: $\alpha = 0$. From left to right: $\gamma = 0.0002$, $\gamma = 0.002$, $\gamma = 0.02$. Top row depicts $\sigma(\rho)$ and bottom row $\sigma(E)$.
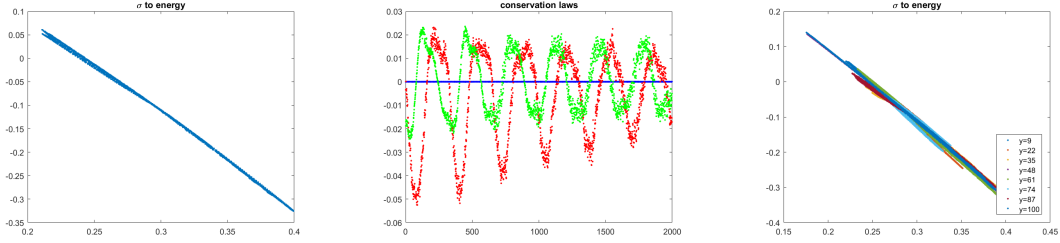
Figure 7: FPUT with LD, the parameters are set to $\gamma = 0.002$ and $\alpha = 0.03$. To the left: $\sigma(E)$. In the middle, the conservation laws: blue is density, red is momentum and green is energy. To the right: $\sigma(E)$ for eight different choices of spatial coordinate y.

4.4 FPUT with LD

In figure 7, $\sigma(E)$ continues to show promising results, there is a clear linear relation between the stress and energy. In the rightmost figure we see that the relation between the stress and energy is independent of both time and the choice of spatial coordinate y.

4.5 Heat flux

The continuum description is not complete without a constitutive relation for the heat flux Q. Unfortunately in our system, the heat flux is small and we are unable to express the heat flux as an easy function of the other variables. However, this does in no way exclude the existence of such a function and we suggest further research upon this subject. In figure 8 we show the heat flux as a function of density, momentum and energy without success. The model is FPUT with a moderate α. Similar results are obtained by letting $\alpha = 0$ and $\gamma \neq 0$. With just the harmonic oscillator one obtains the lying 8-shape one can anticipate from figure 8.
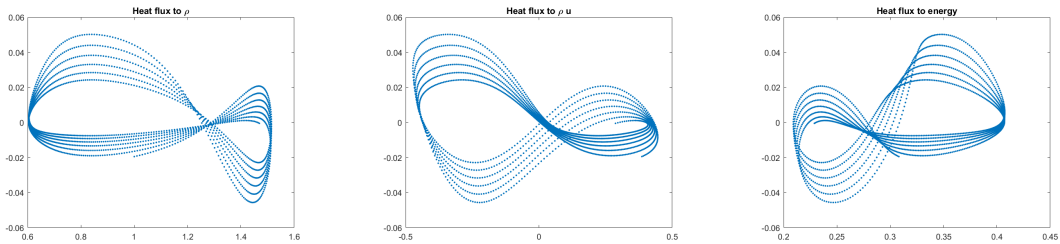

Figure 8: From left to right: Heat flux as a function of density, momentum and energy. $\alpha = 0.03$, $\gamma = 0$.

5   Conclusions

We found that the stress is a linear function of the energy for the FPUT model with LD. This result ratifies that indeed, it is possible to find constitutive relations within the molecular dynamics formulation for the α-FPUT model with LD. Hopefully, this result is not unique for the FPUT model with LD, but that similar relations can be be determined – and perhaps even exploited – for other models as well.

Unfortunately, we were unable to find any such relation for the heat flux, however, the existence of one cannot be excluded. Since a relation for the stress is found, it is even likely that there exists one for the heat flow as well, finding it could be the objective of another study.

Another interesting question which could be pursued in another study is to incorporate the LD model in the macroscopic expressions of Hardy. That is, to investigate if it is possible to reformulate the Langevin equations as a pair potential.

References

[1] Dario Bambusi and Antonio Ponno. "On Metastability in FPU". In: *Communications in Mathematical Physics* 264.2 (June 2006), pp. 539–561.

[2] J. Carlsson et al. *Stochastic differential equations: models and numerics.* draft, 2010.

[3] Fermi E., Pasta J., and Ulam S. "Studies of nonlinear problems". In: *Los Alamos Scientific Laboratory Report* LA-1940 (1955).

[4] Irving J.H. and Kirkwood J.G. "The statistical mechanical theory of transport processes. IV. The equations of hydrodynamics". In: *J. Chem. Phys.* 18.6 (1950), pp. 827–829.

[5] B. Leimkuhler and C. Matthews. *Molecular dynamics with deterministic and stochastic numerical methods.* Springer, 2015.

[6] Onorato M. et al. "Route to thermalization in the α-Fermi-Pasta-Ulam system". In: *PNAS* 112.14 (Apr. 2015), pp. 4208–4213.

[7] Hardy R.J. "Formulas for determining local properties in molecular dynamics simulations: Shock waves". In: *J. Chem. Phys.* 76.1 (1982), pp. 622–628.

[8] Robert Zwanzig. "Nonlinear generalized Langevin equations". In: *Journal of Statistical Physics* 9.3 (Nov. 1973), pp. 215–220.

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