THERMOSTATS: Analysis and Application

by

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Gaussian isokinetic and isoenergetic deterministic thermostats are introduced in the correct historical context with their later justification using Gauss' principle of least constraint. The Nosé-Hoover thermostat for simulating the canonical ensemble is also developed. For some model systems the Lyapunov exponents satisfy the conjugate pairing rule and a Hamiltonian formulation is obtained. We prove the conjugate pairing rule for nonequilibrium systems where the force is derivable from a potential. The generalised symplectic structure and Hamiltonian formulation is discussed. The application of such thermostats to the Lorentz gas is considered in some detail. The periodic orbit expansion methods are used to calculate averages and to categorise the generic transitions in the structure of the attractor. We prove that the conductivity in the nonequilibrium Lorentz gas is non negative.

I. INTRODUCTION

Deterministic thermostats have been used extensively in the molecular dynamics simulation of equilibrium and nonequilibrium fluids for the last 15 years [1,2]. Their use in that context has seemed natural to many workers, but those from different backgrounds have often treated changes to the basic equations of motion with some suspicion. Today with a much better understanding of unthermostatted nonequilibrium systems [3], it is possible to see thermostatted systems in general as a different and complimentary approach to the study of nonequilibrium states.

The fundamental question that is asked when studying nonequilibrium systems, in particular when calculating transport coefficients is the following. Consider a single system or an ensemble of systems which are unperturbed initially (see fig 1). If a constant steady external field is applied (at some arbitrary time origin), what is the subsequent behaviour of the system or the ensemble? We may be interested in the transient response, or simply the steady state response in the long time limit. Regardless of the details of the perturbation, the physical situation is the same. The applied external field does work on the system, and this work is converted to heat, which must be removed to achieve a steady state. Deterministic thermostats are a natural method to remove this heat.

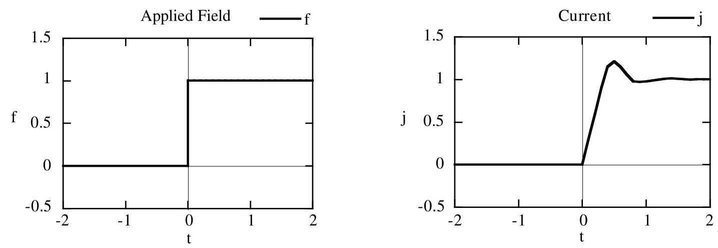


Fig 1. The nonequilibrium "thought experiment".

In molecular dynamics calculations it is almost universal to use periodic boundary conditions. If the number of particles in a fixed volume is small, that is significantly less than 10^{23}, then the fraction of particles near a wall is similar to the fraction in the bulk, and the simulation results will not reflect those of an infinite system. Periodic boundary conditions minimise the effect of boundaries and allows the simulation of homogeneous systems. The homogeneity is particularly useful as it means that it is easy to determine the state point. If we consider a possible experimental setup then the system is maintained at fixed temperature by placing it in contact with a "large" heat reservoir. Clearly this introduces boundary effects as the heat is transported from the place where it is generated to the reservoir, and associated with this flow is a temperature gradient. Once a temperature gradient is produced there will be a density gradient to maintain mechanical stability, and it becomes difficult to determine the state point to which the measured properties correspond.

One of the first realisations for thermostatted systems was that the method has some very important advantages for equilibrium molecular dynamics. The natural ensemble for a system evolving under Newtonian equations of motion is one where (N,V,E) are fixed. However, using a thermostat it is possible to simulate a canonical ensemble with (N,V,T) fixed. Many other ensembles can also be simulated using the techniques developed for thermostats, including constant pressure and constant enthalpy [4] systems.

To use a deterministic thermostat to maintain constant temperature it is necessary to have a phase variable expression for the temperature. At equilibrium we can use the equipartition theorem to define the kinetic temperature, so that

$$\tfrac{3}{2} N k_B T = \tfrac{1}{2} \sum_{i=1}^{N} m_i \mathbf{v}_i^{\,2} \tag{1}$$

The thermodynamic temperature can be defined using

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} \tag{2}$$

The identification of the temperature in the a micro-canonical ensemble has been considered recently [5] .

The definition of the temperature away from equilibrium is problematic. The kinetic and thermodynamic temperatures would be the same if the postulate of local thermodynamic equilibrium was exact. However we know that the energy, pressure, enthalpy etc. are all functions of the thermodynamic forces which drive the system away from equilibrium, and so presumably is the entropy. It is extremely unlikely that the field dependence of the entropy and the energy are precisely those required for the exact equivalence of the kinetic and thermodynamic temperatures for all nonequilibrium systems. The philosophy that is usually adopted is that the kinetic temperature is a convenient **operational** state variable to fix to obtain a steady state, and that there is a unique correspondence between the kinetic temperature and the true temperature.

II. CONSTRAINT DYNAMICS AND THERMOSTATS

Thermostats were first introduced as a practical method of performing nonequilibrium computer simulations at a fixed state point. Only later was it realised that these devices may have a fundamental role in the statistical mechanics of many-body systems. The first deterministic method for thermostatting molecular dynamics simulations was proposed simultaneously and independently by Evans and Hoover. Their method was to introduce a damping term into the equations of motion.

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \alpha m_i \dot{\mathbf{r}}_i \tag{3}$$

where the value of the damping is controlled by α where

$$\alpha = \frac{\sum_{i=1}^{N} \mathbf{F}_i \cdot \dot{\mathbf{r}}_i}{\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2} \tag{4}$$

This value of α keeps the kinetic energy (or kinetic temperature) exactly constant. The damping term removes the natural fluctuations in kinetic energy thus α can be either negative or positive depending upon the instantaneous value of $\{\mathbf{r}_i, \dot{\mathbf{r}}_i\}$. These equations were proposed by Hoover [6], and the same equation (3) with a damping term chosen to keep the internal energy constant, were proposed by Evans [7]. Initially the use of damping terms had no theoretical justification. It was a year before the connection with Gauss' principle was made [8].

A. The Fundamental Equations of Mechanics

Pars [9, 10] constructs mechanics using one of three different forms of what he calls the **fundamental equation**. Consider a general dynamical system with N equations of motion, subject to m constraints. We need to introduce the forces of constraint f_i, so the equations of motion become $m_i \ddot{x}_i = F_i + f_i$. If we consider a virtual displacement δx_i, at fixed time, which is consistent with the constraints, and that the forces of constraint f_i do no work on the system, we obtain the **first** fundamental equation

$$\sum_{i=1}^{N} \left(m_i \ddot{x}_i - F_i\right) \delta x_i = 0 \tag{5}$$

which is valid for an arbitrary virtual displacement. This is d'Alembert's principle, discovered by Lagrange in or about 1760 [11].

To obtain the **second** form of the fundamental equation we consider from the same configuration, and at the same instant, two different velocities for the system $\dot{x}_1, \dot{x}_2, \ldots, \dot{x}_N$ and $\dot{x}_1 + \Delta\dot{x}_1, \dot{x}_2 + \Delta\dot{x}_2, \ldots, \dot{x}_N + \Delta\dot{x}_N$. The (finite) velocity variations $\Delta\dot{x}_1, \ldots, \Delta\dot{x}_N$ then satisfy the **second** form of the fundamental equation (Jourdain 1908)

$$\sum_{i=1}^{N} \left(m_i \ddot{x}_i - F_i\right) \Delta\dot{x}_i = 0 \tag{6}$$

In this form both the configuration and time are given, and we consider the difference (either finite or infinitesimal) between any two possible velocities for the system.

The **third** form of the fundamental equation is obtained by considering two possible motions with the same configuration and velocity at time t, but with different accelerations, $\ddot{x}$ and $\ddot{x} + \Delta\ddot{x}$. The (finite) acceleration-variations $\Delta\ddot{x}_1, \ldots, \Delta\ddot{x}_N$ satisfy the equations for the virtual displacement, and we may write

$$\sum_{i=1}^{N} \left(m_i \ddot{x}_i - F_i\right) \Delta\ddot{x}_i = 0 \tag{7}$$

(used by Gauss and Gibbs). To summarise, in the first form we consider an infinitesimal virtual displacement from a given configuration. In the second form the configuration is not varied, and we use the difference between any two possible velocities. In the third form both coordinates and velocities are unvaried, and we use the difference between any two possible accelerations.

B. Gauss' principle of Least Constraint

Suppose the position and velocity of the system are given, and consider the square of the curvature C, regarded as a function of the accelerations

$$C(\ddot{\mathbf{x}}) = \tfrac{1}{2} \sum_{i=1}^{N} m_i \left(\ddot{x}_i - \frac{F_i}{m_i} \right)^2 \tag{8}$$

The values of $\ddot{x}$ considered are those that are possible for the system. Gauss's principle of least constraint [12] states that the actual acceleration is that for which C is a minimum. If we consider a variation of $\ddot{x}_i$ to $\ddot{x}_i + \Delta\ddot{x}_i$, the proof is straightforward

$$\Delta C = \tfrac{1}{2} \sum_{i=1}^{N} m_i \left(\Delta\ddot{x}_i\right)^2 + \sum_{i=1}^{N} \left(m_i \ddot{x}_i - F_i\right) \Delta\ddot{x}_i$$

If $\ddot{x}_i$ is the actual physical acceleration then last term is zero using the third fundamental form, and any variation about $\ddot{x}_i$ increases C. To find the equations of motion for a given system we need only the less powerful result that C is stationary for the actual motion $\delta C = 0$. Notice that in the application of Gauss's principle we are concerned with the simple algebraic problem of minimising a quadratic form, the curvature C.

C. Geometric Derivation

For an arbitrary constraint problem we can write the constraint as a function of positions, velocities and time

$$g(\mathbf{r}, \dot{\mathbf{r}}, t) = 0 \tag{9}$$

where g is the particular functional form. If this equation is differentiated with respect to time, we obtain an acceleration dependent constraint equation,

$$\mathbf{n}(\mathbf{r}, \dot{\mathbf{r}}, t) \cdot \ddot{\mathbf{r}} = s(\mathbf{r}, \dot{\mathbf{r}}, t) \tag{10}$$

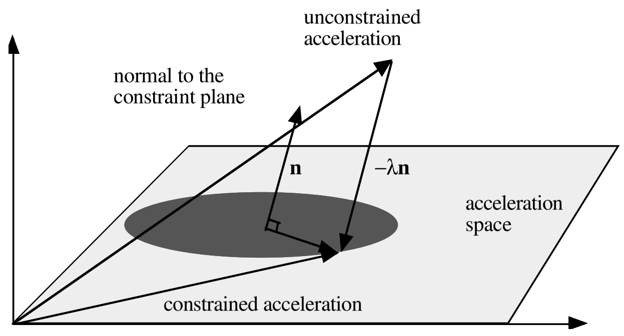


Fig 2 The geometric interpretation of Gauss' principle of least constraint.

