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Statistical Mechanics of Systems Subject to Constraints

L. C. GOMES and R. LOBO

Centro Brasileiro de Pesquisas Físicas — CNPq, Av. Wenceslau Braz, 71, Rio de Janeiro
and
Departamento de Física e Ciências dos Materiais, Instituto de Física e Química, São Carlos, SP

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The statistical mechanics of systems subject to constraints is discussed. For integrable constraint Dirac's method to deal with singular lagrangeans is introduced and a hamiltonian is obtained. From this hamiltonian the phase-space Fokker-Planck equation and the diffusion equation are derived. Another derivation for the diffusion equation is proposed which makes no use of Hamilton's formalism and that may, therefore, be applied both to integrable and non-integrable constraints which preserve volume in coordinate-velocity space. The existence of a diffusion equation for non-integrable constraints and possible analogies to quantum mechanics of similar systems is discussed.

É discutida a mecânica estatística de sistemas sujeitos a vínculos. Para vínculos integráveis o método de Dirac é usado para obter a hamiltoniana da qual a equação de Fokker Planck e de difusão são obtidas. Uma outra derivação da equação de difusão é proposta sem fazer uso do formalismo hamiltoniano e que pode assim ser usada tanto para vínculos integráveis como não-integráveis desde que o vínculo preserve o volume do espaço coordenada-velocidade. É discutida a analogia entre equação de difusão e equação de Schrödinger à luz da existência da equação de difusão para vínculos não-integráveis.

1. INTRODUCTION

The most elegant and compact way of studying statistical mechanics is based on the hamiltonian formalism[1]. A probabilistic interpretation of the dynamical process is introduced by means of Gibbs ensembles, assuming a construction were a large number of copies of the same system, under identical macroscopic conditions, are idealized each one corresponding to a point in phase space, the statistical ensemble is then specified by the distribution function which represents the probability density occupation of the distribution of systems in phase space.

The possibility of introducing such a distribution function is based on Liouville's theorem which proves that the volume in phase space corresponding to a collection of points obeying Hamilton's equations remains constant during the motion of the system. In other words, the motion of the phase points describing the statistical system behaves as an incompressible fluid and the distribution function is constant along the phase trajectories. As a consequence of this theorem one obtains Liouville's equations for classical systems*

$$\frac{\partial f}{\partial t} = \{H,f\}$$

and for quantum systems one replaces $\{,\}$ by $1/i\hbar\,[\,,\,]$. Here f is the distribution function, H the Hamiltonian of the system and $[\,,\,]$ the commutator.

Liouville's equation is essential for the construction of equilibrium and non-equilibrium statistical ensembles. It has the form of a continuity equation is phase space.

When differential constraints are imposed upon the mechanical system several difficulties are easily detected. In general, the hamiltonian formalism breaks down. If the constraint equations are integrable

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* By $\{H,f\}$, is understood the Poisson brackets as usually defined p.Ex., in H.Goldstein, Classical mechanics, Addison Wesley (1973).

one may apply Dirac's method to deal with singular lagrangeans and the hamiltonian formalism is recovered. The problem, in this case, is tractable by Liouville's equation by the use of Dirac's hamiltonian. If, on the other hand, the constraints are non-integrable the Lagrangean formalism is inadequate, as we have shown in reference (2), and the whole problem of doing statistical mechanics has to be reanalysed. From the mechanical equations of motion one may compute the change in the volume along the trajectory of the elementary volume in the coordinate-velocity space. If this volume is conserved, then equilibrium may be defined through the constants of the motion of the system, such as the energy, and evolution equations may be derived.

The purpose of this work is to study the statistical mechanics of constrained systems. In the next section we shall discuss the application of Dirac's method to constrained non-interacting particles. From Dirac's hamiltonian, Fokker-Planck and the diffusion equations are obtained in section 3. The diffusion equation obtained is very similar to the Schrödinger equation for similar constrained quantum mechanical systems.

