Time-Dependent Statistical Mechanics
5. The classical atomic fluid, classical mechanics, and classical equilibrium statistical mechanics

October 1, 2009

Lecture 3 9/29/09 continued from N4

While we know that in principle quantum mechanics is needed for a completely correct theory of the microscopic behavior of materials, it is also well understood that classical mechanics is a very good approximation for many purposes. In particular, as long as we are not concerned with very low temperatures or high frequency vibrations, then classical mechanics can be a good description of many atomic and molecular degrees of freedom - e.g. translation, rotation, and internal rotation.

So we often use classical models and classical mechanics to take advantage of its simplicity relative to that of quantum mechanics.

Today we will start a discussion of classical mechanics and classical statistical mechanics, which will form the basis for much of what this course will deal with. The discussion will at times get very abstract, and one of the points of the discussion will be to demonstrate some of the important features of these subjects in their full generality.

1 Interacting point particles

This section on interacting point particles was not discussed in lecture.

We will now discuss one of the standard models used for atomic gases, liquids, and solids. It consists of a system of interacting point particles.

1.1 Statement of the model

Each particle i has a position $\mathbf{r}_i$ and a momentum $\mathbf{p}_i$. The momentum has the usual meaning of mass times velocity. If we have N such atoms in a volume V of some particular shape, the mechanical state of the system is specified by listing the positions and momenta of all the particles.

$$\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots, \mathbf{r}_N, \mathbf{p}_N$$

We shall usually abbreviate this as $\mathbf{r}^N \mathbf{p}^N$. Since we are using classical mechanics, it is entirely permissible to give labels to the particles or atoms and imagine that we can always tell which particle is particle 47 and which is particle 3450, for example.

The Hamiltonian of the system is

$$H(\mathbf{r}^N, \mathbf{p}^N) = T(\mathbf{p}^N) + U(\mathbf{r}^N)$$

T is the kinetic energy, and it depends only on the momenta, not the positions.

$$T(\mathbf{p}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m}$$

U is the potential energy, and it depends only on the positions, not the momenta. The assumption usually made about U is that it is the sum of the interactions between each pair of particles.

$$U(\mathbf{r}^N) = \sum_{i<j=1}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|)$$

The interaction between a pair of atoms depends on the scalar distance separating them. There are some situations in which this form for the interaction is known to be inadequate. For our purposes, we can carry out much of the discussion without specifying U and without making this assumption, and so we shall delay making this particular assumption.

The separation of the total Hamiltonian into two parts in this way has significant consequences for all sorts of statistical averages, as we shall see.

This is the basic model. These are point particles because we have not included any rotational degrees of freedom. We have been describing a one component system, but this is easily generalized to multicomponent systems. This is a reasonable model for the noble gases, for some metals, and for very round molecules (provided molecular rotation is not important for what is being considered).

1.2 Equilibrium statistical mechanics of the model

1.2.1 Canonical distribution function

Suppose we prepare such a system by putting a precisely measured number of atoms N in a container of volume V, put the container in contact with a heat bath at temperature T, and we wait long enough for the system to come to equilibrium. When the system is ready, we call that time t_0 and we start making measurements. We will assume that t_0 is to be chosen as 0.

For a general experiment, the precise mechanical state of the system at time t_0 is a random variable. It will have a different value each time we do the experiment. In order to carry out statistical mechanical calculations, we need to know the probability distribution function for the initial state. There are two that are most commonly used in theoretical calculations: the canonical distribution function and the grand canonical distribution function.

For the type of experiment just discussed, i.e. and equilibrium system with specified N, V, and T, the appropriate distribution function is canonical distribution function.

The mechanical state of the system at time zero is specified by giving $\mathbf{r}^N(0), \mathbf{p}^N(0)$.

The usual assumption that is made is that[1]

$$P_{\mathbf{r}^N(0),\mathbf{p}^N(0)}(\mathbf{r}^N,\mathbf{p}^N) \propto \exp\Big(-H(\mathbf{r}^N,\mathbf{p}^N)/k_BT\Big)$$

Any state of high energy has a low probability. Any state of low energy has a high probability. From this you might think that the spread in energies is very large. However, with this probability distribution function, the spread of energies in the system is quite narrow, because the number of low energy states is so small compared with the number of higher energy states and the exponential function falls very rapidly with increasing energy.

