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Non-Holonomy and the Diffusion of Particles – II

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We have obtained the equilibrium solution of the Fokker-Planck equation for both liouvillian and non-liouvillian systems. We have exhibited the procedure to solve the diffusion equation for non-holonomic systems. We presented a suggestion to where such systems may be found in nature, at the microscopic level.

Obtivemos a solução de equilíbrio da equação de Fokker-Planck tanto para sistemas liouvillianos quanto para não-liouvillianos. Mostramos o procedimento para resolver a equação de difusão para sistemas não-holônomos. Foi sugerido onde tais sistemas poderão ser encontrados na natureza ao nível microscópico.

1. INTRODUCTION

In a previous paper[1] we have derived the Foller-Planck equation for a system of particles subject to non-holonomic constraint. We have proved that the equation obtained is invariant under general point transformations and we derived from it the equation for the diffusion of particles.

Discussing the diffusion equation we were able to show that systems subject to constraints can be classified in two general classes: (i) the liouvillian systems which contain all holonomic as well as some non-holonomic systems whose major property is to exhibit a static equilibrium state and (ii) the non-liouvillian systems which are necessarily non-holonomic and exhibit in their equilibrium state permanent solenoidal currents. These currents are a direct manifestation of the structure of the non-holonomic constraints and it is independent of how the system was prepared except perhaps for the influence of the shape of the container on the current pattern. This stricking result for non-liouvil1ian systems was obtained by the intermediation of the diffusion equation.

In this paper we derived this same result by exhibiting the structure of the equi1ibrium solution of the Fokker-Planck equation thus avoiding the intermediate step of obtaining the diffusion equation. We have shown that while for liouvillian systems the equation obtained for the equilibrium density is exact, for non-liouvillian systems we could only obtain it approximately by expanding the density in powers of the square of the mean free path of the particles.

The classical result that gives the energy per particle proportional to the nurnber of degrees of freedom could only be proved if one includes besides the random motion of the particles also the' energy associated to the permanent currents. In particular, this result says that the permanent currents are proportional to the temperature of the system.

Having therefore stabilished the diffusion equation by two independent methods we proceeded discussing the Green's formalism for obtaining its solution with given boundary conditions on the surface of the container of the system. We were able to show that the equilibrium solution is unique in both liouvillian and non-liouvillian systems. However, the transient behaviour of these two kind of systems may be substantially different: while liouvillian systems behave as a normal fluid approaching its equilibrium monotonically, non-liouvillian systems may approach its equilibrium by intermediation of an oscillatory regimen.

Before steping into the formalism, we would like to ponder on the physical realization of such systems at the microscopic level. To fix our ideas we may imagine the particles under consideration to be electrons with the molecules being responsible for the non-holonomic structure of their constrained motion.

Such systems has not been observed so far. However the holonomic and non-holonomic molecular organization ca be identified with certain mesomorphic phases of liquid crystals as we will show presently.

Let us first consider the smectic-A mesomorphicphase[2]. In this case, the rod like molecules organize themselves in layers with their mean directions perpendicular to the surface of the layers. If we identify this mean direction with the vector $\vec{a}(\vec{r})$, the form $\vec{a}.d\vec{r}$ is integrable, the foliation corresponding to the layers. These are examples of holonomic molecular organizations.

We now consider the cholesteric mesomorphic phase. Here, the organization of the rod like molecules are tangential to the plane layers and rotates when one moves from one layer to the other. Calling again $\vec{a}(\vec{r})$ the mean direction of the molecules, their organization is described by

$$a_X = \cos\ (q_0 z + \phi)$$
$$a_Y = \sin\ (q_0 z + \phi)$$
$$a_z = 0$$

with the z-axis perpendicular to the layers. Writing

$$w = \vec{a}.d\vec{r} \quad ,$$

we have

$$w \wedge dw = - q_0 \ .$$

This is an example of non-holonomic organization. As $\vec{a}$ is parallel to curl $\vec{a}$, this system is also liouvillian.

Liquid crystals are layered molecular organizations and we do not believe that they can exhibit, as such, a non-liouvillian structure. Besidss, the electrons in the molecules are free to move, as in

the cholesteric mesomorphic phase, in the direction of $\vec{a}(\vec{r})$ and not perpendicular to $\vec{a}(\vec{r})$. Therefore, the field $\vec{a}(\vec{r})$ does not represent a constraint to the motion of the electrons in the sense that will be considered in this paper.

To observe the systems we have in mind one would have to consider building blocks in the form of discs and not of rods as it is common with liquid crystals. Actually, only recently liquid crystals with disc like molecules has been observed[3]. These disc like building blocks would have to articulate themselves in a twisted three-dimensional non-holonomic structure to produce a true non-liouvillian system.

We therefore believe that the realization of non-liouvillian system would come about in large molecular structures possibly of biological origin. We may even speculate that the permanent currents we have predicted will exhibit a kind of superconducting behaviour at room temperature and the magnetic field created could be used by the molecules as a specificity device for its functioning in the biological environment.

2. THE FOKKER-PLANCK EQUATION

We will summarize in this section some of the results we have previously obtained[1]. We assume that the particles move in a n-dimensional riemannian space with kinetic energy T given by

$$T = \frac{1}{2} g_{ij} \dot{q}^i \dot{q}^j \quad . \tag{2.1}$$

We call this the free system. We add to it, first by a set of m independent scleronomic constraints

$$a_i^\alpha(q) dq^i = 0 \qquad \alpha = 1,\ldots,m \quad . \tag{2.2}$$

We observe that the vectors $a^{\prime\prime}$ can always be chosen such that

$$a_\alpha^i a_i^{\alpha'} = \delta_\alpha^{\ \alpha'} \ ,$$

where

$$a^i_\alpha = g^{ij} a^\alpha_j \ .$$

Secondly we add a viscous force $-\xi v^i$ with constant coefficient ξ of viscosity and a Langevin force $F_i(t)$ with constant strength i.e.,

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

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

where K is a constant.

