Non-Equilibrium Molecular Dynamics Simulations: Techniques and Applications

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Abstract. These lectures notes are devoted to the presentation of properties of matter in non-equilibrium conditions by using the techniques of Non-Equilibrium Molecular Dynamics. As a first application, results on the simulation of shock waves in solids are presented. Shock propagation can be modeled by a direct Molecular Dynamics simulation. The shocked state is compared to a modeling through a dynamics constrained by the Hugoniot relations with a uniaxial compression: this new technique, named \textit{Hugoniostat}, allows to compute directly the shocked state properties without having to make a full study of the shock. The next application is concerned with properties of granular fluids. Those systems are always in a non equilibrium state with energy flowing from an external forcing towards the internal elastic energy of the grains. Constant-energy simulation of inelastic hard disks are performed by a rescaling of the velocities at every dissipative collisions, a method we call \textit{Sotostat}. This technique is used to compare flow properties with predictions from continuum equations. Moreover the chaotic indicators of the system behavior, the Lyapunov spectrum, are computed and the influence of the dissipativity of the grains on the spectrum is discussed.

INTRODUCTION

The objective of this paper is to present recent numerical advances based on statistical mechanics and allowing to study non-equilibrium states. There are already a few textbooks with good presentations of the subject of Molecular Dynamics (MD) for equilibrium \cite{1,2} and non-equilibrium systems \cite{3,4}. Here we want to present some new developments devoted to the study of matter in non-equilibrium stationary states.

Atomistic simulations of shock waves seems a quite natural method of investigation since the profiles of the changes in densities across a shock front are limited to a few atomic distances. Early studies have been reported in the late seventies \cite{9,10}; they were dealing with shock propagation in fluids and they attracted much
interest for two reasons: first, they were giving an exact, direct and precise view of a shock profile, providing new insight into a field which had been already described at a macroscopic continuous level [12,14]. And second, they were also a way to realize that the local equilibrium hypothesis and the validity of the linear relations between thermodynamic fluxes and forces were very robust even in those extreme conditions that are encountered in a shock front. One has to go to very high values for the Mach number in order to observe and interpret discrepancies with respect to Navier-Stokes equations [11,12]. Of course, the validity of the approach is limited by the usage of phenomenological potentials and by the ideal geometries realized.

This last aspect is even more crucial in shock waves propagating into a solid where the crystal structure introduces an anisotropy and where one would like to see the interaction of shocks with defects, grain boundaries or free surfaces of a material possibly undergoing some stress. It is easily realized that one has to be able to achieve large sample sizes and the computing cost of the direct simulation methods become rapidly prohibitive. With this idea in mind, we have developed a method where the complete realization of the shock and its propagation inside a sample is replaced by a constraint, forcing the system along the Hugoniot, and which allows to predict in a much more efficient way the state of matter after the shock has passed. There is some physics to solve however and the constraint in pressure has to be applied in a definite direction in order to lead to results comparable to the direct method: this is along the same lines of findings as the dependence of shock properties on the propagation direction which has been observed previously [8]. We present the method as well as the comparison with direct simulations in the first part of this paper. The goal of this part is not to provide an exhaustive review of the work that has been done in this field but rather to point out our recent study. A good introduction to the history of shock wave simulations could be found in [15].

A second kind of physical systems where non-equilibrium properties are crucial is the granular fluid: an assembly of macroscopic grains, with dissipative effective interactions, and which are maintained in a fluid-like state by some external forcing or energy input. Those models have been studied experimentally as well as theoretically by various groups recently with the perspective of being able to use and apply the methods of kinetic theory and hydrodynamics to predict the observed peculiarities of those systems: spontaneous vortex formation and clustering instabilities. Those spontaneous departures from equilibrium are due to the breaking of detailed balance as in non-equilibrium stationary states: however, a peculiarity of those systems is that this symmetry breaking is realized at every collision and not by an external flux.

For those systems too, we have developed a simulation method aimed at producing a stationary state where the energy input is fed homogeneously into the system so as to keep the kinetic energy constant in the course of simulation. We then compare the results of flows and instabilities observed in the system to the predictions of continuum descriptions, very much like what has been done for normal fluid systems [5,6]. We have shown for example that the Fourier's law, describing the heat flux in a system, has to be modified in order to model grain assemblies...
(temperature being identified with peculiar kinetic energy): this is similar to what happens in systems where a change of chemical potential can take place. We then write down the hydrodynamic equations modified accordingly and show a good agreement between a continuum description and granular simulations, at least for small restitution coefficients, that is small dissipativity.

Those systems are also investigated from a more fundamental point of view: there have been recent attempts to build the statistical mechanics of stationary states (for a review, see [7]). An important quantity for this approach is the set of Lyapunov exponents which describe how much the system is chaotic, and how fast nearby trajectories diverge one from another in phase space. A relation of those exponents to transport coefficients has been proposed and we have investigated those properties directly on two-dimensional granular fluid systems maintained in a stationary state. This is described in the last section of the paper in a very phenomenological way: we observe that the modes corresponding to a few of those exponents are similar to long-wavelength small frequencies collective excitations of normal fluid systems, but with also a few differences. The effect of dissipativity on the spectrum is observed: disks are most chaotic when the collisions are elastic, and this corresponds to a maximum for the Kolmogorov-Sinai entropy. The behavior of the spectrum when there is an instability is even more revealing: one observes a sharp drop of the positive exponents at the instability threshold.

We end with a few conclusions.

**SHOCK WAVES IN SOLIDS**

The development of simulations of shock waves has followed the increase of computer capabilities. Nowadays, it is possible to simulate a sample of a mesoscopic size (some shock wave simulations have included up to $10^8$ atoms). When doing MD simulations, it is necessary that the spatial dimension of the phenomenon of interest is contained within the simulation domain. In the case of shock waves, the run has to be long enough to provide a steady profile (i.e. the sample has to be long in the direction of propagation). Moreover, it has been shown that, despite apparent unidimensionality of the shock front, the presence of transverse directions in the simulations is critical for the flow of atoms and for the appearance of plasticity. The size of the sample is particularly important for simulations of solids. For a liquid, the rapid reorganization of atoms makes the system isotropic, and the relaxation processes that are involved are generally fast, as long as chemical changes do not take place. In the case of solids, however, a new, larger length scale is introduced which is the size of defects.

We make a special point here of emphasizing the inherently anisotropic nature of the shock wave. Anisotropy is particularly important for solids, which can sustain nonzero shear stress and also defect structures, making their behavior quite distinct from that of fluids. While we are most interested in the final shocked states, we note that at the shock front, even in the case of fluids, the normal pressure $P_{zz}$ is
typically greater than the transverse components $P_{xx}$ and $P_{yy}$, so that even fluids show transient anisotropic behavior. For later reference, the hydrostatic pressure is one-third the trace of the pressure tensor, $P = (P_{xx} + P_{yy} + P_{zz})/3$, and we define the shear stress in planar shock wave geometry to be half the normal stress difference:

$$2\tau = P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}),$$

where $\tau$ is the shear stress. So that we can write the normal pressure as

$$P_{xx} = P + \frac{4}{3}\tau.$$

In the case of fluids, the shear stress at the shock front is relieved by viscous flow in the transverse directions, so that the final state far behind the shock front is at hydrostatic equilibrium: $P_{zz} = P$ (or $\tau = 0$). In the case of solids, however, transverse motion can occur only if there is sufficient shear stress to overcome the inherent energy barrier to produce defects (e.g., dislocations) or else phase transformations, and thereby, plastic flow (deformation). In any case—whether or not there is plastic deformation—the final state in a solid is still not guaranteed to be hydrostatic, so that there can, in principle, be a residual (nonzero) shear stress.

The next section of this part is devoted to the description of the molecular dynamics technique actually used to performed simulation of a shock wave in solids. It is followed by the description of a recent equilibrium MD method able to predict the thermodynamics properties of a shocked material. Some results are presented at the end of this part.

**Non-Equilibrium Newtonian Dynamics**

We describe here the Non-Equilibrium MD technique that has been used to directly simulate a shock wave propagating in a solid. As in other MD simulations, periodic boundary conditions (PBC) are used, because we are interested in the behavior of atoms in the bulk, and not at the surface of the material. PBC can be used in the directions perpendicular to the propagation of the wave, provided the cross-sectional area is large enough to limit the artefacts of periodicity (limiting the interaction between defects for example and allowing realistic transverse flow). One side of the sample is used to generate the shock wave while the other side is a free surface. All the particles in the sample are given an initial material velocity $-u_p$ in one direction. They collide with an infinitely massive piston at rest (standing at $x = 0$), and are specularly reflected. A shock wave is then generated and propagates at velocity $u_s - u_p$ in the sample. For a liquid, the use of a free surface is not possible (due to the motion of atoms); PBC are then used in three directions, and a inhomogeneous shrinking of one periodic length is used to create two shock waves traveling in opposite directions.
FIGURE 1. snapshots taken at different time during the creation, propagation and reflection of a shock wave in a LJ crystal. The color scaling corresponds to the potential energy of atoms.
In the example displayed in figure 1, a shock wave has been generated with $u_p = 10.5$ in reduced Lennard-Jones (LJ) unit and propagated into a LJ fcc monocrystal in the (100) direction. The sample size is a $50 \times 50 \times 100$ unit cells. The potential energy of atoms are displayed on a color scale. We can see that the front of the wave is very narrow (on the order of 2 or 3 atomic layer). The wave rapidly becomes steady and eventually reaches the free surface. At this stage the thermodynamic properties of the shocked material can be computed, provided the system has reached equilibrium. The properties of the material at the shock front can also be computed. The shock front is associated with a maximum in the shear stress, which is released behind the shock front by the formation of defects.