We refer to this equation as the *differential constraint equation* and it is the equation for the *constraint* plane. $\mathbf{n}$ is the vector normal to the constraint plane and s is the shortest distance between the plane and the origin. In the absence of the constraint the system would evolve according to Newton's equations of motion (see fig 2). This trajectory would in general not satisfy the constraint. The only accelerations which do continuously satisfy the constraint, are those which terminate on the constraint plane. To obtain the constrained acceleration we must uniquely project the unconstrained acceleration back into the constraint plane.

Gauss' principle states that the trajectories actually followed are those which deviate as little as possible, in a least squares sense, from the unconstrained Newtonian trajectories.

The projection which the system actually follows is the one which minimises the magnitude of the constraint force. This means that the force of constraint is parallel to the normal to the constraint surface. The Gaussian equations of motion are then $\ddot{\mathbf{r}} = \mathbf{F} - \lambda\mathbf{n}$ where λ is a Gaussian multiplier which is a function of position, velocity and time.

To calculate the multiplier we use the differential form of the constraint function. Substituting for the acceleration we find that

$$\lambda = \frac{\mathbf{n}\cdot\mathbf{F} - s}{\mathbf{n}\cdot\mathbf{n}} \tag{11}$$

Notice that the original constraint equation is never used explicitly. Gauss' principle only uses the **differential** form of the constraint equation, hence the precise value of the constrained quantity is undetermined. The constraint only acts to stop its value changing.

From an operational point of view a much simpler derivation of constrained equations of motion is possible using Lagrange multipliers. Gauss' principle reduces to finding the minimum of $C(\ddot{\mathbf{r}})$, subject to the constraint. If $G(\ddot{\mathbf{r}})$ is the acceleration dependent form of the constraint, then the constrained equations of motion are obtained from

$$\frac{\partial}{\partial \ddot{\mathbf{r}}}\left(C - \lambda G\right) = 0 \tag{12}$$

It is easy to see that the Lagrange multiplier λ, is equal to minus the Gaussian multiplier.

D. Gaussian Iso-Kinetic Thermostat (GIK)

We illustrate this method by deriving equations of motion for which the kinetic energy is a constant of the motion. The constraint function is

$$g(\mathbf{r},\dot{\mathbf{r}},t) = \sum_{i=1}^{N} \tfrac{1}{2} m_i \dot{\mathbf{r}}_i^2 - K_0 = 0 \tag{13}$$

Differentiating once with respect to time gives the equation for the constraint plane

$$G(\mathbf{r}_i,\dot{\mathbf{r}}_i,\ddot{\mathbf{r}}_i,t) = \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i = 0 \tag{14}$$

Therefore to obtain the constrained Gaussian equations we minimise the curvature C subject to the constraint equation (14). That is

$$\frac{\partial}{\partial \ddot{\mathbf{r}}_i}\left(\tfrac{1}{2}\sum_{j=1}^{N} m_j \left(\ddot{\mathbf{r}}_j - \frac{\mathbf{F}_j}{m_j} \right)^2 + \alpha \sum_{j=1}^{N} m_j \dot{\mathbf{r}}_j \cdot \ddot{\mathbf{r}}_j \right) = 0 \tag{15}$$

This gives the thermostatted equation of motion to be equation (3). Eliminating $\ddot{\mathbf{r}}_i$ using the differential form of the constraint equation (14), we find that the multiplier is again given by equation (4).

E. The GIK Thermostat for External fields

Using Gauss' Principle, the isokinetic equations of motion for a system subject to an external field can be written as,

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i F_e(t) \tag{16}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i F_e(t) - \alpha \mathbf{p}_i \tag{17}$$

where $\mathbf{C}_i$ and $\mathbf{D}_i$ are phase variables which describe the coupling between the system and the external field [1,4]. The Gaussian multiplier is

$$\alpha = \alpha_0 + \alpha_1 F_e(t) = \frac{\sum_i \frac{1}{m_i}\mathbf{F}_i\cdot\mathbf{p}_i}{\sum_i \frac{1}{m_i}\mathbf{p}_i^2} + \frac{\sum_i \frac{1}{m_i}\mathbf{D}_i\cdot\mathbf{p}_i}{\sum_i \frac{1}{m_i}\mathbf{p}_i^2} F_e(t) \tag{18}$$

In writing these equations we are assuming the total momentum is fixed at zero. It is important to keep in mind that the expression for the multiplier depends explicitly on the external field and implicitly on time. Therefore we can separate the multiplier into field dependent and field independent parts α_0, α_1.

If we define the internal energy to be

$$H_0 = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \Phi \tag{19}$$

then we can characterise the energy flow to and from the system. If the system is perturbed by an external field, then that field does work on the system (supplying energy), and that energy must be extracted from the system through the thermostat in order to maintain a steady state. Differentiating equation (19) and substituting the thermostatted equations of motion (16) and (17) gives

$$\dot{H}_0 = -J(\mathbf{q},\mathbf{p})F_e(t) - 3NkT\alpha(\mathbf{q},\mathbf{p}) \tag{20}$$

where the dissipative flux $J(\mathbf{q},\mathbf{p})$ is defined by

$$J(\mathbf{q},\mathbf{p}) = -\sum_{i=1}^{N}\left(\frac{1}{m_i}\mathbf{p}_i \cdot \mathbf{D}_i(\mathbf{q},\mathbf{p}) - \mathbf{F}_i \cdot \mathbf{C}_i(\mathbf{q},\mathbf{p})\right) \tag{21}$$

If a steady state is achieved then we expect a balance between the average energy supplied to the system by the external field, and the average energy removed by the thermostat, so that $\langle \dot{H}_0 \rangle = 0$, and

$$\langle \dot{H}_0 \rangle = -\langle J \rangle F_e - 3NkT\langle \alpha \rangle = 0 \tag{22}$$

Then we can define a field dependent transport coefficient by

$$a(F_e) = -\frac{\langle J \rangle}{F_e} \tag{23}$$

which may be related to a Navier-Stokes transport coefficient a_{NS} in the limit $F_e \to 0$. From equation (22) it follows that the field dependent transport coefficient can also be given by

$$a(F_e) = \frac{3NkT}{F_e^2}\langle \alpha \rangle \tag{24}$$

Thus the transport coefficient can be calculated in two ways; either directly from the average current using equation (23), or from the average thermostatting multiplier.

F. The Gaussian Isoenergetic Thermostat (GIE)

It is easy to show that if Gauss' Principle is used to fix the internal energy, then the equations of motion are the same as those in equations (16) and (17), but the thermostatting multiplier is now

$$\alpha = \frac{\sum_{i=1}^{N}\left(\frac{1}{m_i}\mathbf{D}_i \cdot \mathbf{p}_i - \mathbf{C}_i \cdot \mathbf{F}_i\right)}{\sum_{i=1}^{N}\frac{1}{m_i}\mathbf{p}_i^2} F_e(t) \tag{25}$$

In the isoenergetic case it is clear that the multiplier vanishes when the external field is zero. This is as expected since in the absence of an external field, the total energy is conserved.

Gauss' principle can also be used to fix the value of other phase variables in a many particle simulation, for example the pressure [13]. Indeed, one approach in nonequilibrium systems [1] has been to use Gauss' principle to move between constant field simulations (the Thévenin ensemble) and constant current simulations (the Norton ensemble). However, there appear to be cases where Gauss' principle does not give physically meaningful results. For example, if one uses Gauss' principle to maintain a constant heat flow, then a comparison with linear response theory shows that the Gaussian equations of motion **cannot** be used to calculate thermal conductivity [2]. The correct application of Gauss' principle seems to be limited to arbitrary holonomic constraints and to nonholonomic constraint functions which are **homogeneous** functions of the velocities.

G. The GIK Distribution Function

The ergodically generated equilibrium distribution function f for GIK dynamics, can be obtained by solving the Liouville equation [14]. Here the distribution function is $f(\Gamma) \equiv f(\mathbf{q},\mathbf{p}) \equiv f(\mathbf{q}_1,\ldots,\mathbf{q}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ where the phase point Γ completely describes the state of a single N-particle system. Consider the total time derivative of f, then from the Liouville equation, we see that,

$$\frac{df}{dt} = -f\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = -f\left(\sum_{i=1}^{N}\frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \sum_{i=1}^{N}\frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i\right) \tag{26}$$

At equilibrium the Gaussian isokinetic equations (3) and (4) can be written as a pair of first order equations as

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i - \alpha \mathbf{p}_i \tag{27}$$

$$\alpha = \frac{\sum_i \frac{1}{m_i} \mathbf{F}_i \cdot \mathbf{p}_i}{\sum_i \frac{1}{m_i} \mathbf{p}_i^2} = \frac{-\dot{\Phi}}{2K_0} \tag{28}$$

where $\dot{\Phi}$ is the time derivative of the total potential energy. Notice that the $\dot{\mathbf{q}}_i$ equation is independent of $\mathbf{q}_i$. Computing the second term in equation (26) we get $3N$ identical terms from the $3N$ derivatives, $\alpha(\partial/\partial \mathbf{p}_i)\cdot \mathbf{p}_i$, but using conservation of total momentum only $3N-3$ of these terms are independent. We also get $3N$ terms from $\mathbf{p}_i \cdot \partial\alpha/\partial \mathbf{p}_i$ which sum to give $-\alpha$. Thus equation (26) becomes

$$\frac{df}{dt} = f \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{p}_i} \cdot (\alpha \mathbf{p}_i) = (3N-4)\alpha f = -\frac{(3N-4)}{2K_0} \dot{\Phi} f \tag{29}$$

Integrating both sides with respect to time gives

$$f_T(\Gamma) = \frac{\exp[-\beta\Phi(\Gamma)]\delta(K(\Gamma)-K_0)}{\int d\Gamma \exp[-\beta\Phi(\Gamma)]\delta(K(\Gamma)-K_0)} \tag{30}$$

where we identify $\beta = (k_B T)^{-1} = (3N-4)/2K_0$. This is consistent with the fact that the GIK equations have four constants of the motion; the kinetic energy, and the three components of the total linear momentum. We call this distribution the isokinetic distribution function and it has a very simple form: a microcanonical distribution of kinetic degrees of freedom, and a canonical distribution of configurational degrees of freedom.