In section 4 we proposed a way to derive the evolution equation for the distribution function directly from the newtonian equations for the particle trajectories. As no lagrangean or hamiltonian formalism are invoked, we are able to extend the method to non-integrable constraints, whenever the coordinate-velocity elementary volume is preserved along the trajectory. In the limit of very small relaxation times a diffusion equation is obtained which agrees with the one obtained in section 3 for integrable constraints.

In the conclusion we discuss the results for non-holonomic constraint and the collisionless limit of the theory. We compare the diffusion and Schrödinger equations for constrained systems.

In this work we consider only particles in the euclidean three dimensional space subject to one constraint equation. The introduction of external potentials or interaction among particles are easy to be performed but complicates the formalism and it does not improve the understanding of the problem.

2. DIRAC'S HAMILTONIAN FOR SYSTEMS WITH CONSTRAINTS

Consider a free particle subject to the differential constraint

$$a_i \, \dot{q}_i = 0 \tag{2.1}$$

We may assume, without any loss of generality, a_i as the components of the unit vector $\vec{a}$, what is equivalent to say that $a_i \, dq_i$ is non- singular.

If the constraint equation is integrable we may derive the equations of motion for the particle from the variational principle, as discussed in reference (2).

The procedure we are going to adopt here is the same as that of reference (2) and we summarize it here to make this work self-contained. We assume in this section that the constraint equation is integrable.

Let us define the lagrangean

$$L = \frac{m}{2} (\dot{\vec{q}})^2 - \lambda \, a \cdot \dot{\vec{q}} \, , \tag{2.2}$$

where λ, the usual Lagrange multiplier, is considered as the fourth coordinate of the particle, m is the mass of the particle and $\vec{q}$ its coordinate.

It is easy to show that the Euler-Lagrange equations for such a Lagrangean are

$$m \, \ddot{q}_i = - \, a_i (\partial a_j / \partial q_n) \, \dot{q}_j \, \dot{q}_n \tag{2.3}$$

and

$$a_i \, \dot{q}_i = 0$$

These are the correct equations of motion and constraint as they agree with those derived from D'Alembert's principle[2].

The Lagrangean given in eq. (2.2) is singular since it is independent of $\dot{\lambda}$. Thus the momentum Π canonically conjugated to λ must vanish in the weak sense:

$$\Pi = 0 \tag{2.4}$$

This equation must be valid at all times and is called by Dirac a primary constraint[3].

We may now construct the hamiltonian in the usual way by defining

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$$

The hamiltonian thus found is, nevertheless, not uniquely defined and we may add to it a linear combination of the primary constraints, in our case just Π. We define

$$H_D = H - u\,\Pi = \frac{(\vec{p})^2}{m} + \frac{\lambda^2}{2m} + \lambda\,\frac{\vec{a}\cdot\vec{p}}{m} - u\,\Pi \ . \tag{2.5}$$

The quantity u can be any function of the q's and p's, $\dot{q}$'s and λ. In principle u is an unknown function.

We now impose that $\dot{\Pi}$ must be zero at all times

$$\dot{\Pi} = \{\Pi\ , H_D\} = 0 \tag{2.6}$$

and using H_D given by eq. (2.5) we have

$$a_i\, p_i + \lambda \ = 0 \tag{2.7}$$

This is another constraint called a secondary constraint. It must also be zero at all times, therefore

$$\{a_i p_i \ + \lambda, H_D\} = \frac{\partial a_i}{\partial q_j}\, p_i \left(\frac{p_j}{m} + \frac{a_j}{m} \right) - \frac{\lambda a_i}{m}\,\frac{\partial a_j}{\partial q_i}\, p_j - u = 0 \tag{2.8}$$

The above equation determines the function u,

$$u \ = \frac{1}{m}\,\frac{\partial a_i}{\partial q_j}\, p_i\, p_j$$

Now the problem is completely solved. We have the hamiltonian H_D plus the

constraints given by eqs. (2.4) and (2.7). Since Π and λ form a pair of canonically conjugated variables we may eliminate them in H_D by the use of eqs. (2.4) and (2.7). We are left with

$$H^* = \frac{1}{2m} Q_{ij} p_i p_j \ , \tag{2.9}$$

where $Q_{ij} = \delta_{ij} - a_i a_j$ is the projector on the plane perpendicular to the vector $\vec{a}$.