When the shock wave reaches the free surface, it is reflected and starts to propagate backwards into the sample as a rarefaction wave. The sample expands but the atoms don't recover their initial potential energy (in the figure displayed, the shock strength is just below the melting threshold). We can see that the front of the rarefaction wave spreads as the wave penetrates the sample.

Such type of simulation is routinely performed nowadays and can provide useful insights in the microscopic description of the non-equilibrium processes involved during the shock, particularly for the description of the onset of plasticity or other phase transformations. Another method is thought to be more adapted to describe the equilibrium thermodynamic properties of the shocked material; it is described below.

### The Hugoniostat

We propose in the following an equilibrium MD technique for extracting both thermodynamic and structural properties of shocked crystalline solids and fluid, based on the Hugoniot relations for planar, steady shock waves and their inherently anisotropic nature. The thermodynamic quantities of a material in the initial unshocked state and the final shocked state are linked by the so-called Hugoniot conservation relations of mass, momentum, and energy across the shock front:

**mass:** \[ \rho u_s = \rho (u_s - u_p) \]
\[ \implies \varepsilon = 1 - \frac{\rho_0}{\rho} = 1 - \frac{V}{V_0} = u_p/u_s, \]  

**momentum:** \[ P_{zz} = P_0 + \rho_0 u_s u_p \]
\[ \implies u_s = \sqrt{\frac{P_{zz} - P_0}{\rho_0 \varepsilon}}, \quad u_p = \varepsilon u_s, \]  

**energy:** \[ E = E_0 + \frac{1}{2} (P_{zz} + P_0)(V_0 - V). \]  

$E$ is the internal energy per unit mass, $P_{zz}$ is the normal component of the pressure tensor in the direction of the shockwave (arbitrarily chosen to be the z-direction), and $V = 1/\rho$ is the volume per unit mass of the shocked material; subscript "0" refers to these quantities in the initial unshocked state. $u_s$ is the shock velocity in
the material produced by a piston moving into it at velocity \( u_p \). \( \epsilon \) is the compressive volumetric strain (compression).

When a shock wave propagates into a system, the thermodynamic quantities of the final state should obey the Hugoniot relation: this is a conservation equation linking the characteristic of the final state to those of the unshocked region. This means that, given the thermodynamic parameter of the unshocked region and one of the other parameter, like the shock velocity or the final pressure, all other parameters are determined.

Without simulating a propagating shock wave, the states on the Hugoniot curve can be found by using the Hugoniot relation as a constraint. New equations of motions are build, which constrain the system internal energy to lie on the shock Hugoniot curve (hence, we call this the Hugoniotstat). As a matter of fact, conservation equations also involve mass and momentum conservation, but those conditions will be less important since they are automatically conserved in the equations of motion for the modeled system. We are free to choose one the thermodynamic quantity of the final state (volume, pressure or temperature) and then we will be able to compute the others. There are various techniques to constrain a system to a particular condition. In the following, two different methods, namely the Gauss method and the extended system method, are applied to the problem of constraining the system to the Hugoniot.

**Gauss Constraint Method**

Gauss' principle of least constraint can be applied to force the system to lie on its Hugoniot. It is developed below in the case where the pressure of the final state is chosen (similar techniques can be used with the volume of the final state). The simulation is then performed at constant number of atoms, constant pressure, and on the Hugoniot \((N,P,Hug)\).

The new equations of motion are:

\[
\frac{dq_i}{dt} = \frac{p_i}{m} + \dot{\epsilon} q_i
\]

(6)

\[
\frac{dp_i}{dt} = F_i - (\chi + \dot{\epsilon}) p_i
\]

(7)

where the values of \( \chi \) and \( \dot{\epsilon} \) are given by the microscopic instantaneous state of the system, their roles being to keep the pressure constant and to satisfy the Hugoniot relation.

The volume of the simulation cell is allowed to change, its evolution equation is:

\[
\frac{dV}{dt} = 3V \dot{\epsilon}.
\]

(8)
For numerical convergence, the constraint has to be small, so that the system is weakly perturbed. The Lagrange multipliers are chosen to satisfy the constraint and they in fact minimize the difference between the constrained and the Newtonian dynamics. In order to calculate the value of $\dot{\epsilon}$, we make use of the microscopic expression of the internal energy:

$$
E = \sum_i \frac{p_i^2}{2m} + \sum_{i>j} \phi_{ij}.
$$

(9)

where $\phi_{ij}$ is the interaction potential between two atoms. Introducing the Hugoniot relation and taking the derivative versus time leads to:

$$
\dot{E} = \sum_i \frac{p_i}{m} \dot{r}_i + \sum_{i>j} \frac{d\phi_{ij}}{dr} \dot{r}_i \dot{r}_j
$$

$$
= \frac{1}{2} \dot{P}(V_0 - V) - \frac{1}{2} (P + P_0) \dot{V}.
$$

(10)

The pressure being constant, $\dot{P} = 0$. Introducing equation 6 and 7, we finally get:

$$
\dot{\epsilon} = \frac{3(P_0 - P)V \chi}{2 \sum_i \frac{p_i^2}{m}}.
$$

(11)

The calculation of $\chi$ can be achieved starting with the microscopic expression for the pressure (Irving-Kirkwood formula):

$$
3PV = \sum_i \frac{p_i^2}{m} + f_i r_i.
$$

(12)

Taking the time derivative of equation 12 and introducing eq. 6 and 7 we get:

$$
3\dot{P}V + 3\dot{V}P = \\
\sum_i \frac{2}{m} \dot{p}_i f_i - \sum_i \frac{2}{m} \dot{\epsilon}_i (\chi + \dot{\epsilon}) + \sum_{i>j} \dot{r}_i f_{ij} + \dot{r}_j f_{ij}.
$$

(13)

Newton’s third law is introduced through the following equation:

$$
\sum_i r_{ij} f_i = \sum_i \sum_{j>i} r_{ij} f_{ij} = - \sum_i \sum_{j>i} w(r_{ij})
$$

(14)

where $w(r_{ij})$ is the intermolecular virial. Taking $x = r \frac{dw}{dr}$, we get:

$$
3\dot{P}V + 3\dot{V}P = \\
\sum_i \frac{2}{m} \dot{p}_i f_i - \chi \sum_i \frac{2}{m} \dot{\epsilon}_i [\sum_i \frac{2}{m} \dot{\epsilon}_i (\sum_i \frac{2}{m} \dot{\epsilon}_i) - \sum_i \frac{2}{m} \dot{\epsilon}_i (\sum_i \frac{2}{m} \dot{\epsilon}_i)]
$$

$$
- \sum_i \sum_{j>i} (\frac{2}{m} + \chi r_{ij}) \frac{2\dot{\epsilon}_i}{r_{ij}}.
$$

(15)
The pressure being constant, its derivative is zero. The final expression for \( \chi \) is:

\[
\chi = \frac{2}{m} \sum_i p_i f_i - \frac{1}{m} \sum_i \sum_{j>i} r_{ij} p_{ij} \frac{x(r_{ij})}{r_{ij}} - \sum_{i,j>i} x(r_{ij}) + 2 \sum_i \frac{p_i^2}{m} + 3P_0V + 6PV. \tag{16}
\]

Now the two parameters of the new equations of motions for the Hugoniostat can be computed at each time step of the evolution of the system. These equations are designed to cancel the derivative of the constraint at all times. It means that if the system is put on the Hugoniot curve, then it will stick on it. The first step of the dynamics is then to drive the system on the Hugoniot curve. This is achieved by applying an initial scaling on the volume and temperature of the system as follows:

\[
r_i \leftarrow \lambda r_i \tag{17}
\]

\[
p_i \leftarrow \gamma p_i \tag{18}
\]

The two coefficients \( \lambda \) and \( \gamma \) are chosen such that the system satisfies the Hugoniot relation for the given pressure. To compute these coefficients, we start from the expression of the pressure:

\[
\gamma^2 \sum_i \frac{p_i^2}{m} = 3P\lambda^3V - f(\lambda) \tag{19}
\]

where \( f(\lambda) \) is the result of the scaling 17 on the term \( \sum_i f_i r_i \).