Under these assumptions we may speak of the distribution of probability $W(q,v;t)$ of particles in the phase space of the system. To mantain $W(q,v;t)$ invariant under general point transformations of the configuration space we have introduced the measure weight $\mu(q,v)$ of probability given by

$$\mu(q,v) = g(q) \prod_{\alpha=1}^{m} \delta(a^\alpha_i v^i)$$

with $g = \det (g_{ij})$.

In particular, the normalization of $W(q,v;t)$ is given by

$$1 = \int d^n q \, d^n v \, g(q) \prod_{\alpha=1}^{m} \delta(a^\alpha_i v^i) W(q,v;t) \ .$$

The equation that $W(q,v;t)$ satisfies is a straightforward generalization of the Fokker-Planck equation[4] and we have obtained[1]

$$\frac{\partial W}{\partial t} + \left\{ v^i \frac{\partial W}{\partial q^i} - \Gamma^j_{ik} \frac{\partial W}{\partial v^j} v^k \right\} = \frac{\partial}{\partial v^i} \left\{ \xi \, v^i W + \Delta^i_{jk} \, v^j v^k W + K g^{ij} \frac{\partial W}{\partial v^j} \right\} \tag{2.3}$$

where(*)

(*) We use the semi-colon to denote the covariant derivative associated to the affine conexion Γ^j_{ik}.

$$\Gamma^{j}_{ik} = \frac{1}{2} g^{jl} \left[\frac{\partial g_{li}}{\partial q^{k}} + \frac{\partial g_{lk}}{\partial q^{i}} - \frac{\partial g_{ik}}{\partial q^{l}} \right] ,$$

$$\Delta^{i}_{jk} = \sum_{\alpha=1}^{m} a^{i}_{\alpha} a^{\alpha}_{j;k} \tag{2.4}$$

and

$$Q^{ij} = g^{ij} - \sum_{\alpha=1}^{m} a^{i}_{\alpha} a^{j}_{\alpha} \quad . \tag{2.5}$$

We proved in reference 1 that eq. *(2.3)* is invariant under the following transformation:

$$\bar{q}^{i} = \bar{q}^{i}(q)$$

$$\bar{v}^{i} = \frac{\partial \bar{q}^{i}}{\partial q^{j}} \, v^{j} \quad .$$

Our purpose in this paper is to exhibit a static solution $W(q,v)$ of eq. *(2.3)*.

3. THE STRUCTURE OF THE STATIC SOLUTION

We assume that the static solution of eq. *(2.3)* has the form

$$W = \exp(\psi) \tag{3.1}$$

where ψ is a real function of q and v. This hypothesis is sufficient to guarantee that W is a positive function.

We take for ψ the general form

$$\psi = A(q) = \sum_{\nu=1}^{\infty} \frac{\beta^{\nu/2}}{\nu!} A_{l_1,\ldots,l_\nu}(q) \, v^{l_1} \ldots v^{l_\nu} \tag{3.2}$$

where β, the inverse of the temperature of the system, is introduced in eq. (3.2) to make $A_{l_1,\ldots,l_\nu}$ dimensionless

We will assume, without loss of generality for ψ, that $A_{l_1,\ldots,l_\nu}$ is symmetric in all its indices and satisfies the following equation:

$$a_a^{i_1} A_{\ell_1,\ldots,\ell_\nu} = 0 \quad \text{for} \quad a = 1,\ldots,m \ .$$

Under these restrictions one observes that ψ is independent of v if and only if $A_{\ell_1,\ldots,\ell_\nu} = 0$.

Making use of eqs. (3.1) and (3.2) we arrive at the following results:

$$\left(\frac{\partial W}{\partial q^i} - \Gamma^j_{ik} \frac{\partial W}{\partial v^j} v^k\right) v^i = W\left(v^i \frac{\partial A}{\partial q^i} + \right.$$

$$\left. + \sum_{\nu=2}^{\infty} \frac{\beta^{(\nu-1)/2}}{(\nu-1)!} A_{\ell_1,\ldots,\ell_{\nu-1},\ell_\nu} v^{\ell_1} \ldots v^{\ell_\nu}\right) \tag{3.3}$$

and

$$\frac{\partial}{\partial v^i}(\xi v^i W + \Delta^i_{jk} v^j v^k W) = W\left[(n-m)\xi + b_i v^i + \xi \sum_{\nu=1}^{\infty} \frac{\beta^{\nu/2}}{(\nu-1)!}\right.$$

$$\left. A_{\ell_1,\ldots,\ell_\nu} v^{\ell_1} \ldots v^{\ell_\nu}\right], \tag{3.4}$$

where

$$b_i = \Delta^k_{ik} \ .$$

We further have

$$Q^{ij} \frac{\partial^2 W}{\partial v^i \partial v^j} = Q^{ij}\left(\frac{\partial \psi}{\partial v^i}\frac{\partial \psi}{\partial v^j} + \frac{\partial^2 \psi}{\partial v^i \partial v^j}\right) W \tag{3.5}$$

$$Q^{ij} \frac{\partial^2 \psi}{\partial v^i \partial v^j} = \sum_{\nu=1}^{\infty} \frac{\beta^{(\nu+2)/2}}{\nu!} A^i_{i\ell_1,\ldots,\ell_\nu} v^{\ell_1} \ldots v^{\ell_\nu} + \beta A^i{}_i \tag{3.6}$$

$$Q^{ij} \frac{\partial \psi}{\partial v^i}\frac{\partial \psi}{\partial v^j} = \beta A^i A_i + 2 \sum_{\nu=1}^{\infty} \frac{\beta^{(\nu+2)/2}}{\nu!} A^i A_{i\ell_1,\ldots,\ell_\nu} v^{\ell_1} \ldots v^{\ell_\nu} +$$

$$+ \sum_{\nu=2}^{\infty} \sum_{\nu'=1}^{\nu-1} \frac{\beta^{(\nu+2)/2}}{\nu'!(\nu-\nu')!} A^{\ell}_{\ell_1,\ldots,\ell_{\nu'}} A_{\ell\ell_{\nu'+1}\ldots\ell_\nu} v^{\ell_1}\ldots v^{\ell_\nu} \quad . \tag{3.7}$$