H^* is the hamiltonian to be used.

Notice that the constraint eq. (2.1) is automatically satisfied as, from Hamilton's equation, we have

$$\dot{q}_i = \frac{1}{m} Q_{ij} p_j \ , \tag{2.10}$$

and therefore $a_i \dot{q}_i = 0$. The function H^* is also the energy:

$$E = \frac{m}{2} Q_{ij} \dot{q}_i \dot{q}_j \ . \tag{2.11}$$

We shall show, for completeness, that H^* leads, indeed, to the correct equations of motion for integrable constraints.

From eq. (2.10) we obtain

$$\ddot{q}_i = - \frac{1}{m} a_i \ \partial a_j/\partial q_k \ \dot{q}_j \ \dot{q}_k + a_\ell \dot{q}_\ell \left(- \frac{a_\ell p_\ell}{m} \right) (\partial a_i/\partial q_k - Q_{ij} \ \partial a_k/\partial q_j) \ \dot{q}_k \tag{2.12}$$

We now show that the last term on the right hand side of eq. (2.12) is zero for integrable constraint, i.e., if $\vec{a}$ rot $\vec{a} = 0$. Let us assume we are in a system of coordinates that diagonalise Q_{ij}, i.e., $a_3 = 1$ and $a_1 = a_2 = 0$. Then $\ddot{q}_3 = 0$, as $Q_{3i} = 0$ and the normalization of $\vec{a}$ impose that $\partial a_3/\partial q_i = 0$.

Now

$$\partial a_i/\partial q_k - \partial a_k/\partial q_i = \pm (\text{rot } \vec{a})_3 = \pm a_3 (\text{rot } \vec{a})_3 = 0$$

This proves that for integrable constraints the equations of motion obtained by Dirac's H^* are equivalent to those derived by the D'Alembert's principle.

To conclude this section we summarize the results obtained thus far. If the constraint equation is integrable we are allowed to use lagrangean formalism to obtain the equations of motion form the variational principle. The Lagrangean is, nevertheless, singular and we must extend the hamiltonian using Dirac's prescription for consistency. We finally found, a hamiltonian H^* which correctly describes the motion of the system. We may now proceed to discuss the statistical mechanics of constrained systems.

3. FOKKER-PLANCK AND DIFFUSION EQUATIONS

In this section we obtain, using Dirac's Hamiltonian, the Fokker-Planck equation and then the diffusion equation for constrained systems.

Consider a particle immersed in a liquid. To calculate the motion or, in general, the correlation functions for the particle, we build an ensemble made out of a very large number of similar particle plus liquid systems. The average motion (and the correlation functions) of the particle is the average calculated over the ensemble. If one neglects short time effects, the first and second momenta involving Δq_i and Δp_i can be approximated using Langevin's equation.

Besides the canonical equation of motion we introduce a viscosity λ and a stochastic force F_i for which we assume a white spectrum and zero average

$$\langle F_i(t) \rangle = 0$$

$$\langle F_i(t) F_j(t') \rangle = 2K \, \delta_{ij} \, \delta(t-t')$$

The moments are, to first order in Δt

$$\langle \Delta q_i \rangle = \frac{\partial}{\partial p_i} \Delta t$$

$$\langle \Delta q_i \, \Delta q_j \rangle = \langle \Delta q_i \, \Delta p_j \rangle = 0 \tag{3.1}$$

$$\langle \Delta p_i \rangle = \Delta t \left(- \frac{\partial H}{\partial q_i} - \frac{\gamma}{m} \dot{q}_i + \langle F_i \rangle \right) =$$

$$= - \Delta t \left(\frac{\partial H}{\partial q_i} + \frac{\gamma \dot{q}_i}{m} \right)$$

$$\langle \Delta p_i \, \Delta p_j \rangle = 2K \, \delta_{ij} \, \Delta t$$

where γ is the viscosity.

