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Stochastic motion in phase space on a surface of constant energy

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We study closed systems of particles that are subject to stochastic forces in addition to the conservative forces. The stochastic equations of motion are set up in such a way that the energy is strictly conserved at all times. To ensure this conservation law, the evolution equation for the probability density is derived using an appropriate interpretation of the stochastic equation of motion that is not the Itô nor the Stratonovic interpretation. The trajectories in phase space are restricted to the surface of constant energy. Despite this restriction, the entropy is shown to increase with time, expressing irreversible behavior and relaxation to equilibrium. This main result of the present approach contrasts with that given by the Liouville equation, which also describes closed systems, but does not show irreversibility.

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I. INTRODUCTION

One of the fundamental problems of nonequilibrium statistical mechanics is the explanation of the irreversible decay to equilibrium of closed systems, which is expressed by the increase of entropy. If we consider a closed system of particles interacting through conservative forces, then we are naturally led to a description of the system through the Liouville equation [1–11]. However, a direct result of this equation is the invariance of entropy with time and as a consequence the equation is unable to describe the desired irreversible decay to equilibrium.

The Liouville equation describes appropriately systems in equilibrium. Any probability density ρ which depends on the dynamic variables through the Hamiltonian $\mathscr{H}$ is a stationary solution of this equation. This is the case of the microcanonical Gibbs distribution

$$\rho_e = \frac{1}{\Omega}\delta(E - \mathscr{H}), \tag{1}$$

which describes a system in thermodynamic equilibrium with a fixed energy E [1]. A relevant property of the Liouville equation is the conservation of the energy. If the initial probability density is defined on a surface of a constant given energy, then the density will remain forever defined on this surface.

The Liouville equation predicts that the entropy remains invariant in time, a result which is a direct consequence of the constance of the probability density along a trajectory in phase space. If we start with a probability density with an entropy distinct from that of the Gibbs equilibrium distribution, we conclude that this distribution will never be reached and that the Liouville equation does not account for the irreversibility. This inconvenience may be circumvent by introducing random forces that change the Hamiltonian trajectory while keeping the conservation of energy and momentum.

The Boltzmann kinetc equation [12–16] is, in fact, a realization of this proposal. It incorporates random forces and as a consequence the entropy increases while the energy remains strictly constant. Here we derive a stochastic equation that is similar to the Boltzmann equation in the sense that the entropy also increases at strictly constant energy. To this end we set up a stochastic equation of motion, or Langevin equations, that strictly conserves the energy, that is, the trajectories in phase space lie on the surface of constant energy. From the stochastic equation of motion one derives the associated evolution equation for the probability density, which turns out to be an equation of the Fokker-Planck type [17–20], and it is not an integrodifferential equation as is the case of the Boltzmann equation.

The time evolution equation for the probability density, which incorporates stochastic forces, is a type of equation that is used in approaches to stochastic thermodynamics [21–29], which describe systems in contact with heat reservoirs, including the exchange of heat and entropy as well as the production of entropy. The main difference of these approaches from ours is the strict conservation of energy observed in the present approach. In this sense we may say that the present approach provides a stochastic thermodynamics for closed systems.

To derive the evolution equation, it is necessary to give an interpretation to the stochastic equation of motion because the noise is multiplicative [17]. Usually, the interpretation is that given by Stratonovich and not that given by Itô. However, we find that the proper interpretation necessary to preserve energy at all times is none of them.

The origin of stochastic trajectories may be attributed to forces that are of the hyperbolic type such as those occurring when two hard spheres collide with each other. Given the initial positions and velocities of two hard spheres, then the positions and velocities after the collision will be uniquely determined by the Newton equations of motion. However, if we consider two very similar initial conditions that differ only slightly by the positions, the velocities being the same, then the velocities after the collision will not differ slightly but can be very different. Since the initial condition is almost the same, this result looks as if more than one trajectory is possible from a single initial condition.

We will not pursue in more detail the problem of how stochastic trajectories emerge from pure mechanics, that is, from the Newton equations of motion applied to a system acted by internal conservative forces. Here we adopt the point of view that the stochastic trajectories, or rather the stochastic forces, are an assumption of the present approach.

The stochastic equation of motion that we introduced can be used as a numerical method to simulate a system of interacting particles at constant energy, as is the case of the method of molecular dynamics [30,31]. In equilibrium, the static properties will be the same as those obtained from the molecular dynamics because the stochastic equations of motion lead to the Gibbs distribution. However, the two-time correlations will be distinct due to the presence of stochastic forces.

II. IMPULSIVE STOCHASTIC FORCE

A. Stochastic equation of motion

We consider two particles interacting through random forces that act on a short period of time. We denote by $\mathbf{p}_1 = m_1\mathbf{v}_1$ and $\mathbf{p}_2 = m_2\mathbf{v}_2$ the momenta of the particles, where m_1 and m_2 are their masses and $\mathbf{v}_1$ and $\mathbf{v}_2$ their velocities. The random force acting on particle 1 due to the particle 2 is denoted by $\boldsymbol{\xi}$. The reaction on particle 2 is $-\boldsymbol{\xi}$ and the equations of motion are

$$\frac{d\mathbf{p}_1}{dt} = \boldsymbol{\xi}, \qquad \frac{d\mathbf{p}_2}{dt} = -\boldsymbol{\xi}. \tag{2}$$

The total momentum $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ is conserved because from the stochastic equation of motion it follows that $d\mathbf{P}/dt = 0$.