Let us now observe that for any tensor $B_{\ell_1\ldots\ell_\nu}$ which satisfies

$$B_{\ell_1\ldots\ell_\nu} v^{\ell_1}\ldots v^{\ell_\nu} = 0 \ ,$$

we rnust have

$$PB_{\ell_1\ldots\ell_\nu} = 0$$

where P is the projector

$$P^{\ell_1'\ldots\ell_\nu'}_{\ell_1\ldots\ell_\nu} = \frac{1}{\nu!} \sum_{\text{perm}(\ell_1'\ldots\ell_\nu')} Q^{\ell_1'}_{\ell_1} Q^{\ell_2'}_{\ell_2} \ldots Q^{\ell_\nu'}_{\ell_\nu}$$

with the sum in the above expression running over all $\nu!$ permutations of the set of indices $(\ell_1'\ldots R_\nu')$.

Geometrically P extracts for B its syrnmetric part which is orthogonal to the subspace spanned by the $\vec{a}_\alpha$ vectors.

Substituting eqs. (3.3) to (3.7) into eq. (2.3) and identifying equal powers of v we obtain and infinite set of coupled equations for the tensors $A_{\ell_1\ldots\ell_\nu}$.

The term independent of v gives

$$(n-m)\xi + K\beta(A^i_{\ i} + A^i A_i) = 0 \tag{3.8}$$

Let us set

$$A^i_{\ j} = - Q^i_j + B^i_j$$

and

$$\xi = K\beta \quad . \tag{3.9}$$

From eq. (3.8), we obtain

$$B^{i}_{\ i} = A^{i}A_{i} = 0 \tag{3.10}$$

The terrn linear in v gives:

$$A_{i} = \Lambda(b_{i} - Q^{j}_{i}\ \frac{\partial A}{\partial q^{j}}) + 2B_{ij}A^{j} + A^{j}_{ji} \tag{3.11}$$

where

$$\Lambda = \frac{1}{\xi\sqrt{\beta}} \tag{3.12}$$

is the mean free path of the particles.

We also have

$$B_{\ell_1\ell_2} = -\Lambda P A_{\ell_1;\ell_2} + A^{j}A_{j\ell_1\ell_2} + B^{j}_{\ell_1}B_{j\ell_2} + \frac{1}{2}A^{j}_{j\ell_1\ell_2} \tag{3.13}$$

and in general we obtain (for $\nu \geq 3$):

$$\Lambda P A_{\ell_1\ldots\ell_{\nu-1};\,\ell_\nu} = -A_{\ell_1\ldots\ell_\nu} + \frac{1}{\nu}A^{j}_{j\ell_1\ldots\ell_\nu} + \frac{2}{\nu}(B^{j}_{\ell_1}A_{j\ell_2\ldots\ell_\nu} +$$

$$+ \text{cyclic terms}) + \sum_{\nu'=2}^{\nu-2} \frac{(\nu-1)!}{\nu'!(\nu-\nu')!}\ P\left[A^{j}_{\ell_1\ldots\ell_{\nu'}}A_{j\ell_{\nu'+1}\ldots\ell_\nu}\right]. \tag{3.14}$$

We may look for solutions of eqs. (3.11), (3.13) and (3.14) as power expansions in Λ. By an iterative procedure we can show that if such solutions exist they have the following structure

$$A_{\ell_1\ldots\ell_\nu} \approx \Lambda^{\nu} \sum_{\alpha=0}^{\infty} \Lambda^{2\alpha}A^{\alpha}_{\ell_1\ldots\ell_\nu}\ , \quad \nu \neq 2 \tag{3.15}$$

$$B_{ij} = \Lambda^{2} \sum_{\alpha=0}^{\infty} \Lambda^{2\alpha}\ B^{\alpha}_{ij}$$

In particular we have

$$A^{0}_{i} = b_{i} - \frac{\partial A}{\partial q^{j}}\ Q^{j}_{i} \tag{3.16}$$

$$B^{0}_{ij} = \frac{1}{2}\ (b_{k} - \frac{\partial A}{\partial q^{\ell}}\ Q^{\ell}_{k})_{;m}(Q^{k}_{i}Q^{m}_{j} + Q^{k}_{j}Q^{m}_{i})\ . \tag{3.17}$$

Let us now observe that if

$$A^0_i = 0 \ , \tag{3.18}$$

then every

$$A_{\ell_1 \ldots \ell_\nu} = 0 \qquad \nu \neq 2$$

and

$$B_{ij} = 0$$

Thus $W(q,v)$ takes the simple form

$$W(q,v) = \exp(A - \frac{\beta}{2} Q_{ij} v^i v^j) \ . \tag{3.19}$$

Eq. (3.18) defines the Liouvillian systems and $W(q,v)$ given by eq. (3.19) is the equilibrium solution for such systems. This is an exact solution.

In the case where it is impossible to find A such that eq. (3.18) is fulfilled, the structure of $W(q,v)$ is more complicated and we have to resort to the Λ^2 power expansion.

4. THE Λ^2 APPROXIMATION

We will now discuss the approximation for W in which one includes only terms up to Λ^2. Therefore we have

$$A_i = \Lambda A^0_i = \Lambda \ (b_i - \frac{\partial A}{\partial q^i} Q^j{}_i) + 0 \ (\Lambda^3) \tag{4.1}$$

$$B_{ij} = \Lambda^2 B^0_{ij} = \frac{1}{2} \Lambda^2 \ (Q^k_i Q^m_j + Q^k_j Q^m_i) \ (b_k - \frac{\partial A}{\partial q^\ell} Q^\ell{}_k)_{;m} + 0(\Lambda^4) \tag{4.2}$$

and all other tensors are of order equal to or larger than Λ^3.