If we introduce the hamiltonian obtained in section 2 we are left with the following equation for the first momentum $\langle \Delta p_i \rangle$

$$\langle \Delta p_i \rangle = \Delta t \left(\frac{a_k}{m} \partial a_j / \partial q_i \, p_k \, p_j - \gamma / m \, Q_{ij} \, p_j \right)$$

We are now able to derive the Fokker-Planck equation in phase space for the constrained system which is,

$$\frac{\partial G}{\partial t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left\{ - \frac{\partial}{\partial q_i} \left(\langle \Delta q_i \rangle G \right) - \frac{\partial}{\partial p_i} \left(\langle \Delta p_i \rangle \, G \right) + \right.$$

$$\left. + \frac{1}{2} \frac{\partial^2}{\partial p_i \, \partial p_j} \left(\langle \Delta p_i \, \Delta p_j \rangle G \right) \right\} = - \frac{\partial}{\partial q_i} \left(\frac{Q_{ij}}{m} \, p_j \, G \right) -$$

$$- \frac{\partial}{\partial p_i} \left(\frac{a_k \, \partial a_j}{m} / \partial q_i \, p_j \, p_k \, G \right) + \frac{\partial}{\partial p_i} \left(\frac{\gamma}{m} \, Q_{ij} \, p_j \, G \right) +$$

$$+ K \frac{\partial^2}{\partial p_i \, \partial p_i} G \tag{3.2}$$

We may check the correctness of the above equations if we take the limit $\gamma = D = 0$ and $G(\vec{q},\vec{p},0) = \delta(\vec{q} - \vec{q}_0) \, \delta(\vec{p} - \vec{p}_0)$, where q_0 and p_0 are the initial coordinate and momentum respectively. Substituting the above ansatz in eq. (3.2) we arrive at the correct equations of motion, eq. (2.10) and (2.12).

It is easy to verify that the distribution function

$$G_0(\vec{q},\vec{p}) = f(0(\vec{q})) \exp(-\gamma Q_{ij} \, p_i p_j / 2mk) \, , \tag{3.3}$$

is stationary solution of the Fokker-Planck equation, where $\phi(q)$ = constant is the equation for the constraining surface and, therefore, a_i is proportional to $\partial\phi/\partial q_i$. The function f is arbitrary what means to say that the space is separable into disjoints classes of points lying on the surfaces of constant ϕ. The normalization factors are included in f.

The temperature of the bath is given by $k_B T = K/\gamma m$.

Notice that the component of $\vec{p}$ parallel to $\vec{a}$ does not appear in H and shall not appear anywhere in the calculations. Thus, when normalizing G_0 and G we may integrate this component independently let us say, from $-p_{30}$ to p_{30}.

To obtain the diffusion equation we shall use the projector technique[4]. We define a projector A such that

$$A\Psi(\vec{q},\vec{p}) = G_0(\vec{q},\vec{p}) \int d^3 P \, \Psi(\vec{q},\vec{p})$$

what this projector does is to project on the thermallized state of the particles.

Define the projector B as the complement of A

$$A + B = I ,$$

and the coordinate distribution function $g(\vec{q},t)$ from the application of the projector A on the phase-space distribution function

$$A\, G(\vec{q},\vec{p},t) = G_0(\vec{q},\vec{p}) g(\vec{q},t) \qquad (3.4)$$

We may now decompose the differential operator which appears on the right hand side of the Fokker-Planck equation into two operators

$$\frac{\partial G}{\partial t} = (\Gamma_0 + \Gamma_1)\, G$$

where

$$\Gamma_1 = -\frac{\partial}{\partial q_i} Q_{ij}\, p_j/m - \frac{\partial}{\partial P_i} (\partial a_j/\partial q_i)\, \frac{a_k\, p_j\, p_k}{m} \qquad (3.5)$$

and

$$\Gamma_0 = \frac{\partial}{\partial p_i} \left(\frac{\gamma}{m} Q_{ij} p_j + K \frac{\partial}{\partial p_i} \right) \tag{3.6}$$

It is easy to show that Γ_0 and Γ_1 obey the following equations

$$\begin{aligned} (\Gamma_0 + \Gamma_1)\, G_0 &= 0 \\ \Gamma_0 A = A \Gamma_0 &= 0 \\ A \Gamma_1 A &= 0 \\ \Gamma_0 \Gamma_1 G_0 g &= -\frac{\gamma}{m} G_0 \Gamma_1 g \end{aligned} \tag{3.7}$$