We wish to determine the properties of the stochastic vector variable $\boldsymbol{\xi}$ that makes the energy of the two particles constant. As the forces are supposed to be impulsive, which means that they act during a short period of time, the conservation of energy means the conservation of the kinetic energy

$$\mathscr{K} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}. \tag{3}$$

The derivative of the kinetic energy is

$$\frac{d\mathscr{K}}{dt} = (\mathbf{v}_1 - \mathbf{v}_2)\cdot\boldsymbol{\xi}, \tag{4}$$

Defining the relative velocity $\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2$, we see that the condition

$$\mathbf{v}\cdot\boldsymbol{\xi} = 0 \tag{5}$$

makes the derivative of the kinetic energy to vanish. This condition of orthogonality implies that $\boldsymbol{\xi}$ depend on the relative velocity $\mathbf{v}$.

To proceed further we use a more convenient procedure. As $\mathbf{p}_1$ and $\mathbf{p}_2$ are connected by the conservation of the total momentum, if suffices to use just one independent variable, which we choose to be $\mathbf{p} = m\mathbf{v}$ where m is the reduced mass. The two equations of motion are then reduced to one

$$\frac{d\mathbf{p}}{dt} = \boldsymbol{\xi}. \tag{6}$$

In terms of the new variable $\mathbf{p}$, the kinetic energy, apart from a constant, is given by

$$\mathscr{K} = \frac{p^2}{2m}. \tag{7}$$

The stochastic variable $\boldsymbol{\xi}$ is understood as follows. If we discretize the time in intervals equal to τ the stochastic variable is proportional to $1/\sqrt{\tau}$. Thus in a discretized formulation of the equation of motion (6), we replace $\boldsymbol{\xi}$ by $\boldsymbol{\xi}/\sqrt{\tau}$ with the understanding that $\boldsymbol{\xi}$ has a finite variance. Equation (6) becomes

$$\Delta\mathbf{p} = \sqrt{\tau}\boldsymbol{\xi}. \tag{8}$$

A finite increment of the kinetic energy is

$$\Delta\mathscr{K} = \mathbf{v}\cdot\Delta\mathbf{p} + \frac{1}{2m}(\Delta\mathbf{p})^2. \tag{9}$$

Replacing Eq. (8) in this equation, we find

$$\Delta\mathscr{K} = \sqrt{\tau}\mathbf{v}\cdot\boldsymbol{\xi} + \frac{\tau}{2m}\boldsymbol{\xi}\cdot\boldsymbol{\xi}. \tag{10}$$

Using the condition (5) on $\boldsymbol{\xi}$ established above, $\mathbf{v}\cdot\boldsymbol{\xi} = 0$, we see that $\Delta\mathscr{K}$ vanishes up to order $\sqrt{\tau}$, but not up to order τ. To overcome this inconvenience, we observe that Eq. (8) is not the only possible interpretation of the stochastic equation of motion (6). We may add any random variable proportional to $1/\tau$, which means to interpret the stochastic equation of motion as

$$\Delta\mathbf{p} = \sqrt{\tau}\boldsymbol{\xi} + \tau\boldsymbol{\omega}, \tag{11}$$

where $\boldsymbol{\omega}$ is a random variable with a finite variance. Replacing this expression in Eq. (9), then up to terms of order τ we find

$$\Delta\mathscr{K} = \sqrt{\tau}\mathbf{v}\cdot\boldsymbol{\xi} + \tau\left(\mathbf{v}\cdot\boldsymbol{\omega} + \frac{1}{2m}\boldsymbol{\xi}\cdot\boldsymbol{\xi}\right). \tag{12}$$

The first term vanishes due to the condition (5). If we wish $\Delta\mathscr{K}$ to vanish to order τ, the last term must vanish, which gives the following relation:

$$\boldsymbol{\omega}\cdot\mathbf{p} + \tfrac{1}{2}\boldsymbol{\xi}\cdot\boldsymbol{\xi} = 0, \tag{13}$$

between $\boldsymbol{\omega}$ and $\boldsymbol{\xi}$. To find $\boldsymbol{\omega}$ in terms of $\boldsymbol{\xi}$, we differentiate the condition (5) with respect to $\mathbf{p}$, and perform a dot product with $\boldsymbol{\xi}$ to obtain

$$\boldsymbol{\xi}\cdot\left(\frac{\partial}{\partial\mathbf{p}}\boldsymbol{\xi}\right)\cdot\mathbf{p} + \boldsymbol{\xi}\cdot\boldsymbol{\xi} = 0. \tag{14}$$

Comparing the last two equations, we see that the expression

$$\boldsymbol{\omega}' = \frac{1}{2}\boldsymbol{\xi}\cdot\frac{\partial}{\partial\mathbf{p}}\boldsymbol{\xi}, \tag{15}$$

gives the desired solution. However, this is not the unique solution because we may add to this expression any term orthogonal to $\mathbf{p}$ such as $\boldsymbol{\xi}$ itself. At this point we postpone the problem of determining $\boldsymbol{\omega}$ in terms of $\boldsymbol{\xi}$.

B. Evolution equation

To derive the Fokker-Planck equation associated to the Langevin equation (11), which is the evolution equation for the probability density $\rho(\mathbf{p})$, we use a method that consists in determining the evolution of the characteristic function Φ, which is the Fourier transform of ρ,

$$\Phi = \int e^{i\Omega} \rho \, d\mathbf{p}, \tag{16}$$

where $\Omega = i\mathbf{k}\cdot\mathbf{p}$ and $\mathbf{k}$ is a vector in the Fourier space. The characteristic function is also the average

$$\Phi = \langle e^{i\Omega} \rangle. \tag{17}$$

Denoting by $\Delta\Phi$ the difference of the characteristic functions between times $t+\tau$ and t, then

$$\Delta\Phi = \langle e^{i\Omega}(e^{i\mathbf{k}\cdot\Delta\mathbf{p}} - 1)\rangle, \tag{18}$$

where the average is to be calculated using the probability of the variables $\mathbf{p}$ and $\boldsymbol{\xi}$ considered to be independent of each other. Next we replace $\Delta\mathbf{p}$, given by Eq. (11) in this expression and expand $\Delta\Phi$ up to terms of order τ. Dividing the result by τ, we find the time derivative of the characteristic function in the form

$$\frac{\partial\Phi}{\partial t} = \langle e^{i\Omega} i\mathbf{k}\cdot\boldsymbol{\omega}\rangle + \frac{1}{2}\langle e^{i\Omega} i\mathbf{k}\cdot\boldsymbol{\xi}\boldsymbol{\xi}\cdot i\mathbf{k}\rangle. \tag{19}$$