This relation is introduced into the hugoniot relation:

\[
\epsilon(\lambda) = \frac{1}{2} [3P\lambda^3V - f(\lambda)] + g(\lambda) - E_0 = \frac{1}{2} (P + P_0)(V_0 - \lambda^3 V) \tag{20}
\]

where \( g(\lambda) \) is the result of the scaling 17 on the potential energy of the system. The Hugoniot relation is satisfied if \( \epsilon(\lambda) = 0 \). We use the dichotomy technique to compute \( \lambda \) such that \( \epsilon = 0 \). The value for \( \gamma \) is deduced from equation 19.

**Extended System Method**

Another method, the extended system method, can be used to constrain the system: this is sometimes referred to as the integral feedback mechanism [4]. As in the Gauss constraint method, we make the assumption that only the final state is important: its volume can be fixed at initial time by allowing atoms to vibrate.
around perfect, unstrained lattice sites (at volume $V_0$ and temperature $T_0$ in the cold, unshocked solid), and then applying homogeneous compression $\epsilon$, which can be either uniaxial (in the $z$-direction only, as in the shock wave) or isotropic (in all three spatial directions). The final Hugoniot temperature can be reached by an equilibrium MD method, using a feedback thermostat to constrain the internal energy, according to the Hugoniot relation given by Eq. (5).

We expect that the choice for Hugoniot initial conditions—either uniaxial or isotropic compression—will give rise to different results only in the case of a solid, but not for a fluid. Under isotropic strain in the solid, the time average of the normal pressures are all expected to be equal (so that $\tau = 0$), and we can therefore suppose that an isotropic initial condition will not relax, so as to produce any resulting defect structures, while the uniaxial initial condition will. In fact, we expect that the uniaxial Hugoniot will produce plastic deformation more closely resembling a shock wave, by virtue of the anisotropy inherent in both of these compressive processes. The system sizes required for these two “flavors” of Hugoniot will therefore also be quite different: in order for the uniaxial method to give a faithful rendering of the shock-wave defect structures, the computational box will have to be big enough to contain a reasonable sample of the deformation, which will not in general be uniform in distribution. Moreover, depending on the natural relaxation time for the flow processes, it may still not be possible to observe the deformation on reasonable computational time scales. The model and the new equations of motion for the atoms are described below.

New equations of motion are used, which constrain the system internal energy to lie on the shock Hugoniot curve. The shock strength is determined by the compressive volumetric strain, or compression $\epsilon$. At initial time, we take a configuration of $N$ atoms vibrating about unstrained crystal lattice sites (at volume $V_0$ and low temperature $T_0$), and then apply an instantaneous, homogeneous compression, either uniaxially or isotropically, bringing the system to a highly strained state at the final volume $V$.

The dynamical evolution of the system, in either of the compressional “flavors” of the Hugoniot (either uniaxial or isotropic), is achieved by integral feedback that controls the internal energy, analogous to the method of thermostating initially proposed by Nosé and modified by Hoover [16]. In our approach, in addition to the $3N$ particle coordinates $r_i$ and momenta $p_i$, we introduce a single intensive global degree of freedom—the heat-flow rate $\chi$ (negative into, or positive out of the system)—whose equation of motion depends on the instantaneous values of $E$ and $P_{zz}^i$:

\begin{align}
\dot{r}_i &= \frac{p}_i, \\
\dot{p}_i &= F_i - \chi p_i, \\
\dot{\chi} &= \nu \frac{E - E_0 - \frac{1}{2}(P_{zz} + P_0)(V_0 - V)}{N\epsilon_0}.
\end{align}
FIGURE 2. (a) Time evolution of the temperature under uniaxial Hugoniot (20% strain), with optimal coupling $\nu = 33$; (b) with weak coupling $\nu = 3.3$; (c) with strong coupling $\nu = 100$. 
Eq.(23) above assumes that the final state is in the uniaxially compressed solid phase. [Obviously, for isotropic compression of the solid or for a fluid, one is free to replace $P_{zz}$ by $P$ in this equation, just as in the Hugoniot expression Eq.(5).] The frequency $\nu$ is associated with the heat-flow rate $\chi$: it is an input parameter chosen to optimize the efficiency of the coupling between the Hugoniostat and the system of atoms. ($\epsilon_0$ is the unit of energy for the interaction potential and should not be confused with the symbol for compression.)

The feedback provided by the heat-flow rate $\chi$ guarantees that, at long times, the system reaches a temperature appropriate to the shocked state on the Hugoniot. This "Hugoniostat" provides a new statistical ensemble where the Hugoniot relation is satisfied in the long-time average. We emphasize that, like laboratory shockwave experiments, the Hugoniostat simulation gives the velocities $u_s$ and $u_p$. But, in addition, the Hugoniostat calculation readily yields the shock temperature, which is not easy to measure in experiments.

In the Hugoniostat MD simulations, the response time of the system is dictated by $\nu$, the frequency (coupling strength) of the thermostat. In order to get an efficient coupling between the Hugoniostat and the system, $\nu$ should be chosen to be close to the natural vibrational frequency of the atoms, represented by the Einstein frequency $\omega_E$ under compression [17]. As the compression goes up, so does $\omega_E$, and so should $\nu$. To illustrate this, we show in Fig. 2 the difference in evolution of the temperature under three coupling strengths. When the coupling is chosen to mirror $\omega_E$ at 20% compression (about twice the value at normal density), the temperature comes quickly to its equilibrium value with modest, random-looking fluctuations. A value of $\nu$ that is too small gives rise to large, long-lived undulations in the temperature, while a value of $\nu$ that is too large exhibits large-amplitude oscillations that never seem to settle down.

Care has to be taken also with the initial value of the temperature. When a large strain (either uniaxial or isotropic) is applied to the system, the initial state can be quite far from the final equilibrium state, and the early stages of the simulation can exhibit very large fluctuations in the various mechanical quantities before settling down. In order to prevent unwanted instabilities, the temperature of the system is given an initial value obtained from the Hugoniot energy relation [Eq.(5)], where the potential part of the pressure $P_{zz}^\Phi$ and the potential energy $\Phi$ per unit mass are evaluated at the compressed volume $V$:

$$kT_{(t=0)}/m = 2E_0 + \frac{1}{2}P_{zz}^\Phi(V_0 - V) - \Phi \frac{4 - V_0/V}{4 - V_0/V}. \quad (24)$$

When the initial temperature is set according to Eq.(24), fluctuations larger in amplitude than those expected at equilibrium are still observed in the early stages of the simulation, but they are considerably smaller than when the initial temperature is chosen to be too small. The initial values of $\chi$ and $\dot{\chi}$ are set to zero.
Algorithm

The algorithm used to compute the evolution of the system using the Hugoniostat method - extended system - is described below. Equivalently, Gauss method can be implemented in the same fashion.

We assume the positions \( r(t) \), the velocities \( v(t) \), the accelerations \( a(t) \) and the friction coefficient \( \chi(t) \) to be known at time \( t \). First, the position at time \( t + \delta t \) are computed as:

\[
r(t + \delta t) = r(t) + \delta t v(t) + \frac{\delta t^2}{2} a(t)
\]  

(25)

Then the velocities are computed at mid-step using:

\[
v(t + \frac{\delta t}{2}) = v(t) + \frac{\delta t}{2} a(t)
\]  

(26)

At this stage, the force calculation is performed. The value of the derivative of the friction coefficient at time \( t + \delta t \) is calculated as:

\[
\dot{\chi}(t + \delta t) = \nu^2 \frac{E - E_0 - \frac{1}{2}(P_{zz} + P_0)(V_0 - V)}{N\epsilon_0}.
\]  

(27)

The velocity move is then completed according to the equation:

\[
v(t + \delta t) = v(t + \frac{\delta t}{2}) + \frac{\delta t}{2} f(t + \delta t)
\]  

(28)

The accelerations at time \( t + \delta t \) are finally computed:

\[
a(t + \delta t) = f(t + \delta t) - \dot{\chi}(t + \delta t)v(t + \delta t)
\]  

(29)

This algorithm has the same advantages as the common velocity Verlet algorithm.

Methodology and Applications

Results in this paper are presented for atoms interacting by the well-known Lennard-Jones 6-12 pair potential, using reduced units of distance to the minimum \( r_0 \), bond energy \( \epsilon_0 \), atomic mass \( m \), and time \( \tau = r_0 \sqrt{m/\epsilon_0} \); the potential is set to zero for distances beyond 2.23\( r_0 \). We have performed simulations to compute the Hugoniot curve in three different ways, using the same initial equilibrated configuration, namely, an unstrained, zero-pressure, nearly zero-temperature (\( kT_0/\epsilon_0 = 0.001 \)), face-centered cubic (fcc) crystal (the potential cutoff is just before the 5th neighbor shell).