Now the equation for $g(q,t)$ is easy to obtain using the properties of Γ_0 and Γ_1 shown in eq. (3.7),

$$\frac{\partial (AG)}{\partial t} = (A \Gamma_0 + A \Gamma_1)\, (A G + B G) \tag{3.8}$$

$$\begin{aligned} \frac{\partial (BG)}{\partial t} &= (B \Gamma_0 + B \Gamma_1)\, (A G + B G) \\ &= B \Gamma_1 (A G + B G) + B \Gamma_0 B G. \end{aligned} \tag{3.9}$$

Assuming we started from an initial G such that

$$B\, G(\vec{q}, \vec{P}, 0) = 0 \tag{3.10}$$

what means that locally we have themal equilibrium. (This restriction simplifies the calculations but is not essential since, if it is not satisfied, we are left with a memory of the initial distribution which is exponentially damped.) Eq. (3.9) may be solved directly giving

$$BG = \int_0^t dt' \exp B(\Gamma_0 + \Gamma_1)(t-t')\; B \Gamma_1 A\, G(t') \ . \tag{3.11}$$

If now g is a slow varying function of $\vec{q}$, varying very little for a distance equal to the mean free path, we may keep only the lower ex-

pansion on Γ_1 and we are left with the following solution for eq. (3.8) after substituing of BG as obtained from eq. (3.11),

$$\frac{\partial(AG)}{\partial t} = A\,\Gamma_1 \int_0^t \exp\{(-\gamma/m)\ (t-t')\}\ \Gamma_1\ A\ G(\vec{q},\vec{p},t')dt' \qquad (3.12)$$

The factor γ/m in the exponential comes from the last relation in eq. (3.7) and it can be understood as the inverse of the time necessary to thermalize the system locally. This time is expected to be much smaller than the relaxation time for g and, therefore, we may integrate eq.(3.12) by taking $G(q,p,t)$ outside the time integral. This gives

$$\frac{\partial g}{\partial t} = \frac{m}{\gamma} A\ \Gamma_1^2\ g$$

and, finally,

$$\frac{g(\vec{q},t)}{\partial t} = D\ \frac{\partial}{\partial q_i}\ Q_{ij}\ \frac{\partial}{\partial q_j}\ q(\vec{q},t) \qquad (3.13)$$

where $D = k/2\gamma^2$ is the usual diffusion coefficient. As we stated before the temperature of the heat bath is given by

$$k_B T = K/\gamma$$

and thus

$$D = k_B T/2\gamma \quad ,$$

which is usual expression for the diffusion coefficient.

4. THE DIFFUSION EQUATION

In this section we propose another derivation of the diffusion equation, directly from Newton's equation, no use being made of the Hamiltonian formalism. A collision time and also a relaxation time are assumed so that relaxation effects come out naturally from the evolution equations.

We assume that every particle has a probability of collision in the interval $t_0 \lesssim t \lesssim t_0 + \tau_0$ given by $\tau_0/\tau < 1$ and that after a collision

the particle is thermalized, i.e., it forgets its velocity prior to the collision and leaves the collision with a velocity distribution given by the thermal equilibrium distribution function. Consider a particle reaching a point in coordinate-velocity space $(\vec{q},\dot{\vec{q}})$ at time t. It has either suffered no collisions since the initial time $t=0$ (and thus moves following the mechanical trajectory leaving from the phase point $(\vec{q}',\dot{\vec{q}}')$ uniquely defined by $(\vec{q},\dot{\vec{q}})$ and t) or has suffered at least one collision.