Taking into account that $i\mathbf{k}\cdot e^{i\Omega} = \partial e^{i\Omega}/\partial\mathbf{p}$, the first term on the right-hand side of Eq. (19) is written as

$$\int \left(\frac{\partial e^{i\Omega}}{\partial\mathbf{p}}\right)\cdot\langle\boldsymbol{\omega}\rangle\,\rho\,d\mathbf{p} = -\int e^{i\Omega}\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\omega}\rangle\,\rho\,d\mathbf{p}, \tag{20}$$

where we performed an integration by parts, and now the average is on $\boldsymbol{\xi}$ only. This expression is the Fourier transform of

$$-\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\omega}\rangle\rho. \tag{21}$$

In this and in other integration by parts, we are considering that the integrated part disappears by the assumption of a rapid vanishing of ρ at the boundary of integration.

Using the same procedure, the second term on the right-hand side of Eq. (19) is written as

$$\frac{1}{2}\int e^{i\Omega}\frac{\partial}{\partial\mathbf{p}}\cdot\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle\rho\,d\mathbf{p}, \tag{22}$$

where we performed two successive integrations by parts. This expression is the Fourier transform of

$$\frac{1}{2}\frac{\partial}{\partial\mathbf{p}}\cdot\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle\rho. \tag{23}$$

To determine $\partial\rho/\partial t$, we bear in mind that $\partial\Phi/\partial t$, given by Eq. (19), is its Fourier transform. Therefore, the time derivative of ρ is obtained by adding up the expressions (21) and (23). The result is

$$\frac{\partial\rho}{\partial t} = \frac{1}{2}\frac{\partial}{\partial\mathbf{p}}\cdot\left(\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle\rho - 2\langle\boldsymbol{\omega}\rangle\rho\right). \tag{24}$$

It remains yet to determine $\boldsymbol{\omega}$ in terms of $\boldsymbol{\xi}$.

C. Lagrange multiplier

We saw that the discretized equation of motion (11) preserves the kinetic energy up to time τ. It is not guaranteed that the kinetic energy $\mathscr{K}$ will be preserved forever. To ensure that this will happen for all times, we impose the vanishing of the probability of a trajectory that does not lie on a surface of constant kinetic energy. This amounts to saying that if initially ρ is nonzero only on the surface of constant $\mathscr{K}$, then this property should be preserved as ρ evolves in time. Let us denote by ρ^* a probability density that is zero outside this surface. Then the variation of ρ^* to a point outside the surface vanishes, that is, $d\rho^* = 0$. If ρ is a generic solution of Eq. (24), then ρ^* can be found from ρ by using the method of the Lagrange multipliers, which means

$$d\rho^* = d\rho + \lambda d\mathscr{K}, \tag{25}$$

where λ is a Lagrange multiplier. This equation is equivalent to

$$\rho^* = \rho + \lambda\mathscr{K}. \tag{26}$$

Replacing this expression in the evolution equation (24), written in the simplified form

$$\frac{\partial\rho}{\partial t} = \mathfrak{F}\rho, \tag{27}$$

where $\mathfrak{F}$ is a linear differential operator, we find that ρ^* is a solution of the evolution equation as long as

$$\mathfrak{F}\mathscr{K} = 0. \tag{28}$$

The condition (28) becomes fulfilled if the expression between parentheses in Eq. (24) vanishes when ρ is replaced by $K = p^2/2m$, that is,

$$\frac{\partial}{\partial\mathbf{p}}\cdot\boldsymbol{\xi}\boldsymbol{\xi}p^2 - 2\boldsymbol{\omega}p^2 = 0. \tag{29}$$

Solving for $\boldsymbol{\omega}$, we find

$$\boldsymbol{\omega} = \frac{1}{2p^2}\frac{\partial}{\partial\mathbf{p}}\cdot\boldsymbol{\xi}\boldsymbol{\xi}p^2, \tag{30}$$

which, by the use of the relation $\mathbf{p}\cdot\boldsymbol{\xi} = 0$, can be written in the more simplified form

$$\boldsymbol{\omega} = \frac{1}{2}\frac{\partial}{\partial\mathbf{p}}\cdot\boldsymbol{\xi}\boldsymbol{\xi}, \tag{31}$$

which is the sought relation between $\boldsymbol{\omega}$ and $\boldsymbol{\xi}$.

Replacing Eq. (31) in Eq. (24) we obtain the evolution equation in the simple form

$$\frac{\partial\rho}{\partial t} = \frac{1}{2}\frac{\partial}{\partial\mathbf{p}}\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle\cdot\frac{\partial}{\partial\mathbf{p}}\rho. \tag{32}$$

Using Eq. (31), the discretized stochastic equation of motion (11) becomes

$$\Delta\mathbf{p} = \sqrt{\tau}\boldsymbol{\xi} + \frac{\tau}{2}\frac{\partial}{\partial\mathbf{p}}\cdot\boldsymbol{\xi}\boldsymbol{\xi}, \tag{33}$$

which is the desired interpretation of the stochastic equation of motion leading to the conservation of kinetic energy for all times. It is worth mentioning that this equation *does not* correspond to the Stratonovich interpretation of Eq. (6), which is

$$\Delta\mathbf{p} = \sqrt{\tau}\boldsymbol{\xi} + \frac{\tau}{2}\boldsymbol{\xi}\cdot\frac{\partial}{\partial\mathbf{p}}\boldsymbol{\xi}, \tag{34}$$

and corresponds to use $\boldsymbol{\omega}'$, given by Eq. (15). Of course, it does not correspond either to the Itô interpretation which is simply that given by Eq. (8).