First, we performed direct NEMD shock-wave simulations in the solid, with the shock-wave propagation along the (001) crystal direction (i.e., along the z-axis) for
typical sample sizes $30 \times 30 \times 150$ unit cells. To initiate the shock wave, the sample is given an average initial $z$-velocity of $-u_p$ and thrown into a momentum mirror standing at $z = 0$ [18]. Periodic boundary conditions are applied in the $x$- and $y$-directions. One end of the sample is a free interface, while the other is confined by the momentum mirror. The simulation is run until the shock wave reaches the free end of the sample (a time of usually less than $10\tau_0$). Classical Newtonian equations of motion are integrated by central differences, with the time step ranging from $10^{-3}$ to $2 \times 10^{-3}\tau_0$.

Next, in order to compare with the final states produced by these NEMD shockwave simulations, we performed equilibrium Hugoniostat MD simulations, both isotropic and uniaxial. In each case, the simulation box is originally a cube of size $15 \times 15 \times 15$ unit cells, with periodic boundary conditions applied in all three directions. An instantaneous compression is performed homogeneously, either isotropically or uniaxially along the $(001)$ ($z$-direction) at time $t = 0$. The dynamic evolution of the system is then computed according the equations of motion described in the previous section, typically for times of about $50\tau_0$. (Note that an MD Hugoniostat calculation is about 8 times less expensive than an NEMD shockwave.)

Using the direct NEMD method, shockwave simulations for different piston velocities have been performed, from small shock strength up to the melting transition. When the shock wave reaches the end of the sample, the thermodynamic quantities for the shocked material are averaged in space, excluding a few layers next to the shock front and next to the momentum mirror. In the case of the uniaxial and isotropic Hugoniostats, simulations at a variety of compressions have been performed. Averaging is done when the system has reached a stable state (namely, when the thermodynamic quantities fluctuate around a constant average value). Fig. 3 shows pressures and temperatures along the Hugoniot, calculated using the three methods.

In the two Hugoniostat methods, the Hugoniot relation is guaranteed. In general, as we show in the following section, the uniaxial Hugoniostat produces defect structures very similar to the direct NEMD shockwave simulations, while no defects at all appear in the isotropic Hugoniostat simulations until well after melting has occurred along the shock Hugoniot. The good agreement found between the different Hugoniot curves then demonstrates that the thermodynamic quantities are insensitive to the presence of solid-state defects.

The Hugoniot relation is obeyed in the NEMD shockwave simulation provided the shock wave has traveled far enough to become steady. We note that for the strongest shocks – i.e., those that result in melting – the NEMD simulations have to be run for very long times to ensure steady-wave convergence to the fully melted state. In this regime, both the uniaxial and isotropic Hugoniostat simulations agree well with each other, and give more reliable results for much smaller system sizes than do the NEMD simulations.

In figure 4, the change seen around a pressure $P \approx 580$ is associated with the melting of the material. The uniaxial Hugoniostat MD and NEMD shockwave simulations agree very closely with each other, while the isotropic Hugoniostat dif-
fers noticeably near the melting point. The melting temperature obtained from the isotropic Hugoniostat is indeed found to be greater than the other two, suggesting that the solid is superheated under isotropic compression. When a crystal is isotropically compressed, defects are not produced in the structure, so that a significant mechanism for bulk melting in shock waves is suppressed. The crystal remains perfect up to the melting temperature.

Another example is described below. The same crystal is taken, but the shock is propagated in the (111) direction. The hugoniot curves calculated with the hugoniostat method and with direct NEMD simulations are plotted in a \((T, P)\) diagram (figure 4). We can see that once again, there is a good agreement between the two methods of simulations as far as thermodynamics properties are concerned. The melting transition occurs around \(T = 7, P = 200,\) and \(\frac{V}{V_0} = 0.68\). However, some discrepancies can be seen in the melting domain.

The melting temperatures of the crystal when shocked in either the (100) or the (111) direction are very different (by a factor of two approximatively). This may be related to the underlying structure of the solid which melts. The interesting result comes from the origin of the discrepancies observed between the two methods in the melting region compared to the very good agreement obtained when the crystal is shocked in the (100) direction. The temperature profile extracted from a NEMD simulation of a system shocked in the (111) direction at \(v_p = 8\) is displayed figure 5. The sample size is \(20 \times 20 \times 700\) unit cells.

The temperature of the system increases continuously between the shock front and the end of the sample. This increase takes place on a distance of \(700\sigma\), i.e. \(\sim 0.2\mu m\). It means that the system has not reached equilibrium behind the shock front, i.e. relaxation processes (which involves the motion of atoms) are not yet
FIGURE 4. Pressures and temperatures from simulations of LJ crystal shocked in the (111) direction: NEMD shockwave (diamonds) and uniaxial Hugoniotstat (circles).

achieved. It can be though that at this point, a little increase in temperature would lead to the melting transition. Using the hugoniotstat method, the simulation can be run as long as desired, and there is no need for the sample to be very big. Simulations are routinely run for $50t_0$, and sometimes extended up to $200t_0$. In these conditions, we are more confident that equilibrium has been reached.

GRANULAR FLUIDS

There has been much interest recently devoted to the description of granular media. The understanding of their physical properties is important because they appear in many different phenomena taking place in our daily life as well as in various industrial processes [19,20]. Experiments have been devised which have permitted to focus on many different and new aspects. When subjected to injection of energy (vibrated plates for example), they present many similarities with fluids: convection take place, patterns can form and time-periodicity may be observed [21-25]. But evidence of differences with fluids is also compelling: strain-stress localization, unexpected patterns, long range correlations, large inhomogeneities or absence of spatial scale separation [26-28] call for a more specific description.

In addition to continuum theories, new approaches coming from statistical mechanics have also been proposed. Granular flow peculiarities have been reproduced using molecular dynamics techniques and simplified grain models. The aim of such approaches is to define the simplest possible model for grains able to reproduce, at least qualitatively, the observed behavior and then to use the techniques of statistical mechanics to deduce macroscopic or continuum equations.

In the inelastic hard sphere model (IHS), grains are spherical hard particles with only translational degrees of freedom. The energy dissipation is included through
a restitution coefficient \( r \) lower than one. As for hard spheres, the collision is an instantaneous event and the grain velocities after a collision are given by

\[
v'_{1} = v_{1} + \frac{1}{2} (1 + r) (\hat{n} \cdot (v_{2} - v_{1})) \hat{n},
\]

\[
v'_{2} = v_{2} - \frac{1}{2} (1 + r) (\hat{n} \cdot (v_{2} - v_{1})) \hat{n},
\]

where \( \hat{n} \) is the unit vector pointing from the center of particle 1 towards the center of particle 2. It is convenient to define the dissipation coefficient \( q = (1 - r)/2 \) which vanishes when collisions are elastic. In what follows units are chosen such that the disk diameter \( a \) and the particles masses are set to one.

The IMS model, like the elastic hard-sphere model, does not have an intrinsic energy scale. This means that two systems with the same initial configuration and with the particle velocities of one system being equal to those of the other multiplied by one scaling factor will follow the same trajectory but at different speeds. This lack of an intrinsic energy scale also implies a simple temperature dependence for all hydrodynamic quantities, that may be found by simple dimensional analysis.

This model is not sufficient for a quantitative description of real granular flows where roughness, rotational energy, static friction or polydispersity are needed to be introduced to predict flow properties. But it has proved sufficient to reproduce clustering phenomena, shearing instabilities, vibrated bed convection, pipe flow and so on \cite{26,29-31}. And the simplicity of the model allows to address the question of how the hydrodynamic equations for fluids are modified when dissipativity is introduced in the collision rules.

When the granular system is fluidized due to energy injection, it is common to define the granular temperature in an analogous way to the kinetic definition for
Heat Flux

Hydrodynamic equations, modified by the addition of a sink term in the energy equation, have been proposed in order to describe the long-wavelength long-time behavior of granular fluids with a dissipativity coefficient of only a few percents [32–36]. In those approaches, phenomenological relations (Navier-Stokes and Fourier’s laws) between thermodynamic forces (gradients of density, velocity and temperature) and fluxes as well as equations of states are introduced, extending then the properties of fluids made of elastic hard spheres to dissipative systems. Theoretical results compare generally well with those obtained from simulations done on computers.

Despite the dissipative nature of collisions, if the macroscopic field gradients are not so large, it seems natural to postulate linear relations between fluxes and thermodynamic forces. Then, in general, the heat flux can be expressed as [37]

$$ J = -k \nabla T - \mu \nabla n $$

where $k$ is the thermal conductivity, and $\mu$ is a new transport coefficient. There is no dependence on the velocity gradient because of tensorial arguments (Curie’s theorem).

If the system obeyed the second law of thermodynamics $\mu$ would vanish and $k$ would be positive in order that heat flows from hot to cold. On the other hand, in granular systems—when one neglects the internal heating of the grains on collisions—entropy production is not expected to be positive and there is no a priori reason for discarding the dependence of $J$ on the density gradient, but the new transport coefficient $\mu$ must go to zero with the dissipation coefficient $q$.