H. The Nosé Hamiltonian for the canonical ensemble

The Nosé method [15] considers an extended system with an additional degree of freedom s, which acts as an external heat reservoir, interacting with the system through the velocities of the particles. The potential energy that Nosé chose to associate with this new degree of freedom was $(g+1)k_B T \ln s$, where g is related to the number of degrees of freedom of the system. It is essentially the choice of the potential for s which leads to dynamics which generate the canonical ensemble. The Hamiltonian for N particles moving in a potential Φ (which may contain both interactions between the particles and external fields) is

$$H_N(\mathbf{q}, \pi, s, p_s; \lambda) = \sum_{i=1}^{N} \frac{\pi_i^2}{2ms^2} + \Phi(\mathbf{q}) + \frac{p_s^2}{2Q} + (g+1)k_B T \ln s \tag{31}$$

where Q is an arbitrary constant corresponding to the *mass* of the reservoir. The time variable λ which appears in the Hamilton equations of motion (but not on the RHS of equation 31) need not correspond to physical time. The equations of motion generated by this Hamiltonian are

$$\frac{d\mathbf{q}_i}{d\lambda} = \frac{\pi_i}{ms^2} \qquad \frac{d\mathbf{p}_i}{d\lambda} = \mathbf{F}_i \tag{32}$$

$$\frac{ds}{d\lambda} = \frac{p_s}{Q} \qquad \frac{dp_s}{d\lambda} = \sum_{i=1}^{N} \frac{\pi_i^2}{m_i s^3} - \frac{(g+1)k_B T}{s} \tag{33}$$

Eliminating the variable p_s from the equations of motion, a single second order differential equation for s is obtained. If the system is at equilibrium, the average force on the s coordinate must be zero, so that

$$\left\langle \frac{d^2 s}{d\lambda^2} \right\rangle = \frac{1}{Q} \left\langle \sum_{i=1}^{N} \frac{\pi_i^2}{m_i s^3} - \frac{(g+1)k_B T}{s} \right\rangle = 0 \tag{34}$$

If we choose the Hamiltonian momenta to be related to the physical momenta by $\pi_i = s\mathbf{p}_i$, then

$$\left\langle \sum_{i=1}^{N} \frac{\pi_i^2}{m_i s^3} \right\rangle = \left\langle \sum_{i=1}^{N} \frac{1}{s} \frac{\mathbf{p}_i^2}{m_i} \right\rangle = (g+1)k_B T \left\langle \frac{1}{s} \right\rangle \tag{35}$$

This suggests a particular dynamical average that is equal to the temperature $k_B T$ and hence suggests the general form for the dynamical average of an arbitrary phase variable A,

$$k_B T = \frac{\frac{1}{(g+1)} \left\langle \sum_{i=1}^{N} \frac{1}{s} \frac{\mathbf{p}_i^2}{m_i} \right\rangle}{\left\langle \frac{1}{s} \right\rangle} \quad \Rightarrow \quad \langle A \rangle_\lambda = \frac{\int_0^T \frac{d\lambda}{s} A(\lambda)}{\int_0^T \frac{d\lambda}{s}} \tag{36}$$

Comparing this with the usual physical time average suggests that the physical time is related to the Hamiltonian time by $dt = d\lambda/s$. This type of variable transformation, where both the momenta and the time change $(\pi_i, \lambda) \Rightarrow (\mathbf{p}_i, t)$, will be used many times in what follows.

To calculate the equilibrium distribution function for the Nosé Hamiltonian we use the fact that for an ergodic system, the extended system is microcanonical. Hence from equation (31)

$$Z = \frac{1}{N!}\int d\mathbf{q}d\pi ds dp_s \delta\left(\sum_{i=1}^{N}\frac{\pi_i^2}{2m_i s^2} + \Phi(\mathbf{q}) + \frac{p_s^2}{2Q} + (g+1)k_B T\ln s - E\right) \tag{37}$$

where $\mathbf{q}$ and π are $3N$-dimensional vectors, $\mathbf{q} \equiv (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ and $\pi \equiv (\pi_1, \ldots, \pi_N)$. If we change variables from π to $\mathbf{p}$, where $\mathbf{p} \equiv (\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and $\mathbf{p}_i = \pi_i/s$ for all i, then

$$Z = \frac{1}{N!}\int d\mathbf{q}d\mathbf{p}ds dp_s\, s^{3N}\, \delta\left(H_0(\mathbf{q},\mathbf{p}) + \frac{p_s^2}{2Q} + (g+1)k_B T\ln s - E\right) \tag{38}$$

where $H_0(\mathbf{q},\mathbf{p}) = \sum_i \mathbf{p}_i^2/2m_i + \Phi(\mathbf{q})$ is the usual N particle Hamiltonian. The integral over s can be performed as the only contributions come from the zeros of the argument of the delta function. If $G(s) = H_0(\mathbf{q},\mathbf{p}) + p_s^2/2Q + (g+1)k_B T\ln s - E$, then G has only one zero, that is

$$s_0 = \exp\left(-\frac{H_0(\mathbf{q},\mathbf{p}) + p_s^2/2Q - E}{(g+1)k_B T}\right) \tag{39}$$

Using the identity $\delta(G(s)) = \delta(s - s_0)/G'(s)$ it is easy to show that the integral over s gives

$$Z = \frac{1}{N!}\int d\mathbf{q}d\mathbf{p}dp_s \frac{1}{(g+1)k_B T}\exp\left(-\frac{1}{k_B T}\frac{3N+1}{g+1}\left(H_0(\mathbf{q},\mathbf{p}) + \frac{p_s^2}{2Q} - E\right)\right) \tag{40}$$

Here the choice $g = 3N$ cancels the factor inside the exponent. The integral over p_s is the infinite integral of a Gaussian and the result is

$$Z = \frac{1}{(3N+1)}\left(\frac{2\pi Q}{k_B T}\right)^{1/2}\frac{1}{N!}\int d\mathbf{q}d\mathbf{p}\exp\left(-\frac{H_0(\mathbf{q},\mathbf{p}) - E}{k_B T}\right) \tag{41}$$

If the variables $\mathbf{q}$, π, s, p_s are distributed microcanonically then variables $\mathbf{q}$ and $\mathbf{p}$ are canonically distributed.

I. The Nosé-Hoover Isokinetic Thermostat (NIK)

To compute averages in real physical time the equations of motion can be rewritten in terms of the physical variables $\mathbf{q}$, $\mathbf{p}$ and t, eliminating the Hamiltonian variables π, s, p_s, λ entirely [16]. We use the same transformation as above, $\pi_i = s\mathbf{p}_i$ and $dt = d\lambda/s$ to rewrite the Nosé equations of motion as

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i} \qquad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \zeta\mathbf{p}_i \tag{42}$$

$$\frac{ds}{dt} = \zeta s \qquad \frac{d\zeta}{dt} = \frac{1}{Q}\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - (g+1)k_B T\right) = \frac{1}{\tau^2}\left(\frac{K(\mathbf{p})}{K_0} - 1\right) \tag{43}$$

where $K_0 = (g+1)k_B T/2$ is the value of the kinetic energy corresponding to the target temperature, $K(\mathbf{p})$ is the instantaneous value of the kinetic energy, τ is a relaxation time which is related to the mass of the s degree of freedom ($\tau^2 = Q/2K_0$) and the multiplier $\zeta = p_s/Q$. The motion of the system can now be determined without reference to s. It is an irrelevant variable which can be ignored. The variable $d\zeta/dt$ is a function of $\mathbf{p}$ only, so the complete description of the system can be given in terms of the variables $\mathbf{q}$, $\mathbf{p}$ and ζ. Notice that a Nosé iso-energetic (NIE) thermostat can be constructed from equations (42) and (43) by replacing $K(\mathbf{p})$ by $E(\mathbf{q},\mathbf{p})$, and K_0 by E_0.

The N particle distribution function $f(\Gamma,\zeta)$ generated dynamically by the iso-kinetic Nosé-Hoover equations of motion can be obtained by solving the Liouville equation written in terms of physical variables $\mathbf{q}$, $\mathbf{p}$ and ζ. The Liouville equation for the total time derivative of $f(\Gamma,\zeta)$ is

$$\frac{df}{dt} = -f\left(\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma} + \frac{\partial}{\partial\zeta}\dot{\zeta}\right) \tag{44}$$

From the equations of motion (42) and (43) it is easy to see that $\dot{\zeta}$ is a function of $\mathbf{p}$, and hence independent of ζ. The only nonzero contribution to the right hand side comes from the $\mathbf{p}$ dependence of $\dot{\mathbf{p}}$, so that

$$\frac{d}{dt}\ln f = 3N\zeta \tag{45}$$

Consider the time derivative of the quantity $H_0 + \frac{1}{2}Q\zeta^2$

$$\frac{d}{dt}\left(H_0 + \tfrac{1}{2}Q\zeta^2\right) = \frac{dH_0}{dt} + Q\zeta\frac{d\zeta}{dt} = -(g+1)\zeta k_B T \tag{46}$$

If we take $g + 1 = 3N$, then from equations (45) and (46) we find that the equilibrium distribution function is the extended canonical distribution f_c, where

$$f_c(\Gamma,\zeta) = \frac{\exp\left[-\beta\left(H_0 + \tfrac{1}{2}Q\zeta^2\right)\right]}{\int d\Gamma d\zeta \exp\left[-\beta\left(H_0 + \tfrac{1}{2}Q\zeta^2\right)\right]} \tag{47}$$

In the Hoover representation of the equations of motion, the scaling variable s has been eliminated so the number of degrees of freedom of the system, changes from $3N+1$ to $3N$.