D. Expression of $\boldsymbol{\xi}$

It remains now to determine the explicit expression for the stochastic force $\boldsymbol{\xi}$. The only restriction that has to be fulfilled is the orthogonal condition (5), that is,

$$\mathbf{v}\cdot\boldsymbol{\xi} = 0. \tag{35}$$

To meet this condition, we choose two vectors **a** and **b** that are orthogonal to **v**, and to each other,

$$\mathbf{v}\cdot\mathbf{a} = 0, \quad \mathbf{v}\cdot\mathbf{b} = 0, \quad \mathbf{a}\cdot\mathbf{b} = 0, \tag{36}$$

and write

$$\boldsymbol{\xi} = \mathbf{a}\sigma + \mathbf{b}\eta, \tag{37}$$

where σ and η are independent stochastic variables with zero mean and variance equal to 2γ.

From these definitions we determine the average $\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle$ appearing in the evolution equation (32)

$$\langle\boldsymbol{\xi}\boldsymbol{\xi}\rangle = 2\gamma(\mathbf{aa} + \mathbf{bb}), \tag{38}$$

which replaced in Eq. (24), gives

$$\frac{\partial\rho}{\partial t} = \gamma\frac{\partial}{\partial\mathbf{p}}\cdot(\mathbf{aa} + \mathbf{bb})\cdot\frac{\partial}{\partial\mathbf{p}}\rho. \tag{39}$$

We write the Cartesian coordinates of the relative velocity **v** using spherical coordinates as

$$\mathbf{v} = (v\sin\theta\cos\varphi,\ v\sin\theta\sin\varphi,\ v\cos\theta), \tag{40}$$

where v is the absolute value of the velocity, θ is the polar angle and φ is the azimuthal angle. The vectors **a** and **b** are chosen to be unit vector with Cartesian coordinates given by

$$\mathbf{a} = (\cos\theta\cos\varphi,\ \cos\theta\sin\varphi,\ -\sin\theta), \tag{41}$$

$$\mathbf{b} = (-\sin\theta\sin\varphi,\ \sin\theta\cos\varphi,\ 0). \tag{42}$$

It is easily seen that the conditions of Eq. (36) are satisfied.

Up to now we treated a system in three dimensions. To treat a two-dimensional system, we have to consider that the vector quantities have two Cartesian components. In this case, instead of two vectors orthogonal to **v**, just one is possible. Writing

$$\mathbf{v} = (v\cos\phi,\ v\sin\phi), \tag{43}$$

this vector is

$$\mathbf{b} = (-\sin\phi,\ \cos\phi). \tag{44}$$

In this case there is just one random variable η and

$$\boldsymbol{\xi} = \mathbf{b}\eta. \tag{45}$$

If we wish to treat a system in one dimension, we see that this is unattainable because it is not possible to meet the condition of orthogonality (36). This reflects the following result concerning the collision of two particles in one dimension. Given the velocities of the particles before the collision, they are uniquely determined after the collision if the energy and momentum are conserved. Thus, in one dimension there is no room for a stochastic motion that conserves both the energy and momentum.

E. Entropy production

Although the energy is strictly conserved, this is not the case of the entropy. The entropy is defined by

$$S = -k\int\rho\ln\rho\, d\mathbf{p}, \tag{46}$$

and its time variation can be obtained from the evolution equation (39). Deriving this expression with respect to time, we obtain

$$\frac{dS}{dt} = -k\int\frac{\partial\rho}{\partial t}\ln\rho\, d\mathbf{p}. \tag{47}$$

Replacing the derivative of ρ, given by the evolution equation (39), and after an integration by parts, we reach the result

$$\frac{dS}{dt} = k\gamma\int\frac{1}{\rho}\frac{\partial\rho}{\partial\mathbf{p}}\cdot(\mathbf{aa} + \mathbf{bb})\cdot\frac{\partial\rho}{\partial\mathbf{p}}d\mathbf{p}, \tag{48}$$

which can be written in the form

$$\frac{dS}{dt} = k\gamma\int\frac{1}{\rho}(A^2 + B^2)d\mathbf{p}, \tag{49}$$

where

$$A = \mathbf{a}\cdot\frac{\partial\rho}{\partial\mathbf{p}}, \quad B = \mathbf{b}\cdot\frac{\partial\rho}{\partial\mathbf{p}}. \tag{50}$$

As the integral is positive-definite, $dS \geqslant 0$, the entropy is a monotonic increasing function of time. The right-hand side of Eq. (49) is understood as the rate of entropy production. In the stationary state ρ_e will be a function of K and $\partial\rho/\partial\mathbf{p}$ will be proportional to **p** which is orthogonal to **a** and **b**. Thus A and B vanish, the entropy production vanishes, and the entropy reaches is maximum value.