The solution $W(q,v)$ of the Fokker-Planck equation takes then the form of a gaussian in its dependence on v:

$$W(q,v) = \exp\left\{A + \frac{1}{2} A_i A^i - \frac{\beta}{2} \ (Q_{ij} - B_{ij}) (v^j - \frac{A^j}{\sqrt{\beta}}) (v^i - \frac{A^i}{\sqrt{\beta}})\right\}$$

Let us calculate p, j^i and P^{ij}. We have

$$\rho(q) = \int d^n v \quad \sqrt{g} \sum_{\alpha=1}^{m} \delta(a_i^\alpha v^i) W(q,v) = \frac{\text{const}}{(1-B_i^i)^{1/2}} \exp(A + \tfrac{1}{2} A_i A^i)$$

which, due to eq. (3.10) gives, preserving only terms up to Λ^2:

$$\rho(q) = \text{const } \exp(A)$$

from where we conclude that

$$A = \log \rho(q) + \text{const.} \tag{4.3}$$

Similarly we have

$$j^i = \int v^i \quad \sqrt{g} \prod_{\alpha=1}^{m} \delta(a_i^\alpha v^i) W \, d^n v = \frac{A^i}{\sqrt{\beta}} \rho. \tag{4.4}$$

Making use of eqs. (4.1) and (4.3) we arrive at

$$j^i = D(b^i \rho - Q^{ij} \frac{\partial \rho}{\partial q^i}) \tag{4.5}$$

where $D = \Lambda/\sqrt{\beta}$ is the diffusion coefficient of the system.

One observes therefore that in the equilibrium state, j^i is in general not zero(*).

We also have

$$P^{ij} = \int v^i v^j \sqrt{g} \prod_{\alpha=1}^{m} \delta(a_i^\alpha v^i) \, W \, d^n v$$

thus

$$P^{ij} = -\frac{1}{\beta} A^i A^j \rho + \int \left(v^i - \frac{A^i}{\sqrt{\beta}}\right) \left(v^j - \frac{A^j}{\sqrt{\beta}}\right) \sqrt{g} \prod_{\alpha=1}^{m} \delta(a_i^\alpha v^i) \, W \, d^n v$$

$$= \frac{1}{\beta} A^i A^j \rho + \frac{1}{\beta} (Q^{ij} + B^{ij}) \rho \quad . \tag{4.6}$$

It is interesting to observe that the first term of the se-

(*) This is the same current obtained elsewhere (1).

cond member of the above equation comes from the local collectivemotion of the particles given by $j^{\bar{i}}$ while the second term is the contribution for the random motion of the particles with respect to the local current.

The local density of energy is given by $\frac{1}{2} P^{\bar{i}}_{\bar{i}}$ and, making use of eq. (3.10), we obtain

$$\frac{1}{2} P^{i}_{i} = \frac{(n-m)\rho}{2\beta} \quad ,$$

therefore stablishing the general result of kinetic theory of which states that the average energy by particle is $\frac{1}{2\beta}$ times the number of degrees of freedom $(n-m)$.

One should emphasize that this result is correct in the case of non-Liouvillian systems because we have taken into account also the energy associated with the collective motion described by the local currents, coming from the first term of the left hand side of eq. (4.6).

We still have to examen eq. (3.10) within the Λ^2 approximation. This is an equation for A. Substituting eq. (4.3) into eqs. (4.1) and (4.2) and these latter into eq. (3.10) we obtain:

$$\frac{1}{\rho^2} (\rho b_i - Q^j_i \frac{\partial \rho}{\partial q^j}) (\rho b^i - Q^{ik} \frac{\partial \rho}{\partial q^k}) - \frac{1}{\rho} (\rho b_i - Q^j_i \frac{\partial \rho}{\partial q^j});_k Q^{ik} = 0 \ .$$

After some tedious calculations we finally arrive at

$$(\rho b^k - Q^{ik} \frac{\partial \rho}{\partial q^j});_k = 0 \qquad (4.7)$$

which is the same equation for the equilibrium density for the diffusion of particles, in the Λ^2 approximation, obtained previously (eq. (5.5) of of reference (I)). One shouldobserve that this equation is nothing else that the expression of the conservation of the current.

5. THE LIOUVILLIAN CASE

We have now come to the point where we should discuss the solutions of eq. (4.7). To simplify the discussion we will consider only

the case of a single non-holonomic constraint(*). We further assume in this section that the constraint is liouvillian, i.e., there exists a function ψ such that

$$b^i \equiv a^j a^i{}_{;j} = Q^{ij} \frac{\partial \psi}{\partial q^j} \quad . \tag{5.1}$$

We set

$$\rho = \bar{\rho} \exp \psi$$

and eq. (4.7) takes the form

$$\frac{\partial}{\partial q^i} \left(Q^{ij} \sqrt{g} \exp \psi \frac{\partial \bar{\rho}}{\partial q^j} \right) = 0 \quad . \tag{5.2}$$

Let us consider the operator H defined by

$$Hf \equiv - \frac{1}{\mu} \frac{\partial}{\partial q^i} \left(Q^{ij} \mu \frac{\partial f}{\partial q^j} \right) \tag{5.3}$$

with

$$\mu = \sqrt{g} \exp \psi \quad .$$

We will be looking for solutions of the diffusion equation in a volume Ω bound by a surface C. With this in mind, we define the inner product of two functions f_1 and f_2 as

$$(f_1, f_2) = \int_\Omega f_1^* f_2 \, \mu \, d^n q \tag{5.4}$$

and we take for the space on which H operates the space of all normalizable function with norm given by the inner product defined above.

We further restrict the functions f to those that the derivative at the boundary satisfies the equation(**):

(*) The holonomic case has been discussed in (1) and (5).