III. LYAPUNOV EXPONENTS FOR THERMOSTATTED SYSTEMS

A. The Lyapunov Sum Rule

One of the simplest connections between Lyapunov exponents and transport coefficients is the Lyapunov sum rule. For a GIK thermostat, and field dependent equations of motion, the Liouville equation is given by equation (29) as long as the field does not change phase space volume, or equivalently that the adiabatic incompressibility of phase space AIΓ is satisfied [1]. That is

$$\sum_{i=1}^{N}\left(\frac{\partial}{\partial \mathbf{q}_i}\cdot \mathbf{C}_i + \frac{\partial}{\partial \mathbf{p}_i}\cdot \mathbf{D}_i\right) = 0 \tag{48}$$

For a co-moving phase space volume element located at Γ, the number of ensemble members within the element N_0 does not change, so that the only change in f is due to the changing volume of the element. So

$$f(\Gamma,t) = \frac{N_0}{V(t)} = \frac{N_0}{V_0}\exp\left[-\sum_i \lambda_i t\right] \tag{49}$$

where the λ_i are local Lyapunov exponents (beginning at Γ for a time t). Thus

$$\frac{d}{dt}\ln f = -\sum_i \lambda_i = 3N\alpha + O(1) \tag{50}$$

where both λ_i and α are local properties of the trajectory segment. Combining these and averaging, we find that the field dependent transport coefficient is given

$$a\left(F_e\right) = -\frac{kT}{F_e^2}\sum_i \lambda_i + O(1) \tag{51}$$

The evaluation of the order one terms can often be done exactly, as for example for planar Couette flow [17].

B. The Conjugate Pairing Rule

The conjugate pairing rule is a more subtle connection between Lyapunov exponents and transport coefficients, which is not true in general. However, for those systems where it is satisfied, it shows that the thermostat acts democratically on each pair of degrees of freedom.

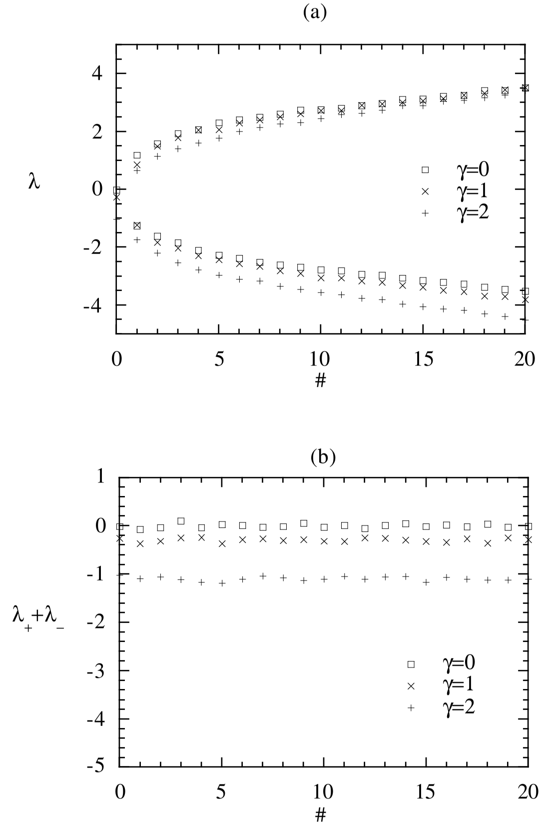


Fig 3: The Lyapunov spectrum for eight particle Couette flow in three-dimensions using the SLLOD algorithm and a GIK thermostat for reduced strain rates of 0, 1, 2 [18] a) The Lyapunov spectrum; b) the sum of conjugate pairs versus pair number.

The conjugate pairing rule states that if λ is a Lyapunov exponent then $C-\lambda$ is also an exponent, where C is the same for all pairs of exponents. For Hamiltonian systems $C=0$.

$$\lambda_+ + \lambda_- = C \tag{52}$$

The conjugate pairing rule was initially a result obtained numerical (from the data in fig 3) for the Lyapunov exponents of four and eight particle simulations of planar Couette flow using the SLLOD algorithm and GIK thermostat [18,1]. Later a proof of the conjugate pairing rule [19] in the limit as the number of particles $N\to\infty$ was obtained, but that argument is flawed. Below we present the correct derivation [20].

C. Proof of the Conjugate Pairing Rule

Here we prove the result exactly for a restricted case, that is, isokinetic thermostats and forces derivable from a potential Φ, for any value of N. There is an important difference between the present result and past statements of the conjugate pairing rule in that here, we explicitly single out two trivial exponents (equal to zero) which do not pair. These are due to the conservation of kinetic energy, and time translation symmetry. They sum to zero, and so should not be included with the other pairs of exponents, which sum to a different constant. Excluding these directions, we define the time evolution in a reduced $6N-2$-dimensional space, in which pairing appears exactly.

The GIK equations of motion in an external field take the form given in equation (27), where $\mathbf{F}$ is the total force given as a sum of inter-particle forces $\mathbf{F}_{int}$ and the external field $\mathbf{F}_{ext}$. Transforming these equations to remove the mass, using $\mathbf{q}_i'=\mathbf{q}_i\sqrt{m_i}$, $\mathbf{p}_i'=\mathbf{p}_i/\sqrt{m_i}$ and $\mathbf{F}_i'=\mathbf{F}_i/\sqrt{m_i}$ then removing the primes, gives

$$\dot{\mathbf{q}}=\mathbf{p} \qquad \dot{\mathbf{p}}=-\nabla\Phi-\alpha\mathbf{p}=\mathbf{F}-\alpha\mathbf{p} \tag{53}$$

$$\alpha=-\frac{\mathbf{p}\cdot\nabla\Phi}{\mathbf{p}\cdot\mathbf{p}} \tag{54}$$

where $\mathbf{q}\equiv(\mathbf{q}_1,\ldots,\mathbf{q}_N)$ and $\mathbf{p}\equiv(\mathbf{p}_1,\ldots,\mathbf{p}_N)$ are $3N$-dimensional vectors. Φ is a scalar potential that generates the total force $\mathbf{F}$.

There are two time dependent matrices which can be used to describe the evolution of a linear perturbation $\delta\Gamma$ in tangent space, and they both depend on the initial phase space point Γ. These are the infinitesimal and finite evolution matrices, T and L, respectively, defined by

$$\delta\dot{\Gamma}(t)=T(t)\delta\Gamma(t) \qquad \delta\Gamma(t)=L(t)\delta\Gamma(0) \tag{55}$$

The matrix T is usually obtained by differentiating the equations of motion, however, we will evaluate it in a restricted subspace of the tangent space, which is slightly more complicated. L can be obtained from T as the solution of

$$\dot{L}(t) = T(t)L(t) \tag{56}$$

with the initial condition $L(0) = I$. The Lyapunov exponents are defined as the logarithms of the eigenvalues of Λ, where

$$\Lambda = \lim_{t\to\infty}\left(L^T(t)L(t)\right)^{1/2t} \tag{57}$$

The co-moving basis vectors, which span the tangent space containing $\delta\Gamma$, rotate with the motion of the trajectory so as to remain perpendicular to the direction of increasing kinetic energy. This means that the finite time eigenvalues may be different to those obtained with fixed basis vectors, but in the long time limit the results are the same. We introduce $6N-2$ orthonormal basis vectors, none of which are exactly along the flow, and demand that a perturbation $\delta\Gamma$ be in the space spanned by these vectors. This effectively means that we are taking a Poincaré section, and considering the perturbed point to be the one at which the perturbed trajectory intersects with the $6N-2$ dimensional space spanned by the vectors. In general, the time elapsed along the perturbed trajectory t', runs at an infinitesimally different rate to t. We scale the time so that $\mathbf{p}\cdot\mathbf{p}=1$, and choose one unit vector $\mathbf{e}_0 = \mathbf{p}$. At an initial time, arbitrarily choose $3N-1$ unit vectors $\mathbf{e}_i$ which together with $\mathbf{e}_0$ form an orthonormal set in $3N$-space. This set of vectors $\mathbf{e}_i$ (where $i = 1,\ldots,3N-1$) is used in **both** position and momentum space to form the required basis. The separation of phase space into position and momentum space, while retaining the symplectic structure is what makes this proof possible in the isokinetic case. The perturbations are taken from the $6N-2$ dimensional subspace defined by the two sets of $\mathbf{e}_i$. This means that there are no perturbations in the direction of increasing kinetic energy and none directly along the flow (which contains a component of $\mathbf{e}_0$ in position space). Now, the equations of motion in $6N$ dimensional space may be written as

$$\frac{d\mathbf{q}}{dt} = \mathbf{p} \qquad \frac{d\mathbf{p}}{dt} = \dot{\mathbf{e}}_0 = \sum_{i=1}^{3N-1}\mathbf{f}\cdot\mathbf{e}_i\mathbf{e}_i \tag{58}$$

where $\mathbf{f} = -\nabla\phi$. If we choose, the unit vectors to have equations of motion

$$\dot{\mathbf{e}}_i = -\mathbf{f}\cdot\mathbf{e}_i\mathbf{e}_0 \tag{59}$$

then the basis remains orthonormal as for all i. The perturbed trajectory $(\mathbf{q}',\mathbf{p}')$ is given by

$$\mathbf{q}' = \mathbf{q} + \sum_{i=1}^{3N-1}\delta q_i\mathbf{e}_i \qquad \mathbf{p}' = \mathbf{p} + \sum_{i=1}^{3N-1}\delta p_i\mathbf{e}_i \tag{60}$$

with equations of motion

$$\frac{d\mathbf{q}'}{dt'} = \mathbf{p}' \qquad \frac{d\mathbf{p}'}{dt'} = \sum_{i=1}^{3N-1}\mathbf{f}'\cdot\mathbf{e}'_i\mathbf{e}'_i \tag{61}$$

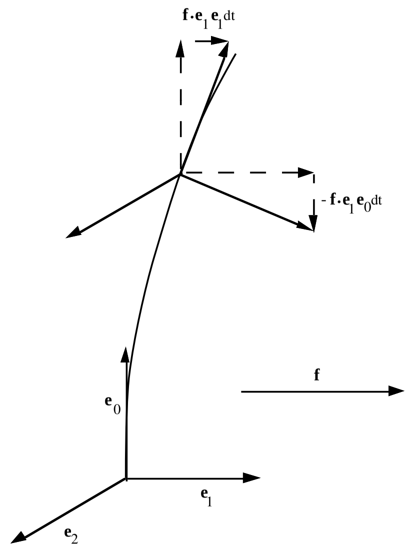


Fig 4: The basis vectors for one particle in three dimensions are parallel transported along the trajectory.