The constitutive equation (33) has been proposed using a Chapman-Enskog type of expansion for the solution of Boltzmann and Enskog equations generalized to the case of dissipative systems [35,38–40]. Here we will use MD simulations of IHS to study the macroscopic behavior of the heat flux. In particular, we examine the relation between the heat flux $J$ and temperature and density gradients. That is, we examine whether Fourier’s law is valid in this granular model or if it must be modified according to (33).

We have done molecular dynamics simulations of dilute two-dimensional systems composed of IHS under the influence of gravity. A total number of $N=1000$ spheres are placed in a square box with horizontal periodic boundary conditions. Energy
is injected in the system through thermal stochastic walls at the top and at the bottom. Each time a particle hits them a new random velocity is sampled out of a Maxwellian distribution at the same temperature $T_0$ for both walls. Since in the IHS model there is no intrinsic energy scale, the wall temperature $T_0$ is set to one.

Three series of simulations were done for different values of gravity acceleration, $g = 0.005, g = 0.01,$ and $g = 0.02$. Global number density was always set to $n_0 = 0.01$ and the dissipation coefficient took the values from $q = 0.01$ to $q = 0.10$.

Given a particular value of the global density $n_0$, gravity acceleration $g$, and dissipation coefficient $q$, the system is simulated until it reaches a stationary state. In these conditions, the number density $n(r)$, the temperature $T(r)$, and the heat flux $J(r)$ are measured using carefully devised measurement routines [41].

Due to the dissipative character of the IHS, even if the top and bottom walls are at the same temperature, the temperature profile is not uniform and has a minimum at some height, $y^*$, in the interior of the system. The energy that is dissipated in the bulk comes from the walls producing a net heat flux that goes from the walls to the bulk.

Gravity produces a non-uniform pressure, monotonically decreasing with height, obeying, in fact, the barometric law

$$\nabla p(r) = -gn(r)$$

(34)

Assuming a local equation of state, $p(r) = p(n(r), T(r))$, the temperature gradient and the density gradient are related by

$$\frac{\partial p}{\partial n} \nabla n + \frac{\partial p}{\partial T} \nabla T = -gn$$

(35)

Then, according to (33) and (35) a non-vanishing heat flux can be measured at $y^*$ only if gravity is different from zero.

Fig. 6 shows the density profile, the temperature profile, and the heat flux obtained in a simulation with $g = 0.01$ and $q = 0.05$. It is clear that the heat flux is not zero at the minimum of $T$, thus contradicting Fourier's law. Also, in the complete region between $y^*$ and the point where the heat flux vanishes, Fourier's law is violated. In effect, in this region the heat flux is parallel to the temperature gradient, that is, heat is flowing from cold to hot contradicting the second law of thermodynamics. Similar results are obtained in all the other simulations.

These results show that the modified heat law (33) must be used. The value of the new transport coefficient $\mu$ can be obtained directly by computing the heat flux and the density gradient at $y^*$. We define first the non-dimensional coefficient $\mu = n\mu/T^{3/2}$.

Fig. 7 shows the computed values of $\mu$ as a function of $q$ for the three series of simulations. A fit to the obtained values of $\mu$ was done including linear density and quadratic dissipation dependence, giving

$$\mu = 0.7q [(1 + 13.3n) + 55.0q (1 + 0.77n)]$$

(36)
FIGURE 6. Density (up), temperature (middle) and heat flux (bottom) profiles as a function of height for a simulation with $g = 0.01$ and $q = 0.05$. The total height of the system is $L = 316$, but only a section is shown. The minimum of $T$ is located at $y^* = 51$ (indicated by the vertical dashed line) whereas the heat flux vanishes at $y = 149$ (outside the plot range).

where the fact that $\mu$ must vanish when $q$ goes to zero was imposed in the fit.

The simulation methodology used to compute $\mu$ can be applied only to a limited range of values for the simulation parameters (global density, dissipation, gravity) since different unwanted phenomena start to happen outside that restricted range. If dissipation or density take larger values, the density at the center of the box increases near to solid values making the approach unsuitable. Also, when gravity is increased a spontaneous convective motion develops [24] which makes the field depend on the $x$ coordinate. In the other extreme, low values of gravity or dissipation produce poor statistics, and a further decrease of density would make the mean free path comparable to the size of the box, not allowing to work with local transport laws.

In conclusion, molecular dynamics simulations for a simple granular model show that the standard Fourier's law of thermal conductivity should be modified, adding a dependence on the density gradient to the usual temperature gradient dependence. Using stationary non-equilibrium techniques we have computed the value of the new transport coefficient $\mu$. 
Non-Equilibrium Steady States from a Hydrodynamic Description

Letting a system composed of IHS grains to evolve freely with periodic boundary conditions, it cools down homogeneously. This homogeneous cooling state (HCS) has been widely studied [26,35,42,43], and because of its simplicity the HCS has been used as a reference state to build up theories for non-homogeneous states. It is the analog of the equilibrium state (with a Maxwellian distribution) for elastic systems. Among other features, it has been shown that, in this state, the velocity distribution function is not Maxwellian, having a non-vanishing fourth cumulant and a long velocity tail [43].

In the HCS the system is in a non-stationary state that does not allow to make time averages of different properties. It is then necessary to inject energy to the system in order to keep it stationary. Different methods have been used, mainly the injection of energy through the walls (vibrating or stochastic), by external fields (like the flow in a pipe) or by stochastic forces acting on the particles (see for example [44]). These methods have the disadvantage of destroying the homogeneity of the fluid or, in the case of the stochastic forces, adding other dynamical effect.

We introduce a thermalizing method that both preserves the homogeneity and the dynamical properties of the granular fluid. Formally, each time two particles collide, the dissipated energy is reinjected immediately into the system by multiplying all particle velocities by the same factor. This factor is chosen each time in order to...
keep kinetic energy constant. This method correspond to the Gaussian or isokinetic thermostat for the IHS [3]. As the IHS model does not have an intrinsic energy (or time) scale the rescaling of all velocities does not change the evolution of the system, the collision sequence (thus all physical phenomena) is preserved but viewed at a different speed. In this sense this thermostating mechanism is the most appropriate for the HCS.

Numerically, the IHS model is simulated using event driven molecular dynamics [45]. A direct implementation of the thermalizing method would lead to a computational cost proportional to the total number of particles for each collision, making impossible to make long simulations. But we can take advantage of the lack of an energy scale to make it much faster. In effect, rescaling all velocities is equivalent to rescaling the time. We define a rescaled time by the relation $ds = \gamma dt$ with

$$
\gamma = \sqrt{\frac{E(t)}{E(0)}}
$$

where $E$ is the total energy in the system. Note that $\gamma$ is a piecewise constant decreasing function. It can directly checked that if rescaled velocities are defined as $\tilde{v} = dr/ds$, then the rescaled kinetic energy ($\tilde{K} = \sum \frac{m}{2} \tilde{v}^2$) is conserved.

Then, the simulation is done for the cooling IHS model (that is, no velocity rescaling is done) but at each collision the new kinetic energy is computed and $\gamma$ is evaluated using Eq. 37. In the simulation, then, the energy and the average velocity decrease, but the rescaled velocities are computed using $\tilde{v} = v/\gamma$.

Finally, to avoid roundoff errors, each time the kinetic energy has decreased by some orders of magnitude (typically $10^{-7}$ of the initial value) a real velocity rescaling is done to put again the temperature equal to one. In this process also the center of mass velocity is subtracted because, otherwise, small errors will be amplified by the rescaling.

At small dissipations, hydrodynamic equation can be written to describe the evolution of granular fluids. At low-density these equations are similar to the usual hydrodynamic equations for fluids except that there is an energy sink term and the already described modification of the Fourier’s law [32–36]. When applying the thermostat, extra source terms are added to the hydrodynamic equations due to the rescaling of time and the hydrodynamic fields. The equations read [46]

$$
\frac{\partial \rho}{\partial s} + \nabla \cdot (\rho \mathbf{v}) = 0,
$$

$$
\rho \left( \frac{\partial \mathbf{v}}{\partial s} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla \cdot \mathbf{P} + \frac{\rho \mathbf{v}}{2E(0)} \int \omega \, dV,
$$

$$
\rho \left( \frac{\partial T}{\partial s} + (\mathbf{v} \cdot \nabla) T \right) = -\nabla \cdot \mathbf{J} - \mathbf{P} : \nabla \mathbf{v} - \omega + \frac{\rho T}{E(0)} \int \omega \, dV.
$$

with the following constitutive equations
\[ P_{ij} = \rho T \delta_{ij} - \eta_0 \sqrt{T} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - (\nabla \cdot \mathbf{v}) \delta_{ij} \right), \tag{39} \]

\[ J = -k_0 \sqrt{T} \nabla T - \mu_0 \frac{T^{3/2}}{\rho} \nabla \rho, \]

\[ \omega = \omega_0 \rho^2 T^{3/2}, \]

where \( \eta_0, k_0, \mu_0, \) and \( \omega_0 \) do not depend on density or temperature but on the dissipation coefficient \( q \). In particular, \( \omega_0 \) and \( \mu_0 \) vanish with \( q \).