(**) The presence of Q^{ij} in eq. (5.5) playing the role of a singular metric could make irrelevant this boundary condition of f. This is impossible for non-holonomic constraints in the neighborhood of C unless Σ is an isolated integrai of the constraint. In this case Ω is a natural boundary to the motion of the particles. Such an example is considered in section 8. In such singular case we may take $\partial_3 f \, d\sigma^j = 0$ to make the solution unique.

$$Q^{ij} \frac{\partial f}{\partial q^j} d\sigma_i = 0 \qquad (5.5)$$

where $d\sigma_i$ is an element of surface at the boundary.

As the current is given by:

$$j^i = Q^{ij} \frac{\partial \rho}{\partial q^j} - b^i \rho = Q^{ij} \frac{\partial \rho}{\partial q^j} e^{\psi} ,$$

the boundary condition given by eq. (5.5) is equivalent to assume that no particle flows in or out of the volume Ω bound by Σ. Thisguarantees the conservation of the number of particles inside C (*) .

Under these assumptions one can easily prove that H is hermitian. Besides, if f_α is an eigenfunction of H:

$$Hf_\alpha = \alpha f_\alpha ,$$

we have:

$$\alpha(f_\alpha, f_\alpha) = \int \partial_i f_\alpha Q^{ij} \partial_j f_\alpha \mu d^n q \geq 0$$

what shows that the spectra of H is non-negative (we can always assume that f_α are real functions).

The equilibrium distribution is given by the eigenfunction f_0 and we have:

$$\int \partial_i f_0 Q^{ij} \partial_j f_0 \mu d^n q = 0$$

what gives

$$Q^{ij} \partial_j f_0 = 0 \qquad (5.6)$$

As

(*) This boundary condition is sufficient but not necessary to guarantee the conservation of the number of particles in the volume R . See the example in section 6 of this paper.

$$\partial_j f_0 \neq \alpha_j$$

for non-holonomic constraint the unique solution of eq. (3.6) is

$$f_0 = \text{constant} .$$

This shows that the equilibrium state of the liouvillian systems is unique and we have

$$\rho = \text{const. } \exp(\psi(q)) .$$

We will consider now the time dependent diffusion equation obtained in [1], which can be put into the following form:

$$\frac{\partial \bar{\rho}}{\partial t} = - D H \bar{\rho}$$

The equation

$$(\frac{\partial G}{\partial t} + DHG) = \delta(t-t_0)\delta^n(q-q_0)$$

has the solution

$$G = \sum_a e^{-D\alpha(t-t_0)} f_\alpha(q) f_\alpha(q_0) \qquad \text{for } t \geq t_0$$

$$G = 0 \qquad \text{for } t < t_0$$

where f_α are the orthonormalized eigenfunctions of H and obey

$$\sum_\alpha f_\alpha(q) f_\alpha(q_0) = \delta^n(q-q_0) .$$

The general solution for $\bar{\rho}(q;t)$ is

$$\bar{\rho}(q,t) = \frac{1}{V} + \sum_{\alpha>0} e^{-D\alpha(t-t_0)} f_\alpha(q) (f_\alpha(q_0), \rho(t_0)) ,$$

with $\rho(t_0)$ the density distribution of the system at the instant t_0 and

$$V = \int_{\Omega} \mu \, d^n q$$

One therefore observes that the modes included in the initial distribution $\rho(t_0)$ damps out each one with this characteristic relaxation time given by

$$t_\alpha = \frac{1}{D\alpha} \quad .$$

6. AN EXAMPLE

We now consider the case of particles of unit masses rnoving in the three dimensional euclidean space subject to the constraint given by the following form:

$$\text{xdy} + x_0 dz = 0 \tag{6.1}$$

where x_0 is a constant length that fixes the scale of the systern. This is a non-holonomic constraint for which

$$b_i \equiv a^j \frac{\partial a_i}{\partial q^j} = 0$$

and therefore liouvillian.

The diffusion equation takes the forrn.

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} + \frac{1}{x_0^2 + x^2}\left\{ x_0^2 \frac{\partial^2 \rho}{\partial y^2} - 2x\, x_0 \frac{\partial^2 \rho}{\partial y \partial z} + x^2 \frac{\partial^2 \rho}{\partial z^2} \right\} \quad . \tag{6.2}$$

One observes that the equation is invariant under translations in the y and z directions. We therefore set periodical boundary conditions in these directions in a retangular box of faces perpendicular to the coordinate axis.

We write

$$\psi_\alpha = \phi_\alpha(x)\, e^{ik_2(y-y_1)}\, e^{ik_3(z-z_1)} \tag{6.3}$$

and we set

$$k_2(y_2-y_1) = 2\, n_2\, \pi$$
$$k_3(z_2-z_1) = 2\, n_3\, \pi \tag{6.4}$$

where

$$x = x_1 \quad ; \quad x = x_2$$
$$y = y_1 \quad ; \quad y = y_2$$
$$z = z_1 \quad ; \quad z = z_2$$

are the equations for the faces of the box. We impose ϕ_α to be an eigenfunction of

$$H = -\left[\frac{\partial^2}{\partial x^2} + \frac{1}{x_0^2 + x^2}\left(x_0\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}\right)^2\right] \tag{6.5}$$

and we have

$$-\frac{\partial^2\phi_\alpha}{\partial x^2} + V(k_2,k_3,x)\phi_\alpha = \alpha\phi_\alpha \tag{6.6}$$

where

$$V(k_2,k_3,x) = \frac{(x_0k_2 - xk_3)^2}{x_0^2 + x^2} \tag{6.7}$$

For $\phi_\alpha(x)$ we impose the boundary conditions

$$\left.\frac{\partial\phi_\alpha}{\partial x}\right|_{x=x_1} = \left.\frac{\partial\phi_\alpha}{\partial x}\right|_{x=x_2} = 0\ . \tag{6.8}$$

With the above boundary conditions for each k_2 and k_3, α takes discrete values which we enumerate from zero starting from the lowest eigenvalue. Thus we write $\psi_{n_1,n_2,n_3}(x,y,z)$ to the eigenfunctions of H given by eq. (6.8).