Here, $\mathbf{f}'$ is the value of $\mathbf{f}$ at the perturbed coordinates,

$$\mathbf{f}' = \mathbf{f} + \sum_{i=1}^{3N-1}\delta q_i\nabla_i\mathbf{f} \tag{62}$$

and the $\mathbf{e}'_i$ are new (arbitrary) unit vectors perpendicular to $\mathbf{p}'$. We choose the orthonormal set ($i = 1,\ldots,(3N-1)$):

$$\mathbf{e}'_0 = \mathbf{p}' \qquad \mathbf{e}'_i = \mathbf{e}_i - \delta p_i\mathbf{e}_0 \tag{63}$$

Then to first order is

$$\delta\dot{q}_i = \delta p_i \qquad \delta\dot{p}_j = -\sum_{i=1}^{3N-1}\left(\nabla_i\nabla_j\phi + (\mathbf{f}\cdot\mathbf{e}_j)(\mathbf{f}\cdot\mathbf{e}_i)\right)\delta q_i - \alpha\delta p_j \tag{64}$$

From these equations, the infinitesimal evolution matrix may be read off as

$$T = \begin{pmatrix} 0 & I \\ M & -\alpha I \end{pmatrix} \tag{65}$$

where each of the elements are $(3N-1)\times(3N-1)$ submatrices. 0 is the zero matrix and I the identity matrix. The crucial point in the derivation is that from equation (64) the M sub-matrix is symmetric. To prove the conjugate pairing rule we need the symplectic eigenvalue theorem [21,22] which we outline below.

DEFINITION 1: The T matrix is infinitesimally α-symplectic if

$$T^T J + JT = -\alpha J \tag{66}$$

where

$$J = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix} \tag{67}$$

DEFINITION 2: The L matrix is globally μ-symplectic if

$$\mu L^T JL = J. \tag{68}$$

If we consider $K(t) = L^T(t)JL(t)$, note that $\dot{K}(t) = -\alpha K(t)$. Solving for K, given that $K(0) = J$, we find that μ is related to α by

$$\mu = \exp\left(\int_0^t \alpha(s)ds\right).$$

THEOREM: a-symplectic eigenvalue theorem

If matrix M satisfies $aM^T JM = J$ for some finite a, and if χ is an eigenvalue of M, then $(\chi a)^{-1}$ is also an eigenvalue of M.

PROOF:

We note that; if χ is an eigenvalue of M, then $\det(M-\chi I)=0$, and M^T has the same eigenvalues as M. The determinant of a product is equal to the product of the determinants and $\det(J)=1$. Therefore

$$\begin{aligned}\det(M-\chi I)=0 \quad &\Rightarrow \quad \det\left(M^T JM - \chi M^T J\right)=0 \\ &\Rightarrow \quad \det\left(a^{-1}J - \chi M^T J\right)=0 \\ &\Rightarrow \quad \det\left(\left((a\chi)^{-1}I - M^T\right)\chi J\right)=0 \\ &\Rightarrow \quad \det\left((a\chi)^{-1}I - M^T\right)=0 \\ &\Rightarrow \quad \det\left(M-(a\chi)^{-1}I\right)=0\end{aligned}$$

QED.

Applying this result to $M = L^T L$, where $a=\mu^2$, we find that for each eigenvalue $\chi > 1$, there is another $\left(\mu^2\chi\right)^{-1}$. The sum of the logarithms of this pair of eigenvalues of $L^T L$ is

$$2\lambda_+ t + 2\lambda_- t = \ln\chi + \ln\left(\mu^2\chi\right)^{-1} = -2\int_0^t \alpha(s)ds \tag{69}$$

which is clearly independent of which pair of eigenvalues we chose.

$$\lambda_+ + \lambda_- = -\tfrac{1}{t}\int_0^t \alpha(s)ds = -\langle\alpha\rangle_t \tag{70}$$

This result applies to any trajectory segment, no matter how small, if the co-moving basis set is used. Finally, we take the $t\to\infty$ limit. The result is that any pair of Lyapunov exponents (except the trivial zeros) sum to $-\langle\alpha\rangle_t$. An important corollary is that, if there is an invariance in the equations of motion leading to a zero exponent, the conjugate exponent is not zero as in the Hamiltonian case, but $-\langle\alpha\rangle_t$. This proof is valid for any number of particles moving in a potential which may contain both external terms and interactions between the particles. There is still no proof of conjugate pairing for SLLOD dynamics where it was first observed numerically. Indeed, now there is a suggestion that conjugate pairing does not hold exactly for SLLOD [23].

D. Pairing of Lyapunov exponents for NIK dynamics

The Nosé Hamiltonian equation (31) is written with variables $(\mathbf{q},\pi,s,p_s,\lambda)$ which satisfy conjugate pairing with each pair summing to zero. However, the equations of motion may be written in terms of the physical variables $(\mathbf{q},\mathbf{p},\zeta,t)$ as equations (42) and (43). In this form, it is apparent that ζ acts like the Gaussian multiplier α. In this representation the equilibrium distribution is canonical in the system variables when $g+1=3N$. We note that the Lyapunov exponents may depend on the variables used to define the phase space if the equations relating different coordinate systems involve exponential functions of time. The total phase space contraction, which is given by minus the sum of the Lyapunov exponents, is proportional to the average of ζ, which is nonzero for a nonequilibrium steady state. Since the sum of the exponents is less than zero, it is clear that the exponents are quite different from the Nosé values. In fact, it has been shown that the conjugate pairing rule holds for NIK thermostats [24]. Numerical simulations also suggest that the conjugate pairing rule holds for iso-energetic Gaussian thermostats (GIE).

IV. HAMILTONIAN FORMULATION OF THE GIK THERMOSTAT

One of the most surprising results is that there is a Hamiltonian formulation of the GIK thermostat. Related to this is a variational formulation in terms of geodesic motion in a curved space. The existence of a Hamiltonian permits a correspondence to be made between Gaussian thermostatted systems, and other Hamiltonian dynamical systems, so that both can be treated on a similar footing. This permits statements to be made about the conservation of phase volume, and the symplectic structure of phase space, for thermostatted systems. An obvious question is how the phase volume conservation of a Hamiltonian system is reconciled with the fact that thermostats cause phase space contraction on the average, leading to steady multifractal distributions and entropy production in nonequilibrium system? The apparent contradiction is resolved by noting the distinction between physical and canonical momenta, (in analogy with a charged particle in a magnetic field). Phase space volume is conserved when written in terms of canonical momenta, but these are not simply proportional to the physical momenta.

Consider the color conductivity algorithm for self-diffusion [1] where there are N particles, in periodic boundary conditions, interacting via a short range potential Φ_{int}. Half of the particles have a positive color charge c, and half have the opposite charge $-c$, which only interacts with the external color field F. The Hamiltonian for this (unthermostatted) system is

$$H_C = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \Phi_{int}(\mathbf{q}) - \sum_{i=1}^{N} c_i z_i F = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{q}) \tag{71}$$

It is clear that the designation internal and external is not necessary as the two terms may be grouped together to give a single potential Φ. If we introduce an isokinetic thermostat this remains the case, but an isoenergetic thermostat distinguishes between the two, conserving the sum of the kinetic energy and Φ_{int}. The response variable is the color current density

$$J_z = \frac{1}{V}\sum_{i=1}^{N} c_i \dot{z}_i \tag{72}$$

Scaling so that the magnitude of the momentum vector is one gives

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{p}_i \qquad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \alpha\mathbf{p}_i \qquad \alpha = \sum_{i=1}^{N} \mathbf{F}_i \cdot \mathbf{p}_i \tag{73}$$

where the total force is $\mathbf{F}_i = -\partial\Phi/\partial\mathbf{q}_i$. In these variables, the total kinetic energy is normalized to $1/2$. Now we come to the central result - a one parameter family of Hamiltonians which generate these equations of motion [25]:

$$H_\beta(\mathbf{q},\pi;\lambda) = \tfrac{1}{2}e^{(\beta+1)\Phi(\mathbf{q})}\sum_{i=1}^{N}\pi_i^2 - \tfrac{1}{2}e^{(\beta-1)\Phi(\mathbf{q})} \tag{74}$$

From this Hamiltonian the equations of motion are

$$\frac{d}{d\lambda}\mathbf{q}_i = \frac{\partial H}{\partial \pi_i} = e^{(\beta+1)\Phi}\pi_i = \left(e^{\Phi}\pi_i\right)e^{\beta\Phi} \tag{75}$$

$$\frac{d}{d\lambda}\pi_i = -\frac{\partial H}{\partial \mathbf{q}_i} = -\frac{1}{2}\frac{\partial \Phi}{\partial \mathbf{q}_i}e^{(\beta-1)\Phi}\left((\beta+1)e^{2\Phi}\sum_i \pi_i^2 - (\beta-1)\right) \tag{76}$$

We are now free to choose the connection between Hamiltonian variables $(\mathbf{q},\pi,\lambda)$ and physical variables $(\mathbf{q},\mathbf{p},t)$. Equation (75) suggests a particular choice

$$\frac{dt}{d\lambda} = e^{\beta\Phi} \qquad \text{and} \qquad \mathbf{p}_i = e^{\Phi}\pi_i \tag{77}$$

But as the physical kinetic energy is equal to $1/2$, $e^{2\Phi}\sum_i \pi_i^2 = 1$, and hence the conserved value of the Hamiltonian is zero. Combining this with equation (76) gives the GIK equations of motion (73).

The phase space contraction factor in the canonical variables is, of course, unity. Thus for the simplest case $\beta = 0$ in which the physical and canonical times are the same, the constant phase space element is

$$d\Gamma = d^{3N}q\, d^{3N}\pi\,\delta(H-E) = 2e^{-(3N-1)\Phi}d^{3N}q\, d^{3N}p\,\delta(\sum_{i=1}^{N}\mathbf{p}_i^2 - 1) \tag{78}$$

with $E = 0$. From this the physical phase-space contraction factor (in the variables $(\mathbf{q},\mathbf{p})$) is seen to be $\exp((3N-1)\Delta\Phi)$, which is easily shown to be the value obtained directly from the equations of motion. Also the nonequilibrium Kawasaki distribution function [26] can be derived from equation (78).

The value of β is completely arbitrary, and does not affect the equations of motion, however there are three particular values of β in which the canonical variables have a simple interpretation. Hamiltonians with different β are not related by any of the usual types of canonical transformation, since the time variables differ in each case.