If the particle suffered collisions it reaches the point $(\vec{q},\dot{\vec{q}})$ at time t after having suffered the last collision at time t' at the phase point $(\vec{Q},\dot{\vec{Q}})$ determined, once again, by $(\vec{q},\dot{\vec{q}})$ and $t-t'$ and the newtonian equations of motion. The probability that there was a particle at time t' at the phase point $(\vec{Q},\dot{\vec{Q}})$ after a collision having occured is given by the product

$$g(\vec{Q},t)\ G_0(\vec{Q},\dot{\vec{Q}})$$

where $g(\vec{Q},t)$ is the space distribution function and $G_0(\vec{Q},\dot{\vec{Q}})$ is the thermal equilibrium distribution function.

It is very easy, from what we have said above, to show that the total distribution functions obeys the following equation

$$G(\vec{q},\dot{\vec{q}},t) = e^{-t/\tau}\ G(\vec{Q},\dot{\vec{Q}},0) + \frac{1}{\tau}\int_0^t \exp(-(t-t')/\tau)g(q',t')\ G_0(\vec{q}',\dot{\vec{q}}') \quad (4.1)$$

where $G(\vec{Q},\dot{\vec{Q}},0)$ is the initial distribution function. The phase point $(\vec{Q},\dot{\vec{Q}})$ reaches $(\vec{q},\dot{\vec{q}})$ after following a mechanical trajectory for a time and the phase point $(\vec{q}',\dot{\vec{q}}')$ reaches $(\vec{q},\dot{\vec{q}})$ after a time $t-t'$.

Energy is conserved in the mechanical system and we may assume as the thermal equilibrium a Boltzmann distribution

$$G_0(\vec{Q},\dot{\vec{Q}}) = A\ \exp(-E(\vec{Q},\dot{\vec{Q}})/k_B T)$$

where k_B is again the Boltzmann constant and T is the temperature.

A serious problem we have to deal with is the conservation of probability in the coordinate-velocity space[5]. If we call Ω a elementary volume in such space, the equation of motion $m\ddot{q}_i = F_i$ leads to

$$\dot{\Omega} = \frac{\partial F_i}{\partial q_i} \Omega ,$$

which is zero for velocity independent forces.

In the case of constrained motion we have

$$\ddot{q}_i = - a_i \frac{\partial a_j}{\partial q_k} \dot{q}_j \dot{q}_k ,$$

and thus

$$\dot{\Omega} = - a_i \frac{\partial a_j}{\partial q_i} \dot{q}_j \Omega .$$

In order for the system to reach thermal equilibrium we must assume that $\dot{\Omega} = 0$. This corresponds to take

$$a_i \frac{\partial a_j}{\partial q_i} = 0 ,$$

since $\vec{q}$ and $\dot{\vec{q}}$ are independent.

The above condition, although restrictive, is valid for several cases of interest. It is valid for motion on spheres, circles and, more important, it is valid for a non-integrable constraint, i.e.,

$$\vec{a} = \left(0, \frac{q_1}{\sqrt{1+q_1^2}} , \frac{1}{\sqrt{1+q_1^2}} \right) .$$

For non-integrable constraint it is known that no hamiltonian formalism is possible and, therefore, the treatment we propose here is, in this case, more general than the usual Fokker-Planck equation obtained from Liouville's equations.

We now apply eq.(4.1) for systems with constraint as was done in section 3.

To obtain the diffusion equation we integrate both sides in $d^3\dot{q}$ and assume τ very small.

This leads, after changing variables $t-t' = \sigma$, to

$$g(\vec{q},t) = \frac{1}{\tau}\int\int_0^t e^{-\sigma/\tau}\, g(q_i + \sigma\dot{q}_i - \frac{1}{2}\sigma^2 a_i \frac{\partial a_j}{\partial q_k}\dot{q}_j\dot{q}_k,\ t-\sigma)\, G_0(\vec{q},\dot{\vec{q}})\, d^3\dot{q}\, d\sigma. \tag{4.2}$$

We used the equations of motion

$$Q_i = q_i + \sigma\,\dot{q}_i - \frac{\sigma^2}{2} a_i \frac{\partial a_j}{\partial q_k}\dot{q}_j\,\dot{q}_k$$

to eliminate Q_i.