III. SYSTEM OF INTERACTING PARTICLES

A. Stochastic equations of motion

Our attention is now directed toward a system of several interacting particles. The position and the momentum of particle i are denoted by $\mathbf{x}_i$ and by $\mathbf{p}_i$, and the system is described by the Hamiltonian function

$$\mathscr{H} = \sum_i\frac{p_i^2}{2m_i} + \mathscr{V}, \tag{51}$$

where $p_1^2 = p_{xi}^2 + p_{yi}^2 + p_{zi}^2$, m_i is the mass of the particle i, and $\mathscr{V}$ is a function of the coordinates and represent the potential energy of the particles. The stochastic equations of motion, or the Langevin equations, are

$$\frac{d\mathbf{x}_i}{dt} = \mathbf{v}_i, \qquad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + \boldsymbol{\zeta}_i, \tag{52}$$

where $\mathbf{v}_i$ and $\mathbf{F}_i$ are the velocity and the conservative force, respectively, associated to the particle i, and are given by

$$\mathbf{v}_i = \frac{\partial\mathscr{H}}{\partial\mathbf{p}_i}, \qquad \mathbf{F}_i = -\frac{\partial\mathscr{H}}{\partial\mathbf{x}_i}. \tag{53}$$

We wish to describe a system by forces that strictly conserves the total momentum of the collection of particles, given by

$$\mathbf{P} = \sum_i \mathbf{p}_i, \tag{54}$$

and the total energy, given by Eq. (51). The particles are subject only to internal forces, which means that, for each force $\mathbf{F}_i$, there is a reaction force with the opposite sign so that the sum of the conservative forces vanish

$$\sum_i \mathbf{F}_i = \mathbf{0}. \tag{55}$$

Deriving $\mathbf{P}$ with respect to time and using Eq. (55), we get

$$\frac{d\mathbf{P}}{dt} = \sum_i \boldsymbol{\zeta}_i. \tag{56}$$

Therefore, the conservation of momentum requires that the sum of the stochastic forces vanishes.

Deriving the function $\mathscr{H}$ with respect to time, we find

$$\frac{d\mathscr{H}}{dt} = \sum_i \mathbf{v}_i \cdot \boldsymbol{\zeta}_i. \tag{57}$$

There is no contribution coming from the conservative forces. The right-hand side of this equation is the total power of the stochastic force, which should vanish.

The stochastic forces are chosen so that the right-hand sides of the Eqs. (56) and (57) vanish identically. To meet the first requirement, we choose $\boldsymbol{\zeta}_i$ as a sum of independent stochastic vector variables $\boldsymbol{\xi}_{ij}$,

$$\boldsymbol{\zeta}_i = \sum_j \boldsymbol{\xi}_{ij}, \tag{58}$$

with the properties

$$\boldsymbol{\xi}_{ji} = -\boldsymbol{\xi}_{ij}, \tag{59}$$

and $\boldsymbol{\xi}_{ii} = 0$. We see that the right-hand side of Eq. (56) vanishes identically, and the total momentum is strictly conserved. The vector $\boldsymbol{\xi}_{ij}$ is understood as the random force acting on particle i due to particle j and $\boldsymbol{\xi}_{ji}$ as the random force on particle j due particle i. Since they were chosen to differ only by their signs, they are interpreted as action and reaction, leading to the conservation of the total momentum. We now replace Eq. (58) in the right-hand side of Eq. (57) to find

$$\frac{d\mathscr{H}}{dt} = \frac{1}{2}\sum_{ij} (\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\xi}_{ij}, \tag{60}$$

where we used the property (59). Requiring that

$$\mathbf{v}_{ij} \cdot \boldsymbol{\xi}_{ij} = 0, \tag{61}$$

for each pair ij, where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity of particles i and j, we see that the right-hand side of Eq. (60) vanishes identically and $d\mathscr{H}/dt = 0$. The random force ξ_{ij} acting on the particles i and j must be orthogonal to their relative velocities $\mathbf{v}_{ij}$ and, therefore, performs no work.

To meet the condition (61), we choose two unit vectors $\mathbf{a}_{ij}$ and $\mathbf{b}_{ij}$, to be orthogonal to $\mathbf{v}_{ij}$, and to each other

$$\mathbf{v}_{ij} \cdot \mathbf{a}_{ij} = 0, \quad \mathbf{v}_{ij} \cdot \mathbf{b}_{ij} = 0, \quad \mathbf{v}_{ij} \cdot \mathbf{b}_{ij} = 0. \tag{62}$$

We also introduce two new scalar random variables σ_{ij} and η_{ij}, and write

$$\boldsymbol{\xi}_{ij} = \mathbf{a}_{ij}\sigma_{ij} + \mathbf{b}_{ij}\eta_{ij}. \tag{63}$$

Due to the orthogonal property (62) of $\mathbf{a}_{ij}$ and $\mathbf{b}_{ij}$, we see that the condition (61) is fulfilled.

The vectors $\mathbf{a}_{ij}$ and $\mathbf{b}_{ij}$ are chose to be given by the expressions (41) and (42). We remark that when we interchange i and j, the vector $\mathbf{a}_{ij}$ preserves its sign and $\mathbf{b}_{ij}$ changes sign. As $\boldsymbol{\xi}_{ij}$ must change sign then the stochastic variable σ_{ij} should change its sign and η_{ij} should preserve its sign.

The random variables σ_{ij} and η_{ij} are chosen to have zero mean and the same variance $2\gamma_{ij}$, which represents the strength of the random forces and might depend on the positions of the particles i and j. It is reasonable to assume that γ_{ij} is nonzero only when the particles i and j are close to each other.