We won't discuss the justification for this assumption. You should have seen this assumption used in previous statistical mechanics courses. All of our experience with this assumption leads to the conclusion that when used to calculate statistical averages for comparison with experiment it in principle gives the correct results for equilibrium experiments when the values of N, V, and T are specified..

Let's calculate the normalization constant. We have

$$1 = C\int_V d\mathbf{r}^N \int d\mathbf{p}^N \,\exp\Big(-H(\mathbf{r}^N,\mathbf{p}^N)/k_BT\Big)$$

$$C = \Big(\int_V d\mathbf{r}^N \int d\mathbf{p}^N \,\exp\Big(-H(\mathbf{r}^N,\mathbf{p}^N)/k_BT\Big)\Big)^{-1}$$

Note that the Hamiltonian can be written in the form

$$H(\mathbf{r}^N,\mathbf{p}^N) = \frac{\mathbf{p}_1\cdot\mathbf{p}_1}{2m} + \ldots + \frac{\mathbf{p}_N\cdot\mathbf{p}_N}{2m} + U(\mathbf{r}^N)$$

Since the probability distribution function depends exponentially on H, it follows that each momentum is statistically independent of each other momentum and of the positions. Moreover, since each kinetic energy contribution is of the form

$$\frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m}$$

it follows that each component of momentum of each particle is statistically independent of each other component of the same particle, as well as of the

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[1] As is common, we will use P as the symbol for a probability density or probability. To avoid confusion, we will sometimes put the names of the variables as subscripts. To distinguish them from the values of the arguments of the function.

momentum components of the other particle and of the positions of all of them.

Moreover, and this can be counterintuitive, the probability distribution of each component of momentum is a Maxwell-Boltzmann distribution and is the same as if the material were an ideal gas.

Discussion of some special cases.

For many of you, you first learned about the Maxwell-Boltzmann distribution in freshman chemistry. The first theoretical derivations of it that you have seen may have been in an undergraduate physical chemistry course and the derivation may have been for a special case of an ideal gas, with no interactions among the molecules. Many students with this experience tend to think that the Maxwell-Boltzmann distribution applies only to ideal gases or at least low density gases. But this postulate of the canonical distribution function assumes that it is true for any material (gas, liquid, or solid), as long as its motion is classical.

In general, however, the positions are all statistically correlated, because of the potential energy. Only in the special case of an ideal gas, with no interactions between the particles, are the positions independent of each other.

1.2.2 Grand canonical distribution function

There is another postulate that is used for the initial statistical distribution. Suppose that when the system is prepared, we do not control the number of particles precisely, but instead we prepare the system by putting it in contact with a source of material that is at a certain chemical potential μ and the system is equilibrated not only at a specific temperature but with a specific chemical potential.

The grand canonical distribution will not be discussed in lecture.

This situation holds whenever the system of interest is really just part of a larger equilibrium system. For example:

- The system of interest might be just some region of volume V of a larger system, with no real walls separating the system from the surroundings.
- The system of interest might be separated from the surroundings by a wall that is permeable to particles.

In this type of situation, the number N of particles as well as their positions $\mathbf{r}^N$ and $\mathbf{p}^N$ are random variables. We need to know $P(N, \mathbf{r}^N, \mathbf{p}^N)$.

The hypothesis that turns out to be correct is the grand canonical distribution function.

$$P_{N,\mathbf{r}^N(0),\mathbf{p}^N(0)}(N, \mathbf{r}^N, \mathbf{p}^N) \propto \frac{1}{N!} e^{N\mu/k_BT} \exp\left(-H(\mathbf{r}^N, \mathbf{p}^N)/k_BT\right)$$

There are various ways of deriving or justifying this hypothesis, but we will not go into them. As with the canonical distribution function, all of our experience with this assumption leads to the conclusion that when used to calculate statistical averages for comparison with experiment it in principle gives the correct results for the type of experiment just mentioned.