Expanding g in its space and time arguments and assuming τ very small, we are left with

$$\tau\frac{\partial g}{\partial t} = \frac{\tau^2}{4}\left[-a_i\frac{\partial a_j}{\partial q_j}\frac{\partial g}{\partial q}\ \frac{k_B T}{m} + \frac{k_B T}{m} Q_{ij}\frac{\partial^2 g}{\partial q_i\,\partial q_j}\right] \tag{4.3}$$

Using the fact that

$$a_i\frac{\partial a_j}{\partial q_i} = 0$$

we may add the term

$$-\frac{\tau^2}{4} a_i\ \frac{\partial a_j}{\partial q_i}\ \frac{\partial g}{\partial q_i}\ \ \frac{k_B T}{m}$$

in eq. (4.3) and we transform it into

$$\frac{\partial g}{\partial t} = +\frac{k_B T}{4m}\ \frac{\partial}{\partial q_i}\, Q_{ij}\, \frac{\partial}{\partial q_j}\ \ g.$$

Defining $D = \frac{k_B T}{4m}$, we finally obtain

$$\frac{\partial g}{\partial t} = D\,\frac{\partial}{\partial q_i}\ \ Q_{ij}\ \frac{\partial}{\partial q_j}\ \ g\ .$$

Notice that this equation is valid in the limit of very small relaxation time and that, in this case, the integrability of the constraint plays no role: it is the same equation for integrable and non-integrable constraints. The only restriction is the conservation of volume in coordinate-velocity space.

It is usually accepted that the free diffusion equation is a closed analog to the Schrödinger equation. In the case of non-integrable

constraint this analog breaks down, since a differential equation of the form we obtained in this section would correspond to the treatment of the problem through a lagrangean formalism which we know to be incorrect.

Our result indicates that after many collisions the system develops as if it was guided by the "wrong hamiltonian". But we must be careful, here, because we know that we are not allowed to apply anything like the correspondence principle in the theory of the brownian motion.

5. CONCLUSIONS

In this work we have shown how to calculate the diffusion equations for constrained systems using two different formalisms. One has its starting point in Dirac's formalism for singular lagrangeans and it has enabled us to derive a hamiltonian and then the Fokker-Planck and diffusion equations for the system. This method is very direct and makes use, naturally, of the hamiltonian formalism. The diffusion equation we have obtained can be transposed directly to the Schrödinger equation for quantum particles subject to the same constraint by the substitution $(t,D) \rightarrow (it, \hbar/2m)$.

The method of Dirac is correct when the constraint is integrable as discussed in reference 2.

For non-integrable constraints no lagrangean formalism is possible and therefore no hamiltonian formalism exists.

A different derivation of the diffusion equation has been proposed, through an integral equation for the space distribution function $g(\vec{q},t)$. In the limit of infinite collisions $\tau \rightarrow 0$, we were able to obtain a differential equation for $g(\vec{q},t)$ which is of the same form as the one obtained from Dirac's method. The derivation made use of the conservation of volume in coordinate-velocity space but it was shown that non-integrable constraints fulfilled this condition and thus that this kind of volume conservation was no restriction on integrability.

The differential equation obtained was of first order in time and second order in space.

To this equation we may derive by analogy the Schrödinger's equation which is the same as the one given by Dirac's method. As this is valid even for non-integrable constraints we conclude that the many collisions approach to the diffusion equation imposed that in this limit the evolution of $g(q,t)$ is comanded by what, in the non-holonomic case, we may call the "wrong hamiltonian". It is a linear operator that has the same form as if it would be derived from a lagrangean for integrable constraint.

It is clear that the same replacement $(t,D) \to (it, \hbar/2m)$ cannot, in the non-integrable case, lead to the correspondent Schrödinger equation since for the quantum case we must satisfy the correspondence principle and the classical limit must coincide with Newton's equation which this hamiltonian does not reproduce.

In statistical mechanics the newtonian mechanics has to be found in the collisionless limit $\tau \to \infty$, where the classical newtonian trajectories provide the evolution of the space distribution function which is the opposite limiting process for the derivation of the diffusion equation. The fact that we obtained the same diffusion equation for holonomic and non-holonomic constraint poses no formal difficulty for the statistical approach to mechanics but points our that the analogy between Schrödinger and diffusion equations breaks down.

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