The variance of $\boldsymbol{\xi}_{ij}$ is $\langle \boldsymbol{\xi}_{ij}\boldsymbol{\xi}_{ij}\rangle = 2\mathbb{K}_{ij}$, where $\mathbb{K}_{ij}$ is a 3×3 symmetric matrix given by

$$\mathbb{K}_{ij} = \gamma_{ij}(\mathbf{a}_{ij}\mathbf{a}_{ij} + \mathbf{b}_{ij}\mathbf{b}_{ij}), \tag{64}$$

and $\mathbb{K}_{ii} = 0$. The covariances of the random vector $\boldsymbol{\zeta}_i$ are obtained from Eq. (58) and is related to this matrix by

$$\langle \boldsymbol{\zeta}_i\boldsymbol{\zeta}_j\rangle = -2\mathbb{K}_{ij}, \quad i \neq j, \tag{65}$$

$$\langle \boldsymbol{\zeta}_i\boldsymbol{\zeta}_i\rangle = 2\sum_j \mathbb{K}_{ij}. \tag{66}$$

B. Evolution equation

To derive the equation that gives the time evolution of the probability density function ρ of the dynamic variables $\mathbf{x}_i$ and $\mathbf{p}_i$, we assume the following discretized equations of motion

$$\Delta\mathbf{x}_i = \tau\mathbf{v}_i, \tag{67}$$

$$\Delta\mathbf{p}_i = \tau\mathbf{F}_i + \sqrt{\tau}\boldsymbol{\zeta}_i + \frac{\tau}{4}\frac{\partial}{\partial\mathbf{p}_i}\cdot\boldsymbol{\zeta}_i\boldsymbol{\zeta}_i, \tag{68}$$

where $\boldsymbol{\zeta}_i$ is the sum of the independent stochastic variables $\boldsymbol{\xi}_{ij}$, each one given by Eq. (63).

We derive the evolution equation by the method that we used above. To this end we define the characteristic function Φ by

$$\Phi = \int e^{i\Omega}\rho\, dq dp, \tag{69}$$

where the integration is over the phase space and

$$\Omega = \sum_j (\mathbf{k}_j \cdot \mathbf{x}_j + \mathbf{q}_j \cdot \mathbf{p}_j), \tag{70}$$

where $\mathbf{k}_i$ and $\mathbf{q}_i$ are vectors in the Fourier space. The characteristic function is also the average over ρ,

$$\Phi = \langle e^{i\Omega}\rangle. \tag{71}$$

The finite variation Φ is given by

$$\Delta\Phi = \langle e^{i\Omega}(e^{i\Delta\Omega} - 1)\rangle. \tag{72}$$

Expanding the right-hand side of this equation up to terms of the order τ, we find the time derivative of Φ as

$$\frac{\partial\Phi}{\partial t} = \sum_j \langle e^{i\Omega}(i\mathbf{k}_j\cdot\mathbf{v}_j + i\mathbf{q}_j\cdot\mathbf{F}_j)\rangle + \frac{1}{2}\sum_j\left\langle e^{i\Omega}\left(\frac{\partial}{\partial\mathbf{p}_j}\cdot\boldsymbol{\zeta}_j\boldsymbol{\zeta}_j + \frac{1}{2}\sum_\ell i\mathbf{q}_\ell\cdot\boldsymbol{\zeta}_\ell\boldsymbol{\zeta}_j\right)\cdot i\mathbf{q}_j\right\rangle. \tag{73}$$

To obtain the evolution equation, it suffices to take the inverse Fourier transform of the Eq. (73). To this end we observe that the first term of Eq. (73) is the Fourier transform of the Poisson brackets

$$\{\mathscr{H},\rho\} = \sum_j\left(\frac{\partial\mathscr{H}}{\partial\mathbf{x}_j}\cdot\frac{\partial\rho}{\partial\mathbf{p}_j} - \frac{\partial\mathscr{H}}{\partial\mathbf{p}_j}\frac{\partial\rho}{\partial\mathbf{x}_j}\right), \tag{74}$$

a result which is reached by using the relations

$$i\mathbf{k}_j e^{i\Omega} = \frac{\partial e^{i\Omega}}{\partial\mathbf{x}_j}, \quad i\mathbf{q}_j e^{i\Omega} = \frac{\partial e^{i\Omega}}{\partial\mathbf{p}_j}. \tag{75}$$

Using Eqs. (65) and (66), the second term of Eq. (73) can be written in the form

$$\frac{1}{2}\sum_{j\neq\ell}\left\langle e^{i\Omega}\left(\frac{\partial}{\partial\mathbf{p}_j}\cdot\mathbb{K}_{j\ell} + \frac{i}{2}(\mathbf{q}_j - \mathbf{q}_\ell)\cdot\mathbb{K}_{j\ell}\right)\cdot i\mathbf{q}_j\right\rangle. \tag{76}$$

Taking into account that $\mathbb{K}_{j\ell}$ depends on $\mathbf{p}_j$ through the difference $\mathbf{p}_j - \mathbf{p}_\ell$, we may write

$$\frac{1}{2}\sum_{j\neq\ell}\langle e^{i\Omega}[\mathbf{D}_{j\ell}\cdot\mathbb{K}_{j\ell} + i(\mathbf{q}_j - \mathbf{q}_\ell)\cdot\mathbb{K}_{j\ell}]\cdot i\mathbf{q}_j\rangle, \tag{77}$$

where

$$\mathbf{D}_{j\ell} = \frac{\partial}{\partial\mathbf{p}_j} - \frac{\partial}{\partial\mathbf{p}_\ell}. \tag{78}$$

This expression is equal to the integral

$$-\frac{1}{2}\sum_{j\neq\ell}\int e^{i\Omega} i\mathbf{q}_j\cdot\mathbb{K}_{j\ell}\cdot\mathbf{D}_{j\ell}\rho\, dx dp, \tag{79}$$

which was obtained by an integration by parts and using the result

$$\mathbf{D}_{j\ell}e^{i\Omega} = i(\mathbf{q}_j - \mathbf{q}_\ell)e^{i\Omega}. \tag{80}$$

Employing again the second equality of Eq. (75) and performing another integration by parts, we find a result which is the Fourier transform of

$$\frac{1}{2}\sum_{j\neq\ell}\frac{\partial}{\partial\mathbf{p}_j}\cdot\mathbb{K}_{j\ell}\cdot\mathbf{D}_{j\ell}\rho. \tag{81}$$