In the thermostated state, the HCS reduces to a non-equilibrium steady state with a continuous energy supply that compensates the energy dissipation. As there is no energy scale, we fix the reference temperature to be one, so that \( E(0) = N \). The HCS is then characterized by \( \{ \rho = \rho_H, T = 1, \mathbf{v} = 0 \} \). The thermostating, then, produces a stationary state for the granular fluids where analysis are simpler.

A linear analysis of the hydrodynamic equations, predicts that this homogeneous state is unstable under certain conditions of density, system size, and dissipativity \([26,29,34,35,46]\). Considering the dissipativity coefficient \( q \) as a bifurcation parameter, while increasing \( q \) at constant density and number of grains, the system first develops an instability characterized by two counterflows, the shearing instability, and then either a clustering regime in which the density becomes inhomogeneous or a vortex state where many small vortices develop throughout the system.

### The Shearing Instability

The thermostating formalism, that puts the HCS into an stationary state, and the relative simplicity of the model allows for a complete nonlinear analysis on the instability. Consider a two-dimensional system composed of \( N \) grains interacting with the IHS model in a square box of size \( L \) that has periodic boundary conditions in both directions.

To study the stability of the HCS, we consider the perturbation \( \rho = \rho_H + \delta \rho, \mathbf{v} = \delta \mathbf{v}, \) and \( T = 1 + \delta T \). Taking the (discrete) Fourier transform of the linearized hydrodynamic equations around HCS, it is easy to check that the transverse velocity perturbation decouples from the rest and satisfies the equation

\[ \rho_H \frac{\partial \delta \mathbf{v}_{k,\perp}}{\partial \tau} = \left( -\frac{4k^2 \eta_0}{L^2} - \eta_0 + \frac{\rho_H^2 \omega_0}{2} \right) \delta \mathbf{v}_{k,\perp}, \quad \{ k_x, k_y \} = 0, \pm 1, \pm 2, \ldots, \tag{40} \]

For small values of \( \omega_0 \) (proportional to the dissipation) the perturbations \( \delta \mathbf{v}_{k,\perp} \) decay exponentially (the case \( k = 0 \) should not be taken into account since the center of mass velocity is strictly zero). But there exists a critical value of \( \omega_0 \) for which the right side vanishes, thus indicating the stability limit of the corresponding mode. The first modes to become unstable correspond to \( |k| = 1 \) (i.e., \( k_x = \pm 1, k_y = 0 \) and \( k_x = 0, k_y = \pm 1 \)). The instability threshold for \( \omega_0 \) is then given by
The stability for the other modes has been studied previously [35]. In this last reference it was shown that for low dissipation, the first instability that arises is indeed the transverse velocity instability.

The origin of the instability can be understood also in terms of the real-time hydrodynamics. In fact, the relaxation of the transverse hydrodynamic velocity is basically due to the viscous diffusion, which depends on the system size, whereas the cooling process is governed by local dissipative collisions. There exists therefore a system length beyond which the dissipation of thermal energy is faster that the relaxation of the transverse hydrodynamic velocity. The latter will then increase, when observed on the scale of thermal motion, thus producing the shearing pattern.

In this section we propose to work out the explicit form of the velocity field beyond the instability. The calculations are tedious and quite lengthy, so that here we only describe explicitly the basic steps. We start by taking the Fourier transform of the full nonlinear hydrodynamic equations, obtaining a set of coupled nonlinear equations for the modes $\{\delta \rho_k, \delta T_k, \delta v_{k1}, \delta v_{k2}\}$, where $\delta v_{k1}$ represents the longitudinal component of the velocity field. Close to the instability ($\omega_0 \approx \tilde{\omega}_0, |k| = 1$), the modes $\delta v_{k1}$ exhibit a critical slowing down, whereas the other hydrodynamic modes decay exponentially (Ref. [35]). On this slow time scale, the “fast” modes $\{\delta \rho_k; \delta T_k; \delta v_{k2}; \delta v_{k1}, k \neq 1\}$ can be considered as stationary, their time dependence arising mainly through $\delta v_{k1}$. Setting the time derivatives of these fast modes to zero one can express them in terms of the slow modes $\delta v_{k1}$. If now one inserts the so-obtained expressions into the evolution equation for the slow modes, one gets a set of closed nonlinear equations for $\delta v_{k1}$ (adiabatic elimination [47,48]), usually referred to as normal form or amplitude equations [48]. Note that such a calculation is only possible close to the instability threshold, where the amplitude of $\delta v_{k1}$ approaches zero as $\omega \to \tilde{\omega}_0$. On the other hand, in this limit the only Fourier modes that will have large amplitudes are the transverse velocity modes with wave-vector equal to $\pm 2\pi/L$ (i.e., $|k| = 1$). There are four such modes

$$\delta v_{k1} = \begin{cases} A_1, & k = (1,0) \\ A_1^*, & k = (-1,0) \\ A_2, & k = (0,1) \\ A_2^*, & k = (0,-1). \end{cases}$$

After some tedious algebra, one finds

$$\rho \frac{dA_1}{ds} = \left( -\frac{4\pi^2}{L^2} \eta_0 + \frac{\rho H^2 \omega_0}{2} \right) A_1 - 4\pi^2 L^{-2} \eta_0 \left( C_1 |A_1|^2 + C_2 |A_2|^2 \right) A_1,$$  

$$\rho \frac{dA_2}{ds} = \left( -\frac{4\pi^2}{L^2} \eta_0 + \frac{\rho H^2 \omega_0}{2} \right) A_2 - 4\pi^2 L^{-2} \eta_0 \left( C_1 |A_2|^2 + C_2 |A_1|^2 \right) A_2,$$

where

$$\tilde{\omega}_0 = \frac{8\pi^2 \eta_0}{\rho H L^2}.$$

The stability for the other modes has been studied previously [35]. In this last reference it was shown that for low dissipation, the first instability that arises is indeed the transverse velocity instability.
The amplitude equations (43) and (44) admit different stationary solutions. Below the critical point, the motionless solution \((A_1 = A_2 = 0)\) is the stable one. As we cross the critical point this solution becomes unstable. A linear stability analysis of the Eqs. (44) shows that the shearing state solution \((|A_1| = \hat{A}, A_2 = 0\) or \(A_1 = 0, |A_2| = \hat{A}\)) is stable, where

\[
\hat{A} = \sqrt{\frac{1}{C_1} \left( \frac{\rho_H^2 L^2 \omega_0}{8 \pi^2 \eta_0} - 1 \right)}
\]  

(47)

The occurrence of the shearing states in either the \(x\) or \(y\) direction depends on the initial state. In a statistical sense, they are equally probable. For example, in the case that the system chooses the solution \(\{A_1 = \hat{A}, A_2 = 0\}\), the velocity field reads

\[
v = 2\hat{A} \cos(2\pi x/L) \hat{y},
\]

(48)

where \(\hat{y}\) represents the unit vector in \(Y\) direction. The density and temperature fields are modified by the presence of the instability

\[
\delta T = -(\hat{A})^2 \left[1 + 4(1 - C_1) \cos(4\pi x/L)\right],
\]

(49)

\[
\delta \rho = 4 \rho_H (\hat{A})^2 (1 - C_1) \cos(4\pi x/L).
\]

(50)

The temperature decreases globally, since part of the energy is taken by the convective motion. Moreover, because of the viscous heating, the temperature profile exhibits a spatial modulation, i.e., it is higher where the viscous heating is higher. The density profile also shows a spatial modulation that keeps the pressure homogeneous.

Assuming the molecular chaos hypothesis, the mean collision rate \(\bar{v}\) and the dissipation rate \(\overline{\omega}\) can be computed as well,

\[
\bar{v} = \frac{2\sqrt{\pi}}{V \rho_H} \int \rho^2 \sqrt{T} \, dV = \nu_0 \rho_H \left(1 - \frac{\hat{A}^2}{2}\right),
\]

(51)

\[
\overline{\omega} = \frac{1}{V} \int \omega \, dV = \omega_0 \rho_H^2 \left(1 - \frac{3\hat{A}^2}{2}\right).
\]

(52)

These relations show that the global decrease of the temperature leads to corresponding decreases of the collision frequency and dissipation rate.

Contrary to elastic fluids, here, the convective energy is comparable to the thermal energy. In fact, as will be shown in the MD simulations, in a well developed
FIGURE 8. Mean collision frequency $\nu$ and dissipation rate $\dot{\omega}$ as a function of the dissipativity $q$ obtained in molecular dynamics simulations with $N = 10000$ particles and density $\rho_H = 0.005$. The lines are drawn for easier reading of the graphs.

Shearing state up to half of the total kinetic energy corresponds to the convective motion. The microscopic source of this phenomenon lies in the fact that only the relative energy is dissipated in binary collisions, i.e., the center-of-mass energy is conserved. In other words, the thermal energy is dissipated but the convective one is conserved. This asymmetry in the energy dissipation mechanism is at the very origin of the shearing instability.

