Chapter 4

Liouville's Equation

4.1 Derivation

[Reference: Any text on Statistical Mechanics. For Example, M. Toda, R. Kubo, and N. Saito, *Statistical Physics I,* 2nd. ed. Springer Verlag, Berlin (1992).]

An N-particle Hamiltonian system is specified at any instant of time by the coordinates and the momenta of all of the particles in the system.. These $2dN$ variables, where d is the number of dimensions for each position or momentum vector, define a space, Γ-space and one point in this space determines all the coordinates and momenta of all of the particles. In the course of time such a point follows a trajectory in Γ-space. A trajectory is uniquely determined by any of its points and the Hamiltonian, $H(\vec{r}, \vec{p})$:

$$\dot{r}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial r_i}. \tag{4.1}$$

Two distinct trajectories cannot intersect or be tangent to each other, but single trajectories can be closed curves in phase space.

An ensemble of N-particle systems is at any instant described as a large collection of points in Γ-space. A continuous set of points can also be taken to form an infinite ensemble. Then $\rho(\Gamma)d\Gamma$ is the probability of finding a member of the ensemble in $d\Gamma = d\vec{r}_1 d\vec{p}_1 \dots d\vec{r}_N d\vec{p}_N$ about the point Γ. The distribution function, $\rho(\Gamma)$, changes with time as the members of the ensemble follow their individual trajectories. Time-evolution neither creates nor destroys members of the ensemble, so for a region, R in Γ-space, there must be a conservation law:

$$\int_R d\Gamma \frac{\partial \rho(\Gamma, t)}{\partial t} = \text{Flux}_{in} - \text{Flux}_{out} = \int_{\delta R} dS(\vec{v}\rho), \tag{4.2}$$

where $\vec{v} = (\dot{\vec{r}}_1, \dot{\vec{p}}_1 \ldots \dot{\vec{r}}_N, \dot{\vec{p}}_N)$. Or $\frac{\partial \rho}{\partial t} + \vec{\nabla}_{6N} \cdot (\vec{v}\rho) = 0$
where $\vec{\nabla}_{6N} = (\frac{\partial}{\partial \vec{r}_1}, \frac{\partial}{\partial \vec{p}_1} \ldots, \frac{\partial}{\partial \vec{r}_N}, \frac{\partial}{\partial \vec{p}_N})$. This leads to

$$\frac{\partial \rho}{\partial t} + \sum_i^N \frac{\partial}{\partial \vec{r}_i}(\dot{\vec{r}}_i \rho) + \sum_i^N \frac{\partial}{\partial \vec{p}_i}(\dot{\vec{p}}_i \rho) = 0$$

The terms that don't contain derivatives of ρ cancel because of the equations of motion which leads to

$$\frac{\partial}{\partial \vec{r}_i}(\frac{d\vec{r}_i}{dt}) + \frac{\partial}{\partial \vec{p}_i}(\frac{d\vec{p}_i}{dt}) = 0.$$

Then

$$\frac{\partial \rho}{\partial t} + \sum_i^N (\dot{\vec{r}}_i \frac{\partial}{\partial \vec{r}_i} + \dot{\vec{p}}_i \frac{\partial}{\partial \vec{p}_i})\rho = 0.$$

This is often expressed as Liouville's theorem

$$\frac{d\rho(\Gamma, t)}{dt} = 0. \tag{4.3}$$

It expresses the conservation of density of members of the ensemble in Γ-space. If R in equation 4.2 denotes the whole Γ-space and $\rho(\Gamma)$ falls off sufficiently rapidly then

$$\int_{\text{allspace}} d\Gamma \frac{\partial \rho(\Gamma, t)}{\partial t} = \frac{d}{dt} \int d\Gamma \rho(\Gamma, t) = 0$$

i.e. the total probability of finding a system somewhere in phase space remains constant (and equal to one if the probability density is normalized).