1]. For $\beta = -1$, the Hamiltonian reduces to kinetic plus potential energy. The thermostatted equations are thus equivalent to a potential problem with zero total energy.

Alternatively, any system of particles with purely attractive forces and zero total energy can be represented in terms of GIK thermostatted dynamics.

2]. For $\beta = 0$, the canonical and physical times are the same, so this is the most natural form in which to derive the thermostatted dynamics.

3]. For $\beta = 1$, the Hamiltonian is a quadratic form.

$$H_{\beta=1}(\mathbf{q},\pi;\lambda) = \tfrac{1}{2}e^{2\Phi(\mathbf{q})}\sum_{i=1}^{N}\pi_i^2 - \tfrac{1}{2} \tag{79}$$

Ignoring the constant, we see that GIK dynamics is equivalent to a geodesic in a curved space with metric $g^{\mu\upsilon}$, that is $H_g(\mathbf{q},\pi) = \tfrac{1}{2}g^{\mu\upsilon}(\mathbf{q})\pi_\mu\pi_\upsilon$. $H_{\beta=1}$ is equivalent to geodesic motion on configuration space with a metric given by

$$ds^2 = e^{-2\Phi}\sum_{i=1}^{N}d\mathbf{q}_i^2\,. \tag{80}$$

The trajectory followed between two points in configuration space has extremal length with respect to the above metric. That is, for any two points in configuration space, the trajectory followed by the system is a minimum value of $\int ds$ among all trajectories from one point to the other. Occasionally it may be only a local minimum, or even (for sufficiently pathological Φ) a maximum. We have also incidentally proved that the dynamics is time reversible, as there is no preferred direction along a geodesic. Thus we have shown that the GIK thermostat is intimately related to more conventional dynamical systems, augmenting the link which has already been made between quadratic Hamiltonians and geodesic motion in a curved manifold [27].

The one particle problem also has direct relevance to some other systems, for which the thermostatted dynamics is exact. For example, the above form of the metric is equivalent to Fermat's principle for light passing through glass with a refractive index $n = \exp(-\varepsilon x)$. In addition, the $\beta = -1$ form of the Hamiltonian is that of an electron moving in a potential $V = \tfrac{1}{2}\exp(-2\varepsilon x)$ with a total energy of zero.

Another important point relates to boundary conditions. For an equilibrium system, periodic boundary conditions may be used without affecting the Hamiltonian structure of the equations. All that happens is that $\mathbf{q}$ becomes a compact manifold. In our case, enforcing periodic boundary conditions results in abrupt changes in Φ, so that the Hamiltonian is not conserved. It is clear that the imposition of periodic boundary conditions breaks the global Hamiltonian structure, as a multifractal attractor appears. Nonetheless, it is still valid to view a periodic system as a Hamiltonian system with a potential which is in some sense periodic.

V. THE LORENTZ GAS

The Lorentz gas is a simple model of electrical conduction in a periodic solid [28] and has been studied as a low dimensional example of a nonequilibrium steady state [2]. The model consists of a single point particle wandering through a triangular lattice of fixed hard scatterers (see fig 5). The wandering point particle experiences an external field ε in the negative x-direction, and a GIK thermostat. The equations of motion are

$$\dot{x} = p_x \qquad \dot{p}_x = F_x - \varepsilon - \alpha p_x \tag{81}$$

$$\dot{y} = p_y \qquad \dot{p}_y = F_y - \alpha p_y, \tag{82}$$

$$\alpha = \mathbf{p} \cdot \mathbf{F} - \varepsilon p_x . \tag{83}$$

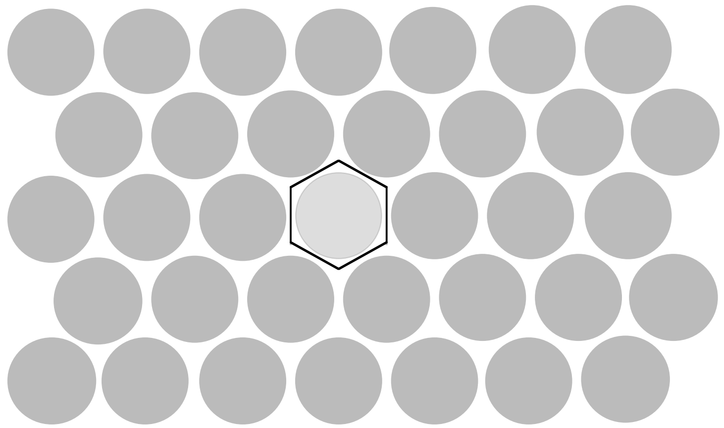


Fig 5. The Lorentz gas showing the "central" scatterer and the surrounding hexagonal boundary which tiles the plane.

It is convenient to write the momentum vector as $\mathbf{p} \equiv (p_x, p_y) = p(\cos\theta, \sin\theta)$ as its magnitude p is fixed by the GIK thermostat. The only free variable in the momentum is θ (see fig 6), and from equations (81) and (82) its equation of motion is $\dot{\theta} = \varepsilon \sin\theta$. Integrating over a time interval, $\Delta t = t_1 - t_0$, in the absence of a collision, gives

$$\tan\left(\frac{\theta}{2}\right) = \tan\left(\frac{\theta_0}{2}\right) \exp\left(\frac{t - t_0}{\varepsilon}\right) \tag{84}$$

The equations of motion for x and y can be parametrised by θ, and are given by

$$x = x_0 + \frac{1}{\varepsilon} \ln\left(\frac{\sin\theta}{\sin\theta_0}\right) \qquad y = y_0 + \left(\frac{\theta - \theta_0}{\varepsilon}\right) \tag{85}$$

where a subscript zero indicates the initial value of the variable. In this form it is straightforward to see that the Lorentz gas described by the equations of motion (84) and (85) is equivalent to two particles with equal masses, in triangular boundary conditions, subject to an external field and GIK thermostat.

As the free motion of the wandering particle is analytic, a complete trajectory can be specified by noting the phase point after each collision. The position of the wandering particle can be specified by $(x, y) = r(\cos\phi, \sin\phi)$, and $r = 1$ on the scatterer surface (the Poincaré surface of section), so the complete phase point is specified by (ϕ, θ). In this picture the time evolution of the Lorentz gas is given by the mapping M which moves the phase point from one collision to the next.

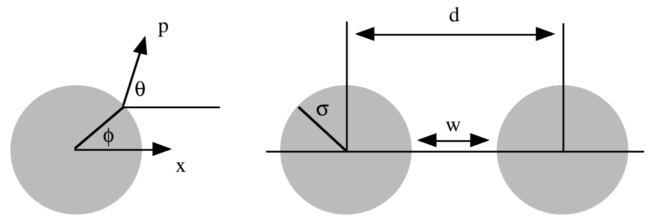


Fig 6. Specifying the thermodynamic state point for the Lorentz gas.

From fig 6, we use a scatterer spacing $w = d - 2\sigma = 0.236$ which is small enough to ensure a finite horizon (that is $w \le 4/\sqrt{3} - 2$). We first consider the Lorentz gas as a geodesic problem to help give a more intuitive understanding of the Hamiltonian formulation outlined previously, and to explore new techniques for numerical and possibly experimental investigation of the nonequilibrium Lorentz gas.

A. The Lorentz Gas as a Geodesic Problem

For a single particle moving in two dimensions under the influence of a constant field $\mathbf{F} = -\varepsilon\hat{\mathbf{x}}$ (or potential $\Phi = \varepsilon x$) and GIK thermostat, the metric is

$$ds^2 = e^{-2\varepsilon x}\left(dx^2 + dy^2\right) \tag{86}$$

Notice also that the Hamiltonian is cyclic in y, so the conjugate momentum is conserved $\pi_y = e^{-\varepsilon x} p_y$. This is not at all obvious from the equations of motion (82). We consider the trajectory between two points which differ only by a separation in the y direction. The intermediate points have larger values of x because lengths as defined by the metric are smaller for larger values of x. First we observe that there is a maximum y separation, so that if the y separation is larger than π/ε, then no trajectory exists. This happens because the initial and final values of θ in equation (85) can differ by at most π. In the limit as $\Delta y \to \pi/\varepsilon$ the total length of the path from a point to infinity along the x direction is finite,

$$S_{x_0,\infty} = \int_{x_0}^{\infty} ds = \int_{x_0}^{\infty} e^{-\varepsilon x} dx = \frac{e^{-\varepsilon x_0}}{\varepsilon} \qquad (87)$$

so the shortest path between the two points with y separation equal to π/ε, consists of two straight lines projecting from the two end-points in the $+x$ direction.

To set-up the general geodesic problem we write the path length S as a function of the initial and final coordinates and find the extremal path. The path length is given by

$$S = \int_0^s ds = \int_0^y f(x,\dot{x},y)dy \qquad (88)$$

Here x is a function of y, as the reverse is not necessarily true. The integrand is given by $f(x,\dot{x},y) = e^{-\varepsilon x}(\dot{x}^2+1)^{1/2}$, so the Euler-Lagrange equation gives $\ddot{x} + \varepsilon\dot{x}^2 + \varepsilon = 0$ which has a solution $\dot{x} = \cot\theta$. Or in Cartesian variables this reduces to equation (85). Notice that θ and θ_0 must have the same sign, therefore they differ by at most than π. Also the total length of a path can be written as $\frac{1}{\varepsilon} e^{-\varepsilon x_0} \sin\theta_0 \left(\cot\theta_0 - \cot\theta\right)$.

B. Symbolic Dynamics

A very useful technique for obtaining a coarse-grained description of a trajectory is to label each piece of trajectory between two collisions using the relative position of the second scattered [29]. If the last collision was with the central scatterer, we assign a label to the free flight according to the next scatterer. For a finite length of trajectory its symbolic code provides a coarse grained description, but for a periodic orbit the symbolic code uniquely specifies the orbit (for a two-dimensional hyperbolic system).