We have done MD simulations of the IHS system in the thermostated regime. Simulations were done for system made of $N = 10000$ hard disks with a global number density $\rho_H = 0.005$. Inelastic collision rules are adopted, with a dissipativity varying from $q = 0.0$ to $0.12$. The boundary conditions are periodic in all directions.

In Fig. 8 the collision frequency and the temperature dissipation rate are presented as a function of the dissipating coefficient $q$. As expected, the shearing instability is associated with an abrupt decrease of these functions. It must be
noted that the decreasing of the collision frequency is more than 30%, which corresponds to a global decrease of the temperature of more than 50%. This means that when the shearing is fully developed, about half the total kinetic energy is taken by the macroscopic motion. This phenomenon is typical of granular media and has no counterpart in elastic fluids.

The critical dissipativity $\eta_0$ and the slopes of the collision frequency and dissipation rate above the critical point are computed from the simulation results.

$$q_0 = 0.0686$$  \hspace{1cm} (53)

$$\left. \frac{d\eta}{dq} \right|_{q=q_0^+} = -0.167$$  \hspace{1cm} (54)

$$\left. \frac{d\Delta}{dq} \right|_{q=q_0^+} = -0.00466$$  \hspace{1cm} (55)

To compare these results with our theoretical predictions we need the explicit form of the transport coefficients, up to critical dissipativity. As the critical dissipativity is small we can use the quasi-elastic approximation for the transport coefficients (that is, taking the first nontrivial order in $q$) [49,33]

$$\omega_0 = 4\sqrt{\pi q}, \quad \eta_0 = \frac{1}{2\sqrt{\pi}}, \quad k_0 = 2/\sqrt{\pi}, \quad \mu_0 = 0. \hspace{1cm} (56)$$

Replacing the above approximations for the transport coefficients in Eq. (41) and in Eqs. (45) and (47), the critical dissipativity and the amplitude of the shearing state are given by

$$\hat{q} = \frac{\pi}{\rho_0 L^2}, \quad \hat{A} = \sqrt{\frac{30 \delta q}{29 q}} \hspace{1cm} (57)$$

Then, for the presented simulation, we predict

$$q_0 = 0.0628$$  \hspace{1cm} (58)

$$\left. \frac{d\eta}{dq} \right|_{q=q_0^+} = -0.146$$  \hspace{1cm} (59)

$$\left. \frac{d\Delta}{dq} \right|_{q=q_0^+} = -0.00438$$  \hspace{1cm} (60)

which shows a good accord with the observed values. The discrepancy is due to the quasi-elastic approximation for the transport coefficients.
FIGURE 9. (a) Amplitude of the $k_x = \pi/L$ cosine component of the momentum density field as a function of the dissipativity $q$. (b) Amplitude of the $k_x = 2\pi/L$ cosine component of the density field as a function of the dissipativity $q$. The dots are the results of molecular dynamics simulations, the dashed line is the full nonlinear theory prediction, and the solid line is the nonlinear theory prediction where the critical point is taken from the fit. The simulations were done in a channel with $N = 10000$ particles and density $\rho_H = 0.005$. 
Since the system is periodic, the developed convective patterns can diffuse in
the direction perpendicular to the flow (the phases of the complex amplitudes \(A_i\)
are arbitrary due to Galilean invariance). As a result, the average hydrodynamic
fields remain vanishingly small, mainly because of “destructive” interference. To
overcome this difficulty we have performed another series of simulations, keeping
periodic boundary conditions in the vertical direction, while introducing a pair of
stress-free and perfectly insulating parallel walls in the horizontal direction (in a
collision with a wall the tangential velocity is conserved whereas the normal one is
inverted). As a consequence, the total vertical momentum is conserved, which will
be simply set to zero initially.

The nonlinear analysis for this case is similar to the periodic one, except that here
the direction of the flow pattern remains always parallel to the walls. Furthermore,
the unstable wave-vector is now \(k = \pi/L\), because of the fixed boundary conditions.
As a result all the previous predictions remain valid, except that everywhere \(L\) must
be replaced by \(2L\).

We have used the very same number of particles and density for this series of
simulations, but, of course, the different boundary conditions produce a new critical
dissipativity. The observed critical value is \(q_0 = 0.0163\) and the predicted one is
\(q_0 = 0.0157\).

Equations (48) and (50), once \(L\) is replaced by \(2L\), indicate that the perturbation
of the transverse momentum density \((j = \rho v)\) has a wave-vector equal to \(k_x = \pi/L\),
while the density has a wave-vector \(k_x = 2\pi/L\). In the simulations we computed the
amplitudes of these Fourier modes using the microscopic definitions for the particle
and momentum densities. Figure 9 show the predicted and computed Fourier modes
amplitudes. The predictions are in good agreement with the simulations in the
neighborhood of the critical point, showing that not only the average quantities
like the collision frequency are well predicted, but also the whole hydrodynamic
picture is correct.

THE LYAPUNOV SPECTRUM

The Lyapunov spectrum describes how quickly two identical systems with almost
identical initial conditions diverge in phase space, and is one of the few quantitative
measures of chaos. In this chapter, we calculate the Lyapunov spectrum of freely
cooling granular gas. \(N\) particles of radius \(a\) are placed in a two-dimensional domain
of size \(L_x \times L_y\). An initial condition is prepared by running a simulation with the
restitution coefficient \(r = 1\) so that the system attains an equilibrium state. Then,
\(r\) is set to the chosen value at \(t = 0\). The gas is kept in a steady state using the
method described in the previous chapter. In addition to the traditional choice
of \(r < 1\), we also consider \(r > 1\). This second choice does not correspond to any
physical granular material, but it is useful from a theoretical perspective.

The granular gas is very useful for comparing equilibrium and nonequilibrium
steady states. If we set \(r = 1\), we have the much studied hard sphere fluid, which is
an equilibrium system. It is then easy to generate a closely related nonequilibrium system by changing $r$ while leaving all the other parameters ($N$, $a$, $L_x$, and $L_y$) the same. We can approach the equilibrium system as closely as we like by making $r \to 1$. Furthermore, we can approach equilibrium from two directions: $r \to 1_-$ and $r \to 1_+$. 

**Definition of the Lyapunov Spectrum**

Consider a system at the point $\Gamma(0)$ in phase space of $L$ dimensions. The system follows some trajectory through phase space, arriving at $\Gamma(t)$ at time $t$. Next, consider a second system at at $\Gamma(0) + \delta \Gamma(0)$, where $\delta \Gamma(0)$ is infinitesimally small. After a time $t$, this system moves to $\Gamma(t) + \delta \Gamma(t)$. Then the Lyapunov exponent $\lambda$ is defined to be

$$\lambda = \lim_{t \to \infty} \frac{1}{t} \log \frac{|\delta \Gamma(t)|}{|\delta \Gamma(0)|}. \quad (61)$$

Note that $\lambda$ has units of inverse time. It is the growth (or decay) rate of the perturbation $\delta \Gamma$. It must therefore depend on $\delta \Gamma$. But since the perturbations $\delta \Gamma$ are infinitesimal, their dynamics are linear. Thus, once we know the Lyapunov exponent $\lambda$ associated with $L$ independent perturbations, we can calculate $\lambda$ for any other perturbation. This set of $L$ exponents is the Lyapunov spectrum. By convention, we associate $\lambda_1$ with the fastest growing direction $\delta \Gamma_1$; $\lambda_2$ with the fastest growing direction $\delta \Gamma_2$ which is also perpendicular to $\delta \Gamma_1 (\delta \Gamma_1 \cdot \delta \Gamma_2 = 0)$, and $\lambda_i$ with the fastest growing direction $\delta \Gamma_i$ with $\delta \Gamma_j \cdot \delta \Gamma_i = 0$ for $j < i$.

The number of dimensions $L$ of the phase space is typically large. For the two-dimensional granular gas $L = 4N$, because each particle contributes four degrees of freedom (two for its position and two for its velocity). In this paper, we consider $N = 100$. We calculate the Lyapunov spectrum using the algorithm of Dellago, Posch and Hoover [50]. When $r \neq 1$, nontrivial modifications are necessary [53].

**Equilibrium Spectra**

Equilibrium spectra of the hard sphere fluid (equivalent to the granular gas at $r = 1$) have already been discussed in the literature. [50-52], so we present only a very brief outline here. Equilibrium spectra have the special property that they are symmetric about $\lambda = 0$: each exponent $\lambda$ has a partner which is its negative. If we order the exponents according to the convention presented in Sec., we have $\lambda_i = -\lambda_{4N-i+1}$. This is called the “conjugate pairing rule”; $\lambda_i$ and $\lambda_{4N-i+1}$ form a “conjugate pair”. Thanks to the conjugate pairing rule, it is necessary to calculate only the first half ($1 \leq i \leq 2N$) of the spectrum at equilibrium. A typical example is shown in Fig. 10.