Equation 4.3 has important consequences; consider at $t = 0$ a set A in Γ-space and take for the initial ensemble-density the characteristic function of A :

$$\rho(\Gamma, 0) = \chi_A(\Gamma) = \begin{cases} 1 \text{ if } \Gamma \in A \\ 0 \text{ if } \Gamma \notin A \end{cases}$$

The volume of A is given by $V(A) = \int_{\text{allspace}} d\Gamma \chi_A(\Gamma)$. Now Liouville's equation implies $\rho(\Gamma(t), t) = \rho(\Gamma, 0)$. After some time t

$$\rho(\Gamma, t) = \begin{cases} 1 \text{ if } \Gamma \text{ evolved from } A, \text{ or } \Gamma(-t) \in A \\ 0 \text{ if } \Gamma \text{ did not evolve from } A, \text{ or } \Gamma(-t) \notin A \end{cases}$$

So $\rho(\Gamma, t) = \chi_{A(t)}(\Gamma)$. An integration over Γ-space gives

$$\int d\Gamma \rho(\Gamma, t) = V(A(t)) \tag{4.4}$$

From Eq. 4.3 it then follows that $\frac{d}{dt} V(A(t)) = 0$. In others words : time-evolution is a volume-preserving transformation. Consider points in phase-space that are distributed uniformly over the region where $E < H < E + \delta E$. Let dS be the differential surface area for the constant energy surfaces and δn be the infinitesimal (perpendicular) distance between the two surfaces. Then the differential for the volume can be written as $d\text{Vol} = dS\delta n$. Using $\delta E = \delta n |\nabla H|$ we see that the volume element $d\text{Vol} = \frac{dS\delta E}{|\nabla H|}$ is conserved in the course of time. Since the left-hand side is constant in time, and since δE is fixed, one can define an invariant measure on the constant energy surface by $\mu(dS) = \frac{dS}{|\nabla H|}$.

4.2 The BBGKY Hierarchy Equations

[References: J.R. Dorfman and H. van Beijeren, "The Kinetic Theory of Gases", in *Statistical Mechanics, Part B,* B. Berne, ed., op. cit.; P. Resibois and M. de Leener, *Classical Kinetic Theory of Fluids,* John Wiley, New York (1977); E.G.D. Cohen, Physica A **194**, 229, (1993); N.N. Bogoliubov, in *Studies in Statistical Mechanics, Vol.I,* G.E. Uhlenbeck and J. de Boer, eds. North Holland, Amsterdam, (1962).]

In our discussion of the Boltzmann equation we concluded that this equation had to be understood as describing the average behavior of an ensemble of similarly prepared dilute gases, rather than the behavior of one particular member of the ensemble. If this is true, then we ought to be able to derive the Boltzmann equation from the Liouville equation by integrating the N-particle distribution function $\rho(\Gamma, t)$ over the phases of all but one of the particles. This is in fact true, and the work of N.N. Bogoliubov, M.S. Green and E.G.D. Cohen showed how this could be accomplished. These workers provided the foundation for a very advanced kinetic theory which has led to a derivation of the Boltzmann equation, allowed for a generalization the Boltzmann equation to higher densities, and uncovered a variety of physical phenomena which have been studied by means of computer simulations and experiments on laboratory systems. We will not discuss this here, since this would take us away from the main topic of the connections with dynamical systems theory, but interested readers should consult the references listed above.

Here we will only show how this procedure is initiated by carrying out the integration of the phase space distribution function over the phases of all but one of the particles. We begin by writing the Liouville equation Eq. 4.3 as

$$\frac{\partial \rho(\Gamma, t)}{\partial t} + \sum_{i=1}^{N} \frac{\vec{p}_i}{m} \cdot \nabla_{\vec{r}_i} \rho(\Gamma, t) - \sum_{i<j}^{N} \theta_{ij} \rho(\Gamma, t) = 0 \qquad (4.5)$$

where we have used the explicit form of the total time derivative in Eq. 4.3, and defined the operator θ_{ij} by

$$\theta_{ij} = \theta(\vec{r}_i, \vec{p}_i, \vec{r}_j, \vec{p}_j) = \frac{\partial \varphi(r_{ij})}{\partial \vec{r}_i} \cdot \left(\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right)$$

and $\varphi(r_{ij})$is the intermolecular pair potential energy which is a function of $r_{ij} = |\vec{r}_i - \vec{r}_j|$. From our discussion of the Boltzmann equation we know that the quantity of interest to us is $F(\vec{r}, \vec{v}, t)$ which we now think of as the ensemble average of the density of particles in the region $\delta\vec{r}\delta\vec{v}$ at time t. Since Γ-space is most properly formulated in terms of $\vec{r}$ and $\vec{p}$ instead of $\vec{r}$ and $\vec{v}$ we simply define a new function of position and momentum, $\hat{F}(\vec{r}, \vec{p}, t)$ such that