C. Periodic Orbit Expansions

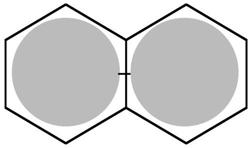
We consider the Lorentz gas as the mapping from Poincaré section to Poincaré section from which we want to extract the classical averages of some phase variable. To construct a measure that is valid at equilibrium (zero field), and also away from equilibrium, we use periodic orbits. These techniques have recently been developed and applied to systems with few degrees of freedom [29,30, 31]. For a mapping the measure of a cell C_k can be written as [32]

$$\mu(C_k) = \lim_{n\to\infty}\left(\sum_{\substack{\text{points of}\\ \text{period } n \text{ in } C_k}} \Lambda_{1,j}^{-1}\right) \tag{89}$$

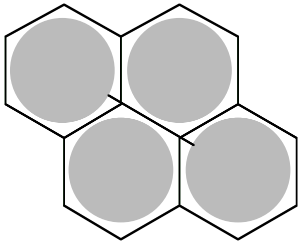
where Λ_i^{-1} is the product of the expanding Lyapunov numbers. Using this measure, the classical average of a phase variable B for a flow is

$$< B >= \lim_{n\to\infty} \frac{\sum_{i\in P_n} \Lambda_i^{-1}\int_0^{\tau_i} B(s)ds}{\sum_{i\in P_n} \tau_i \Lambda_i^{-1}} \tag{90}$$

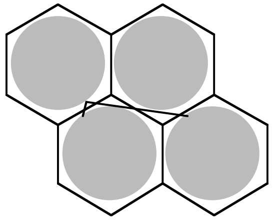
where τ_i is the period of the i^{th} orbit and $\int_0^{\tau_i} B(s)ds$ is the contribution of the i^{th} periodic orbit to the average. P_n is the set of periodic orbits of length n. The symbolic dynamics is used to enumerate the set of periodic orbits. It is possible to give a physical motivation based on the idea that because the periodic orbits are dense in the attractor, each orbit represents the typical behaviour of a group of finite (non-periodic) orbits with the same symbol sequence. The inverse Lyapunov numbers we call stability weights, and the most unstable orbits are least probable, so have the smallest weight, while the least unstable orbits have the highest weight. The advantage of this approach is that the same arguments give both the equilibrium and nonequilibrium averages [33].



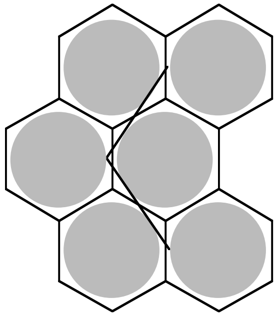
S-orbit (0 6) $\lambda\tau = 1.3486$



L-orbit (1 7) $\lambda\tau = 3.4334$



T-orbit (4 11) $\lambda\tau = 3.0983$



V-orbit (1 5) $\lambda\tau = 4.6348$

Fig 9 The length 2 periodic orbits for the Lorentz gas and their stabilities $\lambda\tau = \ln\Lambda$.

To illustrate the periodic orbit expansions in fig 9 we give all of the length 2 periodic orbits for the Lorentz gas. There are 4 topologically distinct orbits {S, L, T, V}, the full 24 orbits consist of rotations and reflections of {S, L, T, V}. Notice that there are two types of periodic orbit; those that are strictly periodic returning to the same point {S, L} and those whose periodicity relies upon the triangular lattice {T, V} which return to the same relative position in a different cell. Clearly the set {S, L} cannot contribute to a current, whereas the set {T, V} do contribute.

Table 1: A typical result from a periodic orbit calculation for the nonequilibrium Lorentz gas at a field of $\varepsilon = 0.005$. Notice the exponential profileration of orbits and the slow convergence of the averages.

n	# orbits	L_{xx}	L_{xx}^{Shanks}	$p^{\phi}V$	λ	λ^{Shanks}
2	24	0.3769		0.5429	1.4052	
3	64	0.0902	0.2130	0.6455	2.0751	1.8233
4	98	0.3051	0.2077	0.5527	1.6716	1.8465
5	232	0.1269	0.2028	0.6325	1.9803	1.8691
6	674	0.2589	0.2105	0.6301	1.8065	1.9050
7	1902	0.1825	0.2078	0.6527	2.0339	1.9491
8	5343	0.2203	0.2019	0.6565	1.8987	1.9468
9	14138	0.1845	0.1967	0.6578	1.9724	1.9535
10	31475	0.2030		0.6771	1.9434	
exact		0.1978	0.1978	0.6608		1.9625

A typical periodic orbit expansion calculation, as in table 1, enumerates all of the periodic orbits to some length and constructs a sequence of approximations to the classical average. From this sequence we extract the limit as the length of the orbits approaches infinity. In practical terms we are limited to some maximum orbit length, and the exponential proliferation of orbits with length, can make the estimation of the average difficult (see fig 10).

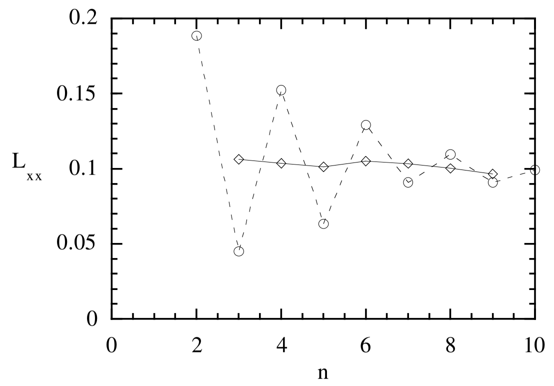


Fig 10: The convergence of the conductivity from the periodic orbit expansion results in table 1. The odd-even effect in the raw data can be removed using a convergence enhancing technique such as the shanks transformation [34].

D. The Bifurcation Diagram

For the Lorentz gas, the behaviour of the attractor in the (ϕ, θ) phase space can be studied, but to look at the behaviour as a function of field it is more convenient to eliminate one of these variables. If we project the full Poincaré section in (ϕ, θ) onto the θ axis we can observe the way a projection of the attractor behaves as the field varies, see fig 11. A similar picture is obtained by projecting onto the ϕ axis, so the choice of projection is not critical.

The essential features of the bifurcation diagram for the Lorentz gas are;

[a] Ergodic region	$0 < \varepsilon < 2.2$
[b] Crisis	$\varepsilon = 2.2$ and $\varepsilon = 2.34$
[c] Elliptic region	$2.3 < \varepsilon < 2.46$
[d] Complex	$2.407 < \varepsilon < 2.52$
[e] Stable orbits	$2.52 < \varepsilon$

There is overlap between the elliptic and complex region at this value of the spacing, but at other values of the spacing the ergodic and elliptic regions overlap [35]. We now give a brief

description of each region and then concentrate the crisis at $\varepsilon = 2.2$ and the emergence of the elliptic region at $\varepsilon = 2.3$.

collision of a family of hyperbolic fixed points (see fig 13), of which (0 4 8) and (0 4 10 6) are the first two members, to form the neutrally stable (4 10). The end of the elliptic region can be considered as the collision between the hyperbolic (4 10) orbit and the elliptic (4 10) orbit. The existence of the elliptic region signals a breakdown in the ergodicity of the Lorentz gas [38] as the phase space is decomposable into two separate regions in which trajectories remain for all time.

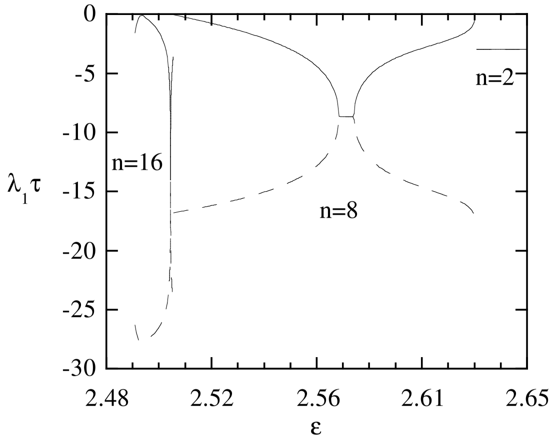


Fig 12: Lyapunov exponents for stable periodic orbits.

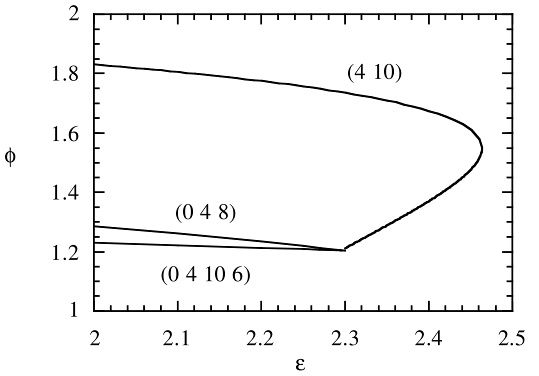


Fig 13: The initial ϕ value for the periodic orbits (0 4 8) and (0 4 10 6) which converge to the same initial condition as that for the elliptic (4 10) at $\varepsilon = 2.3$

[b] At about $\varepsilon = 2.2$ the attractor suddenly changes from a space filling object to one with a much smaller support [35]. At this point the attractor and repeller become disjoint objects [36]. Such a transition has been termed a crisis [37]. Although this transition should be observed as a sudden change in the value of capacity or box counting dimension D_0, from two to something smaller, the numerical difficulties in calculating D_0 make this a poor indicator of the position of the transition [35]. The information dimension D_1 and Kaplan-Yorke dimension D_{KY} change smoothly through the transition, indicating that the attractor is multifractal, but giving no indication of a transition, see table 2.

Table 2: Information dimension D_1 and Kaplan-Yorke dimension D_{KY} near the crisis.

Field	2.1	2.15	2.2	2.25	2.3
D_1	1.45	1.37	1.30	1.25	1.22
D_{KY}	1.451	1.381	1.321	1.270	1.221

In order to find a better indicator of the crisis we return to the symbolic dynamic description of a generic trajectory. At the crisis point the symbolic dynamics reduces suddenly from 10 symbols to five (see fig 14), with the probability of observing a some symbols becoming zero.

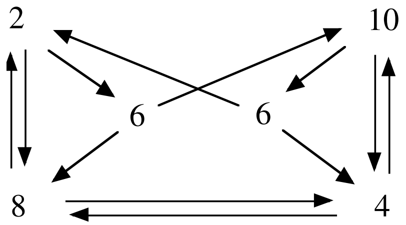


Fig 14: At the onset of the crises, $\varepsilon = 2.2$, the possible symbol sequences are restricted.

By studying the symbolic dynamics the following order parameters all give consistent indications of the position of the crises.

1] Above the crisis a generic trajectory never has more than one segment opposite the field direction, we term this mesoscopic irreversibility.