The evolution equation is obtained by observing that $\partial\Phi/\partial t$ is the Fourier transform of $\partial\rho/\partial t$. Therefore, to reach the equation it suffices to add up the results of Eqs. (74) and (81),

$$\frac{\partial\rho}{\partial t} = \{\mathscr{H},\rho\} + \frac{1}{2}\sum_{(ij)}\mathbf{D}_{ij}\cdot\mathbb{K}_{ij}\cdot\mathbf{D}_{ij}\rho. \tag{82}$$

Replacing $\mathbb{K}_{ij}$ in this expression, the evolution equation acquires the form

$$\frac{\partial\rho}{\partial t} = \{\mathscr{H},\rho\} + \frac{1}{2}\sum_{(ij)}\gamma_{ij}\mathbf{D}_{ij}\cdot(\mathbf{a}_{ij}A_{ij} + \mathbf{b}_{ij}B_{ij}), \tag{83}$$

where

$$A_{ij} = \mathbf{a}_{ij}\cdot\mathbf{D}_{ij}\rho, \quad B_{ij} = \mathbf{b}_{ij}\cdot\mathbf{D}_{ij}\rho. \tag{84}$$

We argued above in the analysis of the stochastic motion of two particles that the kinetic energy is a stationary solution of the evolution equation. The reasoning based on the Lagrange multipliers can be generalized leading to the rule that a *conserved quantity is a stationary solution of the evolution equation*. This is indeed the case of $\mathscr{H}$ and $\mathbf{P}$ in relation to the evolution Eq. (83), which can be verified by inspection. The Poisson brackets vanish trivially when ρ is replaced by $\mathscr{H}$. When it is replaced by $\mathbf{P}$ it vanishes as well if we use the condition (55). The quantities A_{ij} and B_{ij} given by Eq. (84) vanish when ρ is replaced by $\mathscr{H}$ because $\mathbf{D}_{ij}\mathscr{H}$ equals $\mathbf{v}_{ij}$ which is orthogonal to $\mathbf{a}_{ij}$ and $\mathbf{b}_{ij}$. The quantities A_{ij} and B_{ij} also vanish when ρ is replaced by $\mathbf{P}$ because $\mathbf{D}_{ij}\cdot\mathbf{P} = 0$.

From the results just obtained, it follows that any function of the conserved quantities will be a stationary solution of the evolution equation. In particular, the microcanonical Gibbs distribution (1) is a stationary solution of the evolution equation, and represents the state of thermodynamic equilibrium of the system. If we start with a probability distribution ρ defined on a surface of constant energy, then it will remain on this surface. If the energy is equal to E, the probability density will eventually reach the Gibbs distribution (1). In other words, the system will relax to equilibrium. This result can be demonstrated by showing that the entropy is a nondecreasing function of time and that its maximum value is the one corresponding to the Gibbs distribution (1). This will be shown in the following.

C. Entropy production

Let us determine the time evolution of the average U of $\mathscr{H}$. Multiplying Eq. (82) by $\mathscr{H}$ and integrating in the phase space, we arrive at the equation

$$\frac{dU}{dt} = -\frac{1}{2}\sum_{(ij)}\int\mathbf{v}_{ij}\cdot\mathbb{K}_{ij}\cdot\mathbf{D}_{ij}\rho\, dx dp, \tag{85}$$

where we performed an integration by parts and used the result $\mathbf{D}_{ij}\mathscr{H} = \mathbf{v}_{ij}$. Taking into account the orthogonality (62), it follows that the right-hand side of Eq. (85) vanishes and $dU/dt = 0$. That is, U remains constant in time, which is expected because $\mathscr{H}$ is conserved by the evolution equation.

We determine now the time evolution of the entropy S, defined by

$$S = -k\int\rho\ln\rho\, dx dp. \tag{86}$$

Multiplying the evolution Eq. (82) by $-\ln\rho$ and integrating in the phase space, we find

$$\frac{dS}{dt} = \frac{k}{2}\sum_{(ij)}\int\frac{1}{\rho}(\mathbf{D}_{ij}\rho)\cdot\mathbb{K}_{ij}\cdot(\mathbf{D}_{ij}\rho), \tag{87}$$

where we performed an integration by parts. Replacing $\mathbb{K}_{ij}$ given by Eq. (64), we reach the following expression:

$$\frac{dS}{dt}=\frac{k}{2}\sum_{(ij)}\int\frac{\gamma_{ij}}{\rho}\left(A_{ij}^2+B_{ij}^2\right)dxdp. \tag{88}$$

We see that the right-hand side of Eq. (88), which we denote by Π, is positive-definite and should be interpreted as the rate of entropy production since there is no exchange of energy with the environment, in fact no exchange of heat occurs since there is no external work involved. We remark that Π vanishes in equilibrium because each one of the terms A_{ij} and B_{ij} vanish when ρ is replaced by the equilibrium distribution ρ_e, given by Eq. (1). Since S is monotonically increasing in time because $dS/dt=\Pi\geqslant 0$, it reaches a maximum when $\Pi=0$, that is, when the distribution is ρ_e.

IV. LIOUVILLE EQUATION

If we set γ_{ij} equal to zero in the Fokker-Planck Eq. (82), which means that no stochastic forces are involved, it reduces to the form

$$\frac{\partial\rho}{\partial t}+\{\rho,\mathscr{H}\}=0, \tag{89}$$

which is the Liouville equation. Here we present the usual derivation of the Liouville equation, which is carried out by the use of the Liouville theorem. We also present some of its properties to compare with those of the Fokker-Planck Eq. (82). We consider a system described by a Hamiltonian $\mathscr{H}$, and the equations of motion are

$$\frac{dx_i}{dt}=\frac{\partial\mathscr{H}}{\partial p_i},\qquad\frac{dp_i}{dt}=-\frac{\partial\mathscr{H}}{\partial x_i}. \tag{90}$$

If at time t we consider a region $\mathscr{R}$ in phase space which is transformed, through the Hamiltonian motion, in a region $\mathscr{R}'$ at time t', then the Liouville theorem states that the volume of these regions are equal, that is,

$$\int_{\mathscr{R}}dxdp=\int_{\mathscr{R}'}dx'dp'. \tag{91}$$

We may also write this result as $dxdp=dx'dp'$, which means that the Jacobian of the transformation $(x,p)\to(x',p')$ equals the unity.