The spectrum has two parts: a continuous part, where the exponents fall onto a well defined continuous curve, and the discrete part, where the exponents appear
FIGURE 10. The spectrum of a $N = 100$ hard disk fluid ($r = 1$) in a rectangular domain ($L_x = 15a$, $L_y = 37.5a$). (a) The first $2N$ Lyapunov exponents (the second $2N$ are just the negative of the displayed exponents.) (b) The smallest positive exponents (note difference in the $x$-axis). The stars indicate the exponents shown in Fig. 11.

FIGURE 11. Lyapunov vectors $\delta \Gamma_1$, $\delta \Gamma_{195}$, $\delta \Gamma_{197}$ and $\delta \Gamma_{199}$ of a hard disk fluid with $N = 100$, $r = 1$, $L_x = 15a$, and $L_y = 37.5a$. The circles show the positions of the particles at the end of the simulation. Since all exponents were calculated during the same simulation, all the panels have circles in exactly the same position. The arrows show the components of $\delta \Gamma_i$ which describe the displacement in physical space of each particle. (The displacements in velocity space are nearly equivalent.) The lengths of the vectors are scaled by the maximum length. If the length of a vector is less than 0.16, no vector is shown.
FIGURE 12. The Lyapunov spectra of the freely cooling granular gas with \( N = 100, L_x = 15\alpha, L_y = 37.5\alpha \), and \( 0.7 \leq r \leq 1.3 \). Equilibrium \((r = 1)\) is marked with a thin solid line, and the transition to the shearing state at \( r \approx 0.945 \) is marked with the dashed line. The spectrum shown in Fig. 10 appears as a single column at \( r = 1 \); for each exponent, a dot is placed on the graph. Since all the exponents of Fig. 10 have the same value of \( r \), they fall in a vertical column. The spectra for the other values of \( r \) are displayed in the same way. This method of graphing allows the eye to easily follow the evolution of \( \lambda \) with \( r \). These spectra were computed by averaging over 2000 collisions per particle.

in small separated groups at certain values. The discrete exponents are associated with hydrodynamic-like perturbations [52], whereas the continuous exponents are linked to disorganized perturbations. Fig. 11 shows the perturbations underlying the exponents marked by the stars in Fig. 10.

The appearance of discrete groups of exponents can be explained by examining the Lyapunov vectors. For example, \( \lambda_{196} = \lambda_{197} \) because both exponents correspond to transverse, sinusoidal shearing perturbations (\( \delta \Gamma_{197} \) is shown in Fig. 11c, and \( \delta \Gamma_{196} \) is the same as \( \delta \Gamma_{197} \), but with a phase shift of \( \pi/2 \).) Likewise, the family of four exponents \( \lambda_{192} \ldots \lambda_{195} \) correspond to longitudinal sound waves. The compressive motion of the wave is visible in Fig. 11b. Changing \( L_y \) while keeping the density constant shows that the hydrodynamic exponents obey \( \lambda \sim 1/L_y \). The growth or decay of these perturbations, therefore, is not dissipative.
Non-Equilibrium Spectra

In Fig. 12, we show how the Lyapunov spectrum changes with $r$. The only thing which distinguishes the equilibrium spectrum from the nearby non-equilibrium ones is its symmetry about $\lambda = 0$. Not only are the exponents continuous functions of $r$, but so are their derivatives with respect to $r$. On the other hand, the spectrum's dependence on $r$ changes abruptly at $r = 0.945$. This is where the shearing instability that was discussed in the previous section occurs. On the level of the microscopic dynamics, the shearing transition is more significant than equilibrium.

Fig. 12 also shows that sound and shear waves behave differently as $r$ is varied. For sound waves, $\lambda$ increases as $r$ decreases, whereas the opposite occurs for sound waves.

The vanishing exponents split when $r \neq 1$. This happens because the thermostat causes a freely moving particle to accelerate (or deaccelerate if $r > 1$). Two vanishing exponents correspond to adding a constant vector to the velocities of all the particles. This sets the center of mass in motion. The thermostat accelerates this motion, causing these perturbations to grow (or shrink for $r > 1$). Another zero exponent corresponds to multiplying all the velocities by a constant factor. The thermostat causes this exponent to grow at twice the rate of the the velocity translation perturbation.

The Conjugate Pairing Rule

Another way to show the effect of inelasticity is to check the conjugate pairing rule, which states that the sum $\lambda_i + \lambda_{4N-i+1}$ is a constant independent of $i$. As discussed in Sec. , the Lyapunov spectra of equilibrium systems obey $\lambda_i + \lambda_{4N-i+1} = 0$. In nonequilibrium systems, this is no longer true, but in some [54] (but not all [55]) systems obey the conjugate pairing rule. In Fig. 13, we show $\lambda_i + \lambda_{4N-i+1}$ as a function of $i$ for two spectra from Fig. 11. In our case, $\lambda_i + \lambda_{4N-i+1}$ depends on $i$; even its sign can be change with $i$. For $i < 50$, $\lambda_i + \lambda_{4N-i+1} < 0$. For $i > 50$, the sum of the conjugate pairs seems to be slightly positive, but it is difficult to be certain because of the noise. However, for the vanishing exponents and the shearing exponents ($i \geq 196$), $\lambda_i + \lambda_{4N-i+1}$ is significantly positive. Note that the sum is also positive for $i = 190$ and $i = 191$. Inspecting $\delta\Gamma_{190}$ and $\delta\Gamma_{191}$, we find that these exponents are noisy second harmonics of the shearing wave. If $L_y$ and $N$ are increased while keeping density constant, these two modes separate from the continuum. Examining the spectra of systems with large $L_y$ and $N$ reveal several harmonics of the shear and sound waves. For the shearing waves, $\lambda_i + \lambda_{4N-i+1} > 0$ is independent of wavelength.
FIGURE 13. A check of the conjugate pairing rule, that is obeyed for $r = 1.0$ (circles), but not for $r = 0.95$ (stars). The behavior of $\lambda_i + \lambda_{4N-i+1} = 0$ is very different in the continuous (left panel) and discrete (right panel) parts of the spectrum.

FIGURE 14. Kolmogorov-Sinai entropy (solid line) and the collision frequency (dashed line), divided by the number of particles $N$. These two quantities are closely related, but not equivalent.
The Kolmogorov–Sinai Entropy

The Kolmogorov-Sinai entropy $h_{KS}$ gives the rate at which a forecast made from finite precision data loses accuracy. For closed systems, like the one considered in this paper, it is equal to the sum of all the positive Lyapunov exponents. In Ref. [50], this quantity has been calculated as a function of density and shown to be closely related to the collision frequency. In Fig. 14, we show the Kolmogorov-Sinai entropy and the collision frequency, normalized by the number of particles $N$. As a function of $r$, $h_{KS}$ is almost constant at equilibrium, and seems to have a maximum at a value of $r$ slightly larger than 1 (although it is difficult to be certain because of the noise). The biggest change in behavior occurs at the shearing instability, not at equilibrium. Fig. 14 reveals that $h_{KS}$ is roughly proportional to the collision rate $dC/ds$ (where $s$ is the rescaled time described in the previous chapter). This is to be expected, since the perturbations are magnified most rapidly during collisions.

CONCLUSIONS

We have presented MD methods for investigating non-equilibrium states. In the case of shock waves, it has been possible to formulate and apply a new method which is able to provide a detailed description of the microscopic processes involved in the appearance of plasticity or phase transformations. The Hugoniostat method has been successfully applied to the calculation of shock-Hugoniot curves for a Lennard-Jones crystal. It appears to be reliable for both thermodynamics and structural properties of the shocked material. The understanding of phenomena at this scale is essential if one wants to provide reliable input for macroscopic constitutive models.

This new method can now be applied to investigate in a more systematic way the effect of adding in the sample some realistic inhomogeneities like polycrystallinity or impurities. Preliminary results are confident that it is indeed possible to bridge the time and length scales up to mesoscopic scales where experimental results are available.

In the case of granular fluids, hydrodynamic equations for low dissipation grains are able to predict accurately the non-linear regime of the shearing instability. The equations are similar to those for normal fluids with, however, the inclusion of a new heat flux law (Eqs. 33 and 36) and the adding of a sink term. The fully developed nonlinear regime is characterized by an important transfer of thermal kinetic energy into convective energy. This process is characteristic of granular fluids and it is a consequence that energy is dissipated at collisions, that is at the microscopic scale.

We have computed the Lyapunov spectra for the same systems and we have compared closely related equilibrium and nonequilibrium systems. The equilibrium spectrum is distinguished by its symmetry, but the hydrodynamic exponents and the Kolmogorov–Sinai entropy change smoothly and continuously away from equilibrium. Not only are these Lyapunov exponents continuous functions of $r$ at
equilibrium, but so are their derivatives. On the other hand, the derivatives change discontinuously at the onset of the shearing instability. The relation of the hydrodynamic Lyapunov exponents to the hydrodynamic modes of a fluid is currently an open question which we are currently investigating.

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