The Green's function for H can be written as

$$G(\vec{r},t;\vec{r}',t') =$$

$$= \sum_{n_1 n_2 n_3} \psi_{n_1 n_2 n_3}(x,y,z)\psi^*_{n_1 n_2 n_3}(x',y',z')e^{-\alpha(n_1,n_2,n_3)(t-t')}$$

$$\text{for } t \geq t' \qquad (6.9)$$

and

$$G(\vec{r},t;\vec{r}',t') = 0 \qquad \text{for } t < t' .$$

From the fact that

$$\psi_{n_1,-n_2,-n_3}(x,y,z) = \psi^*_{n_1,n_2,n_3}(x,y,z)$$

and that the sum in eq. *(6.9)* runs over all integers n_2 and n_3, we conclude that G given by eq. *(6.9)* is real.

The time dependent solution is

$$\rho(\vec{r};t) = \int G(\vec{r},t;\vec{r}',t')\rho(\vec{r}';t')d^3\vec{r}' .$$

Therefore, with the above equation we can calculate ρ fromthe knowledge of ρ at an earlier time.

We will now compare the behaviour of the system when the box which contains the particles is situated in different regions of the space. Translations in the y and z-directions do not affect the system as the diffusion equation is invariant with respect to these dislocations. We will therefore compare only two systems, one positioned at the oriqin and another shifted in the x-direction

We assume, for simplification that

$$|x_1-x_2| = |y_1-y_2| = |z_1-z_2| = 2x_0 .$$

Let us estimate the smallest relaxation time for the system. From eq. *(6.6)* we obtain:

$$\alpha = \left\{ \int_{x_1}^{x_2} \phi_\alpha'^2 \, dx + \int_{x_1}^{x_2} V \, \phi_\alpha^2 \, dx \right\},$$

assuming that

$$\int_{x^1}^{x_2} \phi_\alpha^2 \, dx = 1 .$$

To estimate the lowest α we take $\phi_a^2 = \frac{1}{2x_0}$ then we have:

$$\alpha \simeq \frac{1}{2x_0} \int_{x_1}^{x_1+2x_0} V(k_2, k_3, x) \, dx .$$

From where we obtain:

$$\alpha = k_3^2 + \frac{(k_2^2-k_3^2)}{2} \left\{ \tan^{-1} (\lambda_1+2) - \tan^{-1} \lambda_1 \right\} \frac{k_2 k_3}{2} \log \frac{1+(\lambda_1+2)^2}{1+\lambda_1^2}$$

where

$$\lambda_1 = \frac{x_1}{x_0} .$$

For the box at the origin we have $\lambda_1 = -1$ and

$$\alpha = \frac{\pi}{4} k_2^2 + (1 - \frac{\pi}{4}) k_3^2$$

The lowest value is for $k_2 = 0$ and $k_3 = \frac{\pi}{x_0}$ and we finally set

$$\tau_{\alpha} = \frac{4 x_0^2}{(4-\pi)}$$

for the lowest relaxation time for the box at the origin. In this box the system has a slightly faster tendency to be homogeneous in the y--direction than the z-direction as the constraint in this region of space predominantly inhibits motion in the z-direction.

For the box away from the plane $x=0$, we have

$$\lambda_1 >> 1 .$$

We immediatly observes that the lowest mode is associated with $k_3 = 0$ and we get, for $k_2 = \frac{\pi}{x_0}$

$$\alpha \simeq \frac{\pi^2}{x_0^2} \frac{1}{1 + (\lambda_1 + 2)^2}$$

or

$$\tau_0 = \frac{x_0^2 [1 + (\lambda_1 + 2)^2]}{D \pi^2}$$

Here, the inhomogeneity in the y-direction has a tendency to persist for a long time as compared with the previous case. The reason is again the constraint, as, in this region of space, it predominantly inhibits the motion in the y-direction.

This strong dependence of the relaxation time of the system with respect to where we set the box signs to us that one should be careful with taking the thermodynamic limit in the case of non-holonomy. In general we have no uniformity of behaviour of the system in different regions of space and the relaxation of the system may come to be forbiddingly high to guarantee uniformity of the thermodynamic limit.

7. THE NON-LIOUVILLIAN CASE

We will now discuss eq. (4.7) when the constraint is non-liouvillian. We set

$$b_i = Q^{ij} \frac{\partial \chi}{\partial q^j} + C^i \tag{7.1}$$

and we assume that

$$C^i{}_{;i} = 0 \tag{7.2}$$

Thus, the equation for χ takes the forrn

$$\frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} \left\{ \sqrt{g}\, Q^{ij} \frac{\partial \chi}{\partial q^j} \right\} = S(q) \tag{7.3}$$

where

$$S(q) = \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} (\sqrt{g}\, b^i) \tag{7.4}$$

Let us define the Green's function by

$$\frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} \left[\sqrt{g}\, Q^{ij} G(q,q') \right] = \delta^n(q-q') \tag{7.5}$$

with the following boundary condition over the surface C enclosing the fluid(*)

$$Q^{ij} \frac{\partial G(q,q')}{\partial q^j} d\sigma_i = 0 .$$

For the function χ we assume

$$Q^{ij} \frac{\partial \chi}{\partial q^j} d\sigma_i = b^i d\sigma_i \tag{7.6}$$

as its boundary condition. In this way we are taking $C^i(q)$ tangent to the surface Σ. Under these assumptions we obtain

$$\chi(q) = \int_\Omega G(q,q') S(q) \sqrt{g}\, d^n q' + \int_\Sigma G(q,q') \sqrt{g}\, b^i(q') d\sigma_i \quad . \tag{7.7}$$