2] The disappearance of the symbols 0 and 5 & 7.

3] The disappearance of backward collisions, where the backward collision is defined in fig 16.

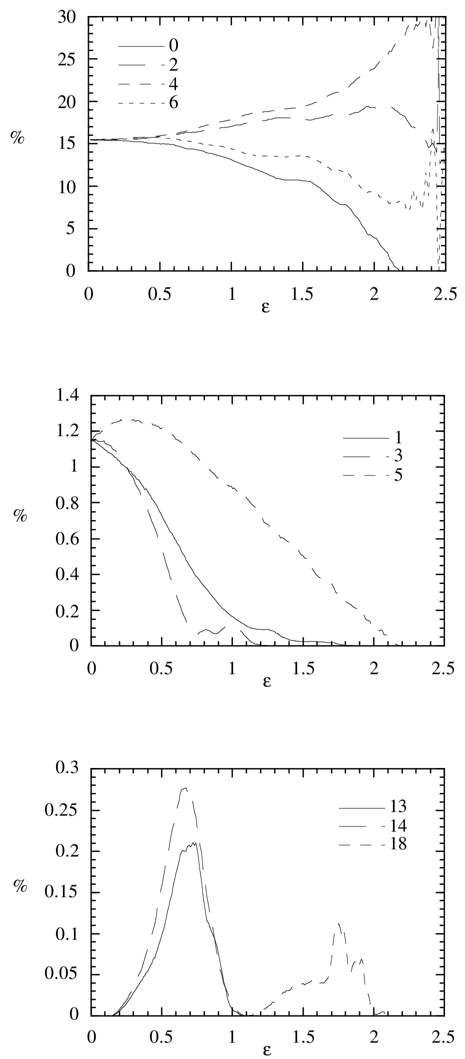


Fig 15: a) Percentage probability of even symbols 0, 2, 4, 6; b) Percentage probability of odd symbols 1, 3, 5. c) Percentage probability of extra symbols 13, 14, 18.

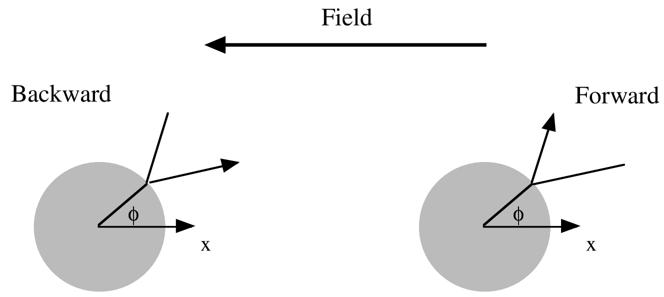


Fig 16: The definitions of backward and forward collisions.

E. The Dynamical Partition Function

The partition function has a dual role in statistical mechanics, it normalises the distribution function, and also generates the thermodynamic properties, as for example

$$p = kT\frac{\partial}{\partial V}\ln Z_c(N,V,T) \tag{91}$$

A dynamical partition function for the Lorentz gas has been proposed [39] by connecting the normalisation factor in the POE average formula with the canonical partition function. Thus

$$Z_d(V) = \lim_{n\to\infty} Z^{(n)}(V) = \lim_{n\to\infty}\sum_{i\in P_n}\tau_i \exp(-\tau_i\lambda_i) \tag{92}$$

We observe that this partition function has the dimensions of time, but this is analogous to the classical partition function for an N particle system which has the units of action to the N^{th} power (the semi-classical partition function has no units, as h sets a minimum length scale). This characteristic time unit required to make the dynamical partition function a pure number can be expected to set a minimum time scale. The value of this minimum time scale only affects thermodynamic functions by at most a constant. Chernov [40] has recently shown that the partition function formula is exact for the Lorentz gas, and that the time corresponds to the mean time between collisions.

F. Analytic Expressions for the Lyapunov Numbers

We have already seen that the evolution of the Lorentz gas can then be written as a mapping from surface of section to surface of section. We can calculate the stability matrix for a trajectory or orbit J_{orbit} by considering products of free flight stability matrices and collision stability matrices [33]. Thus

$$J_{orbit} = \prod_{i=1}^{n} J_M(i) = \prod_{i=1}^{n} J_C(i) J_F(i) \tag{93}$$

where the collision stability matrix is

$$J_C(1) = \begin{pmatrix} -1 & 2 \\ 0 & 1 \end{pmatrix} \tag{94}$$

and the free flight stability matrix is

$$J_F(1) = \begin{pmatrix} \dfrac{\sin\theta_0'}{\sin\theta_0}\dfrac{\cos(\phi_1-\theta_0)}{\cos(\phi_1-\theta_0')} & -\varepsilon\sin\theta_0'\dfrac{\sin(\phi_1-\phi_0)}{\cos(\phi_1-\theta_0')} \\ \dfrac{1}{\varepsilon\sin\theta_0}\dfrac{\sin(\theta_0'-\theta_0)}{\cos(\phi_1-\theta_0')} & \dfrac{\cos(\phi_0-\theta_0')}{\cos(\phi_1-\theta_0')} \end{pmatrix} \tag{95}$$

Given the trajectory details, (θ_i, ϕ_i) at the beginning of the free flight, and θ_i' at the end, the Lyapunov numbers Λ_1 and Λ_2 can be calculated as the eigenvalues of $\left(J_{orbit} J_{orbit}^*\right)^{1/2}$. The determinant of J_{orbit} can be calculated from the determinants of the constituent matrix factors. Thus for a periodic orbit

$$\det(J_n) = \prod_{i=1}^{n} \det(J_F(i)) \det(J_C) = \prod_{i=1}^{n} \frac{\sin\theta_{i-1}'}{\sin\theta_{i-1}}. \tag{96}$$

The x displacement for the i^{th} free flight is $\Delta x_i = x_i - x_{i-1} = (1/\varepsilon)\ln\left(\sin\theta_{i-1}'/\sin\theta_{i-1}\right)$ so the total displacement for a periodic orbit Δx is

$$\varepsilon\Delta x = \sum_{i=1}^{n} \varepsilon\Delta x_i = \ln\left(\det|J_n|\right) \tag{97}$$

Therefore the Lyapunov exponent sum rule $\varepsilon\Delta x_i = \left(\lambda_i + \lambda_{-i}\right)\tau_i$ is obeyed for individual periodic orbits.

G. Positivity of the Conductivity

For the Lorentz gas in an external field there a very simple argument based on periodic orbit theory that shows that the transport coefficient, in this case the conductivity, is strictly non-negative. The average conductivity from the periodic orbit expansion is given by

$$L_{xx}(\varepsilon) = -\lim_{n\to\infty} \frac{1}{\varepsilon} \frac{\sum_{i\in P_n} \Delta x_i \Lambda_i^{-1}}{\sum_{i\in P_n} \tau_i \Lambda_i^{-1}} \tag{98}$$

At every level in the expansion there are two classes of periodic orbits: those with $\Delta x_i = 0$, and those for which $\Delta x_i \neq 0$. Each orbit with $\Delta x_i \neq 0$ has a time reverse, with exactly opposite displacement, $\Delta x_{-i} = -\Delta x_i$. The contribution to the average conductivity for each time reverse pair of orbits is

$$\begin{aligned} -\varepsilon\Delta x_i\left(\Lambda_i^{-1} - \Lambda_{-i}^{-1}\right) &= -\varepsilon\Delta x_i\left(e^{-\lambda_i\tau_i} - e^{\lambda_{-i}\tau_i}\right) = \Delta x_i e^{-\lambda_i\tau_i}\left(1 - e^{(\lambda_i+\lambda_{-i})\tau_i}\right) \\ &= -\varepsilon\Delta x_i\left(1 - e^{\varepsilon\Delta x_i}\right)\Lambda_i^{-1} \end{aligned} \tag{99}$$

where the last equality follows from Lyapunov exponent sum rule for individual periodic orbits. As $\Lambda_i^{-1} = \exp(-\lambda_1\tau)$ is positive, and $-\varepsilon\Delta x_i\left(1 - e^{\varepsilon\Delta x_i}\right)$ is **never negative**, so all contributions to the average conductivity are positive, and hence the average conductivity itself is positive [36] (that is, in the same direction as the field). The observed irreversibility in this microscopically reversible system is due to the different stability weights assigned to forward and backward periodic orbits, but these stability weight are derived from the microscopic (reversible) dynamics. This result can be generalised to many particle color conductivity systems [41]. Ruelle [42] has recently proposed formulas for the entropy production rate for Gaussian thermostatted systems and can sometimes prove that the entropy production is positive.

VI. CONCLUSIONS

We have shown how deterministic thermostatting mechanisms have developed from the arbitrary inclusion of a damping-like term in the equations of motion, to a set of methods based on firm mechanical foundations, which extract energy from nonequilibrium systems to achieve a steady state, or change ensembles in equilibrium systems, or move from Thévenin (constant field) to Norton (constant current) ensembles away from equilibrium. The linear and nonlinear response theory of these thermostatted systems is also well developed [1].

Since the first demonstration that thermostatted systems exhibit phase space contraction (on average) and that the nonequilibrium distribution (or measure) is multifractal [43], these systems have been studied as dynamical systems using the usual tools - Lyapunov exponents and generalised dimensions. One of the most important results from this work is the conjugate pairing rule for Lyapunov exponents. Although not valid in general, the conjugate pairing rule demonstrates that the thermostatting mechanism acts democratically on all pairs of degrees of freedom. This result is related to that of Gaspard for open systems [44].

Thermostatted nonequilibrium systems are dissipative, and have until now been considered as non-Hamiltonian systems. Now that a class of thermostatted nonequilibrium systems have been shown to be Hamiltonian and to have a generalised symplectic structure, their status is equivalent to that of the well studied case of non-dissipative Hamiltonian systems. A further consequence of this is a variational principle for the microscopic dynamics which can be regarded as an extension of Hamilton's principle.

The application of these techniques to the nonequilibrium Lorentz gas illustrates their use. For this system we map out the range of behaviour as the field varies, identifying the major generic transitions in such nonequilibrium systems. The periodic orbit expansion is used to calculate averages, and several results (such as the non-negativity of the conductivity) are shown to be simple consequences of the periodic orbit approach. Indeed studies of the application of cycle expansions to the Lorentz gas have also led to improvements in cycle expansion methods, as for example with the introduction of stability ordering [45].

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