In the usual derivation, the Liouville equation is obtained by postulating that the probability of the region $\mathscr{R}$ at time t is equal to that of the region $\mathscr{R}'$ at time t', that is,

$$\int_{\mathscr{R}}\rho(x,p,t)dxdp=\int_{\mathscr{R}'}\rho(x',p',t')dx'dp', \tag{92}$$

or $\rho(x,p,t)dxdp=\rho(x',p',t')dx'dp'$. From this equation and the Liouville theorem, we find

$$\rho(x,p,t)=\rho(x',p',t'), \tag{93}$$

and the probability density is invariant along a trajectory. This is equivalent to say that the material time derivative of ρ vanishes, that is,

$$\frac{\partial\rho}{\partial t}+\sum_i\left(\frac{\partial\rho}{\partial x_i}\frac{\partial x_i}{dt}+\frac{\partial\rho}{\partial p_i}\frac{\partial p_i}{dt}\right)=0. \tag{94}$$

Taking into account the Hamilton equations of motion, the second term becomes the Poisson brackets $\{\rho,\mathscr{H}\}$ and we arrive at the Liouville Eq. (89).

The most relevant property of the Liouville equation is that the microcanonical Gibbs distribution (1) is a stationary distribution of the equation. However, not all initial distribution will relax to this distribution. To discuss this point we use the property coming from the Liouville equation that the entropy is invariant in time.

The entropy $S(t)$ at time t is defined by Eq. (86). Using the invariance of the probability density along a trajectory, given by Eq. (93), we reach the result $S(t)=S(t')$, at distinct instants of time. Alternatively, we may employ the procedure used above in the stochastic approach. We multiply the Liouville Eq. (89) by $k\ln\rho$ and integrate in the phase space. After an integration by parts we find that $dS/dt=0$, and the entropy is invariant.

To proceed in our analysis it is convenient to define the measure of a surface A of constant energy E in phase space. We consider another surface A$'$ of constant energy E', with E' differing little from E. The measure of A, which we denote by $\Omega_{\rm A}$, is the volume between the two surfaces A' and A divided by $E'-E$. Thus Ω appearing in Eq. (1) is the measure of the entire surface of constant energy E.

Let us consider a probability distribution, denoted by $\rho_{\rm A}$, which is nonzero only in a surface A which is a subset of the whole surface of constant energy E. Within A it is given by

$$\rho_{\rm A}=\frac{1}{\Omega_{\rm A}}\delta(E-\mathscr{H}), \tag{95}$$

where $\Omega_{\rm A}$ is the measure of A. The corresponding entropy is $S_A=k\ln\Omega_A$.

Suppose that the initial condition to the Liouville equation is ρ_A. As time evolves, the surface A changes to another surface A' and become intertwined with the complementary surface to the whole surface. However, by the Liouville theorem, the measure of A' is the same as that of A, and the entropy remains constant and equal to S_A. Therefore, the Gibbs distribution will never be reached because the entropy of this distribution is $S_e=k\ln\Omega$ which is larger than S_A.

We present now an example where the initial distribution is nonzero and given by

$$\rho=a\rho_A+b\rho_B, \tag{96}$$

where $a+b=1$, and the surfaces A and B are complementary surfaces and make up the entire surface of constant energy E. The corresponding entropy is

$$S=ka\ln\frac{\Omega_A}{a}+kb\ln\frac{\Omega_{\rm B}}{b}, \tag{97}$$

and it differs from $S_e=k\ln\Omega$, where $\Omega=\Omega_{\rm A}+\Omega_B$. In fact, we can show that $S_e\geqslant S$, the equality occurring when ρ is the Gibbs distribution in which case $a=\Omega_A/\Omega$ and $b=\Omega_B/\Omega$. Therefore, if the initial distribution is of the type (96) but is not the Gibbs distribution, this Gibbs distribution will never be reached.

V. CONCLUSION

We proposed a stochastic equation of motion that emerges as a consequence of stochastic forces acting on each pair of particles. The random forces acting on a pair of particles are action and reaction leading to the conservation of momentum. These forces are perpendicular to the relative velocity between the particles, performing, therefore, zero work on the two particles and thus preserving their kinetic energy.

These stochastic forces and the conservative forces leads to the conservation of energy along a trajectory in phase space. The trajectories in phase space are restricted to the surface of constant energy and is thus similar in this aspect to the Hamiltonian flow. From the stochastic motion, we derived the evolution equation for the density which turns out to be a Fokker-Planck equation, but distinct from the usual Fokker-Planck equation that describes the contact of system with a heat reservoir.

To derive the evolution equation we introduced an appropriate interpretation of the stochastic equation of motion that does not correspond neither to the interpretation proposed by Itô nor that proposed by Stratonovich. The interpretation proposed here makes the energy be conserved at all times, a result that was demonstrated by showing that the Hamiltonian function is a stationary solution of the evolution equation.

In contrast to the Liouville equation, which also describes a closed system and conserves the energy, the evolution equation that we set up predicts the increase of entropy and the relaxation to equilibrium. In other terms, the equation describes an irreversible decay to equilibrium, but we cannot ascertain whether the present approach could describe correctly the actual decay observed in real closed systems.

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