Let us write

$$\rho = \exp\psi(q)$$

and

$$\bar{\chi} = \psi - \chi .$$

Thus, eq. (4.7) takes the form

$$\frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} (\sqrt{g}\, Q^{ij} \cdot \bar{\chi}) = \frac{\partial \chi}{\partial q^i} C^i + \bar{S}[\bar{\chi}] \tag{7.8}$$

where

$$\bar{S}[\bar{\chi}] = \frac{\partial \bar{\chi}}{\partial q^i} \left(C^i + Q^{ij} \frac{\partial \bar{\chi}}{\partial q^j} \right) - \frac{\partial \chi}{\partial q^i} Q^{ij} \frac{\partial \bar{\chi}}{\partial q^j} . \tag{7.9}$$

(*) See footnote on page 675

We take for $\bar{\chi}$ the same boundary condition as that taken for $G(q,q')$, i.e.,

$$Q^{ij} \frac{\partial \bar{\chi}}{\partial q^j} da_i = 0 \ .$$

Therefore we have for $\bar{\chi}(q)$:

$$\bar{\chi}(q) = \bar{\chi}_0(q) + \int G(q,q') \bar{S}[\chi(q')] \sqrt{g} \, d^n q' \qquad (7.10)$$

where

$$\bar{\chi}_0(q) = \int G(q,q') \frac{\partial \chi(q')}{\partial q'^j} C^j(q') \sqrt{g} \, d^n q' \ . \qquad (7.11)$$

Eq. (7.10) can be solved by the usual iterative method.

The equilibrium solution is thus given by

$$\rho_0 = \text{const.} \exp(\bar{\chi} + \chi) \ . \qquad (7.12)$$

Let us observe that, from the discussion of section 5, the Green function $G(q,q')$ is uniquely defined apart from a constant. So it is also $\chi(q)$. The function $\bar{\chi}$ is also uniquely defined by the iterative method applied to the eq. (7.10) and thus ρ_0, given by eq. (7.12), comes to be known apart from a multiplicative constant.

We now turn our attention to the time dependent solutions of the diffusion equation in the case of non-liouvillian constraints:

$$\frac{\partial \rho}{\partial t} = \frac{D}{\sqrt{g}} \frac{\partial}{\partial q^i} \left[\sqrt{g} \, (Q^{ij} \frac{\partial}{\partial q^j} - b^i \rho) \right] \ . \qquad (7.13)$$

We write

$$\rho(q,t) = \bar{\rho}(q,t) \rho_0(q)$$

$$\mu(q) = \rho_0(q) \sqrt{g}$$

$$\rho_0 = e^{\psi}$$

and

$$\gamma^i = Q^{ij} \frac{\partial \psi}{\partial q^j} - b^i \ .$$

With these definitions we may rewrite eq. (7.13) as

$$\frac{\partial \bar{\rho}}{\partial t} = D\left[\frac{1}{\mu}\frac{\partial}{\partial q^j}\left(\mu\, Q^{ij}\frac{\partial \bar{\rho}}{\partial q^j}\right) + \gamma^i\frac{\partial \bar{\rho}}{\partial q^i}\right] . \tag{7.14}$$

We observe that

$$\frac{\partial}{\partial q^i}(\mu\,\gamma^i) = 0$$

it is another form of saying that ρ is the equilibrium solution

The boundary condition for $\rho(q,t)$ is obtained by imposing that no current flows through the surface C of the container and we must have

$$\left(Q^{ij}\frac{\partial \rho}{\partial q^j} - b^i\rho\right) d\sigma_i = 0$$

or, equivalently

$$Q^{ij}\frac{\partial \bar{\rho}}{\partial q^j}\, d\sigma_i = 0 . \tag{7.15}$$

Let us now consider the vector space of the functions defined in the volume Ω with normal derivative at the boundary C satisfying eq. (7.15). In such a space we define the operator

$$H = H_0 + H_1$$

with

$$H_0 f \equiv -\frac{1}{\mu}\frac{\partial}{\partial q^i}\left(\mu\, Q^{ij}\frac{\partial f}{\partial q^j}\right) \tag{7.16}$$

and

$$H_1 f \equiv -\gamma^i\frac{\partial f}{\partial q^i} . \tag{7.16a}$$

We observe that H_0 and H_1 are hermitean and anti-hermitean operators respectively.

To construct the Green's function for H we will consider the bi-orthogonal basis generated by H and its adjoint H^+.

Let us call f_α the eigenfunction of H corresponding to the eigenvalue α. We have

$$Hf_\alpha = \alpha f_\alpha \ .$$

In general a will be a complex number. In this case f_α^* is the eigenfunction corresponding to the eigenvalue a* and we have

$$f_\alpha^* = f_{\alpha *} \ .$$

Because of that, the spectrum of H is the same as the spectrum of H^+ and to every f_α there corresponds a f_a^+ such that(*)

$$H^+ f_\alpha^+ = \alpha f_\alpha^+ \ .$$

We further have

$$\int f_\alpha^+ f_{\alpha'} \mu \, d^n q = 0 \quad \text{if} \quad \alpha \neq \alpha'$$

and we normalize these functions by the condition

$$\int f_\alpha^+ f_\alpha \mu \, d^n q = 1 \ .$$

The Green's function satisfying the following equation

$$\left(\frac{\partial}{\partial t} + DH \right) G(q,q';t-t') = \delta^n(q-q')\delta(t-t')$$

is

$$\begin{aligned} G &= \sum_\alpha e^{-D\alpha(t-t')} f_\alpha(q) f_\alpha^+(q') \qquad \text{for} \quad t \geq t' \\ G &= 0 \qquad\qquad\qquad\qquad\qquad\quad \text{for} \quad t < t' \ . \end{aligned} \tag{7.17}$$

Its is a simple rnatter to show, from the fact that complex eigenvalues alwaysoccurs is conjugate pairs that $G(q,q';t-t')$, defined by eq. (7.17), is a real, non-symrnetric function with respect to exchange of q by q'.