$$\hat{F}(\vec{r}, \vec{p}, t)\delta\vec{r}\delta\vec{p} = F(\vec{r}, \vec{v}, t)\delta\vec{r}\delta\vec{v},$$

and continue the discussion for $\hat{F}$. Let us now suppose that the phase space distribution function is normalized to unity, that is

$$\int d\Gamma \rho(\Gamma, t) = 1$$

where $d\Gamma = d\vec{r}_1 d\vec{p}_1 d\vec{r}_2 d\vec{p}_2 ... d\vec{r}_N d\vec{p}_N$ is the volume element in phase space. Then the single particle distribution function function $\hat{F}(\vec{r}, \vec{p}, t)$ is defined by taking the average value of the microscopic density of particles at $\vec{r}, \vec{p}$ as

$$\hat{F}(\vec{r}, \vec{p}, t) = \int d\Gamma \rho\left(\Gamma, t\right) \sum_{i=1}^{N} \delta\left(\vec{r}_i - \vec{r}\right) \delta\left(\vec{p}_i - \vec{p}\right). \tag{4.6}$$

This then is the proper formulation of the single particle distribution function as a phase space average. We should expect this function to satisfy the Boltzmann equation if our system is a dilute gas. An equation of motion for $\hat{F}$ can be found by differentiating Eq. 4.6 with respect to time and by using the Liouville equation, Eq. 4.5 to determine the time derivative of $\rho\left(\Gamma, t\right)$. When this is carried out one obtains (the proof is left to the reader)

$$\begin{aligned} & \frac{\partial \hat{F}(\vec{r}, \vec{p}, t)}{\partial t} + \frac{\vec{p}}{m} \cdot \nabla_{\vec{r}} \hat{F}(\vec{r}, \vec{p}, t) \\ = & \int d\vec{r'} \int d\vec{p'} \theta\left(\vec{r}, \vec{p}, \vec{r'}, \vec{p'}\right) \hat{F}_2\left(\vec{r}, \vec{p}, \vec{r'}, \vec{p'}, t\right) \end{aligned} \tag{4.7}$$

where the θ-operator is defined above, and $\hat{F}_2$ is the two particle distribution function defined by

$$\begin{aligned} & \hat{F}_2(\vec{r}, \vec{p}, \vec{r'}, \vec{p'}, t) \\ = & \int d\Gamma \rho\left(\Gamma, t\right) \sum_{i \neq j}^{N} \delta\left(\vec{r}_i - \vec{r}\right) \delta\left(\vec{p}_i - \vec{p}\right) \delta\left(\vec{r}_j - \vec{r'}\right) \delta\left(\vec{p}_j - \vec{p'}\right) \end{aligned} \tag{4.8}$$

which is the average probability density of finding *two* particles in the fluid one at $\vec{r}, \vec{p}$ and the other at $\vec{r'}, \vec{p'}$. Equation 4.7 is called the first BBGKY hierarchy equation. Hierarchy is used to denote the fact that if one wants to find the equation of motion for $\hat{F}_2$ one finds that it depends on a three particle probability density, and so on. There is in fact an open-ended chain of equations for the $\hat{F}_n$ functions derived by Born, Bogoliubov, Green, Kirkwood, and Yvon. The extraction of the Boltzmann equation from this chain of equations is no small task, but it can be done, and a lot more besides.

We will not pursue this issue here, other than to say that the derivation of the Boltzmann equation from the hierarchy equations requires some assumptions about the properties of the n-particle distribution functions $\hat{F}_n$ at some *initial* time. These assumptions usually are that the initial values of the $\hat{F}_n$

are smooth functions of their arguments and that for initial configurations of particles where some are far from the others, then the $\hat{F}_n$ can be written as a product of lower order distribution functions involving the separated groups of particles.

This very rough outline of the derivation of the Boltzmann equation is all that we will need for our further discussions here.

Chapter 5

Poincare Recurrence Theorem

5.1 Proof

[References: Articles by M. Kac and by S. Chandrasekhar in *Noise and Stochastic Processes,* N. Wax, ed., Dover Publishing Co. New York, (1954); S. Brush, *The Kind of Motion We Call Heat*, Vol.2, North Holland Publishing Co., Amsterdam, (1976); M. Kac, *Probability and Related Topics in Physical Science,* op. cit.]

One of the most interesting consequences of Liouville's theorem is the famous Poincaré recurrence theorem, which states, roughly, that almost every initial state of a system will occur again in the course of the time evolution of the system. This theorem was stated by F. Nietzsche who called it the "law of universal return". In this form even Woody Allen referred to it in one of his movies, *Hannah and Her Sisters.* We turn to a careful statement and proof.

Consider a classical system confined to a phase space of finite measure, $\mu = \int \frac{dS}{|\nabla H|} < \infty$. For example think of a system with finite energy and extension, so that for all particles i

$$0 < \frac{p_i^2}{2m} < M_p$$

and

$$0 < |\vec{r}_i| < M_r$$

In this case Poincare's Recurrence Theorem states that *almost every point in phase space is recurrent* (i.e. the set of points that do not return arbitrarily close to their starting-point after a sufficiently long time, has measure zero).

To prove it consider a set of points, A, in phase-space with finite measure. Next consider in A a set of points, B_0 that leave A after a time τ and that never return to A. We let the time τ be arbitrary, and B_0 is a non-recurrent set of points. We wish to show that $\mu\left(B_0\right) = 0$. Let B_n denote the set of points that B_0 evolves to after time $n\tau$.

Claim: the intersection between B_n and B_k is empty for every set of integers (k, n) with $k > n$. If this were not the case then some $x_n \in (B_n \cap B_k)$ would have evolved from $x_{n-1} \in B_{n-1} \cap B_{k-1}$. So $B_{n-1} \cap B_{k-1} \neq \oslash$. Repeating this n times we get $B_0 \cap B_{k-n} \neq \oslash$, implying that a point in B_0 has returned to A after a time $(k-n)\tau$. This contradicts the assumption and proves the claim. Because time-evolution is measure-preserving according to Liouville's equation, the total measure of the sets $B_0 \ldots B_n$ after a time $n\tau$ is $n\mu(B_0)$. For a non-zero $\mu(B_0)$, and some large enough n, this number will exceed the total measure of Γ-space, meaning either that overlap must occur between the B_k's which we just proved is impossible or $\mu(B_0)$ must be zero.

Poincare's Recurrence Theorem has strange implications; for example, the particles in a bottle of gas that have an exceptional configuration will, even after equilibrium has been established, eventually return to their original positions. Very large fluctuations will occur after enough time. Zermelo used the theorem to argue that Boltzmann should not try to reconcile the Second Law of Thermodynamics and Classical Mechanics. In his reply, Boltzmann compared Zermelo to a dice player who complains that a die is false because he has never thrown 1000 ones in a row, even though this possibility has non-zero measure. The recurrence of an ordinary system to an unlikely state has never been recorded, because the recurrence-times are *very* large. It is still true that when a system is not in equilibrium, the most likely movement will be towards equilibrium. Poincare's theorem just doesn't exclude the possibility that a system can also move away from it. A similar theorem can also be proved for quantum systems (see exercise 3.2).

Chandrasekhar has given an instructive calculation of Poincaré recurrence times. He considers a sphere of radius a in the middle of a container of air at STP. He then computes the recurrence time, t_r, for a one percent fluctuation in the density of the air. The results are:

For $a \sim 10^{-5} cm$, $t_r \approx\ 10^{-11} sec$
For $a \sim 2.5 \times 10^{-5} cm$, $t_r \approx\ 1 sec$
For $a \sim 3 \times 10^{-5} cm$, $t_r \approx\ 10^{6} sec$
For $a \sim 5 \times 10^{-5} cm$, $t_r \approx\ 10^{68} sec$

For $a \sim 1cm$, $t_r \approx 10^{10^{14}} sec$

5.2 Ehrenfests' Urn Model.

Consider two urns, I and II, and a bag. One hundred balls are distributed between the urns. These balls are labelled with numbers from 1 to 100. The bag contains pieces of paper that also carry numbers from 1 to 100. Each time-step somebody draws a number out of the bag at random and moves the corresponding ball to the other urn. This person then puts the piece of paper back in the bag. This is repeated an infinite number of times. Consider the (absolute) difference between the number of balls in I and in II as a function of time. The chance that a ball will move from the fuller urn to the emptier urn is always greater than the chance that the opposite will happen, therefore the system has a tendency to approach an equilibrium, where the balls are distributed equally between the urns. Fluctuations will also occur, even very large ones. (See the article by M. Kac referred to above, and Problem 2.2)