(*) See, for example, P.M.Morse and H.Feshbach, *Methods of Theoretical Physics*, Vol.1, MacGraw-Hill Book (N.York) 1953.

The time dependent solution $\rho(q;t)$ is

$$\rho(q;t) = \rho_0(q) \int G(q,q';t)\rho(q';0)\rho_0(q') \sqrt{g}\, d^n q .$$

We should observe that the non-hermitian character of the diffusion operator H may lead to unexpected behaviour of the system. If the imaginisry parts of some eigenvalues of H are larger than their corresponding real parts, the system, exciting these rnodes, comes to equilibrium through an oscillatory behaviour, unusual in the transient behaviour for diffusion.

8. AN EXAMPLE

To illustrate the formalism we consider a simple exarnple of non-liouvillian systems. Let us consider the three-dimensional euclidean space and let us introduce toroidal coordinate (r,ϕ,θ) by the following transformation

$$\begin{aligned} x &= (a + r\sin\phi)\cos\theta \\ y &= (a + r\sin\phi)\sin\theta \\ z &= r\cos\phi \end{aligned} \tag{8.1}$$

We take for the surface of the container, two tori defined by $r = r_1$ and $r = r_2$ and we will assume

$$a > r_0 > r_1$$

We will set D, the diffusion coefflcient, equal to unit.

For the constraint we take the form:

$$\omega = a dr + \Delta(r d\phi + (a + r\sin\phi) d\theta) \tag{8.2}$$

where

$$A = \frac{(r-r_1)(r-r_0)}{(r_0-r_1)^2} \tag{8.3}$$

The choice of A given by the previous equation makes the cons-

traint self-confining in the sense that the surfaces $r = r_1$ and $r = r_2$ are natural boundaries for particles moving between these two tori as the field a_i is everywhere normal to these two surfaces. To see this better let us first introduce the metric in the toroidal coordinates. We observe that

$$dx^2 + dy^2 + dz^2 = dr^2 + r^2 d\phi^2 + (a + r\sin\phi)^2 \, d\theta^2 ,$$

and we therefore set

$$(g_{ij}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & (a+r\sin\phi)^2 \end{pmatrix}$$

where the indices (1,2,3) corresponds to the $(dr, d\phi, d\theta)$ directions respectively. We also have

$$(a_i) = \Lambda \, (a, \Delta r, \Delta(a+r\sin\phi))$$

and

$$a^i a_i = 1 = \Lambda^2 \, (a^2 + 2\Delta^2)$$

from where we obtain

$$\Lambda = \frac{1}{\sqrt{a^2+2\Delta^2}} \quad .$$

At the surface of the container, where $\Delta = 0$, we have

$$(a_i) = (1,0,0).$$

To calculate (b_i) we use the formula

$$b_i = a^j \left(\frac{\partial a_i}{\partial q^j} - \frac{\partial a_j}{\partial q^i} \right)$$

which avoids calculating the affine conexion. On the surface of the container, we obtained:

$$(b_i) = \begin{cases} \dfrac{1}{a(r_0-r_1)}\ (0,\ r_0,\ a+r_0\sin\phi) & \text{for } r = r_0 \\ \dfrac{1}{a(r_0-r_1)}\ (0,-r_1,-(a+r_1\sin\phi) & \text{for } r = r, \end{cases}$$

As (b_i) is tangent to the surface of the container, ψ satisfies the boundary condition

$$\frac{\partial\psi}{\partial\rho} = 0 \quad \text{and} \quad r = r_0 \text{ and } r = r_1 .$$

If one would calculate the divergence of (b_i) in the bulk of the fluid one would find it to be different from zero, what would say that ψ is not constant over the volume of the system. We cannot calculate the divergence of ψ in the $d\phi$ and d directions on the surface unless we solve its equation explicitly. To get an idea of the solenoidal currents on the surface of the container, we observe that Q^{ij} is the identity operator in the tangent plane of these surfaces and we have

$$\gamma_\phi = -\frac{1}{r_0-r_1} + \frac{\partial\psi}{\partial\phi} \qquad \text{for } r = r_0$$

and

$$\gamma_\theta = -\frac{(a+r_0\sin\phi)}{a(r_0-r_1)} + \frac{\partial\psi}{a\theta} \quad \text{for } r = r .$$

Because (a_i) does not depend on θ we may assume that ψ is also independent of θ and

$$\gamma_\theta = -\frac{(a+r_0\sin\phi)}{a(r_0-r_1)} \qquad \text{for } r = r_0$$

what shows that there exists, in this example, a permanent solenoidal current in the opposite directions of $d\theta$, everywhere on the outer surface of the container. On the inner surface, this current is in the positive direction of $d\theta$. We also have a current in the negative $d\phi$ direction on the outer surface whose circulation is given by

$$\oint \gamma_{\phi} \, d\phi = - \frac{2\pi}{r_0 - r_1}$$

Such an example should be easily simulated on computers and the solenoidal currents observed.

9. CONCLUSIONS

We have stabilished by two different approaches the diffusion equation for non-holonomic systems. We have also specified the procedures for solving it for both liouvillian and non-liouvillian systems and discussed the equilibrium and transient states of such systems. With these results we believe that, unless microscopic physical systems with non-holonomic constraints are found in nature, further development of the theory here developed is pointless. We have even suggested in the introduction, where we should look for such systenis in nature. However, two aspects of the theory seen to us worth while pursuing its development. One is the probability of classifying the constraints, let us say in three dimensional space, by applying group theoretical considerations. We have in mind a development somewhat similar to the applications of homotopy theory to crystal defects[6]. Though we believe that the situation here is complicated by the lack of translational invariance of the non-holonomic structures. The other direction is tha large Λ^2 limit which cannot be reached by the method here presented.

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