1.3 Ensemble

An ensemble is a collection of systems whose coordinates and momenta have a certain probability distribution function. (In some sense, an ensemble is the same thing as a probability distribution function.) Some ensembles have probability distributions that are appropriate for equilibrium systems. Thus we often talk about the canonical ensemble, which is just a collection of systems distributed according to the canonical distribution function. Some are appropriate for nonequilibrium situations. In general, an ensemble is a collection of systems prepared according to a certain prescription and having a certain probability distribution function for their mechanical state.

1.4 Classical dynamics of the model

The coordinates and momenta change with time according to Newton's laws.

$$\begin{aligned} \dot{\mathbf{r}}_i(t) &= \mathbf{p}_i(t)/m \\ \dot{\mathbf{p}}_i(t) &= \mathbf{f}_i(t) = -\nabla_{\mathbf{r}_i} U(\mathbf{r}^N) \end{aligned}$$

Here $\mathbf{f}_i(t)$ is the force on particle i at time t.

These are also special cases of Hamilton's equations, which can be written in the following form.

$$\dot{\mathbf{r}}_i = \nabla_{\mathbf{p}_i} H$$

$$\dot{\mathbf{p}}_i = -\nabla_{\mathbf{r}_i} H$$

where it is to be understood that both sides are evaluated at the same time.

An important feature of classical dynamics is that the equations of motion are deterministic. The values of $\mathbf{r}^N(t), \mathbf{p}^N(t)$ are completely determined by the values of $\mathbf{r}^N(0), \mathbf{p}^N(0)$.

End of material not discussed in lecture

2 Classical mechanics

We consider a material containing molecules and perhaps atomic species. We assume that classical mechanics is adequate for discussing the mechanics and statistical mechanics. The molecules are labeled witn an index i, and molecules are in principle distinguishable.

2.1 Degrees of freedom

Each molecule i has more than just x, y and z center of mass degrees of freedom. Corresponding to each degree of freedom there will be a position variable and a momentum variable. Thus, we will always have $\mathbf{r}_i$ and $\mathbf{p}_i$, the position and momentum associated with center of mass motion. But we will also have additional coordinates; e.g.

- orientational angles (e.g. two angles for a rigid linear molecule and three for a rigid nonlinear molecule)
- vibrational coordinates (e.g. amplitudes of normal modes of vibration)
- internal rotation coordinates (typically chosen as angles)

In some cases, we may use entirely different coordinates.

In any case, each molecule has a set of coordinates, and for each coordinate there is a corresponding momentum. (For an angular coordinate, the corresponding momentum is usuall called an angular momentum.) The set of all coordinates for a set of N molecules will be called Q^N and the momenta will be called P^N. Each Q_i corresponds to three or more variables, depending on the model. Let $Q_{i\alpha}$ be the αth coordinate for molecule i and $P_{i\alpha}$ be the corresponding momentum.

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Notation

$Q_{i\alpha}$ = the αth coordinate for molecule i

$P_{i\alpha}$ = the αth momentum for molecule i

Q^N = the set of all coordinates for all N molecules

P^N = the set of all momenta for all N molecules

Hamiltonian

$$H(Q^N, P^N) = T(Q^N, P^N) + V(Q^N)$$

$T(Q^N, P^N)$ = kinetic energy of all the molecules

$V(Q^N)$ = potential energy of all the molecules

The Hamiltonian function gives the energy of system.

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2.2 Hamiltonian

The Hamiltonian depends on the coordinates and momenta.

$$H(Q^N, P^N) = T(Q^N, P^N) + V(Q^N)$$

In the general case, unlike the case of the atomic fluid, the kinetic energy may depend on some of the coordinates. This is the case for rotational degrees of freedom. (Thus, the momenta are not statistically independent of the positions in the most general situation.)

The physical meaning of the Hamiltonian is the energy of the system.

2.3 Equilibrium statistical mechanics

The canonical distribution function is of the form

$$P(Q^N, P^N) \propto \exp(-H(Q^N, P^N)/k_BT)$$

The grand canonical distribution function is still of the form

$$P(N, Q^N, P^N) \propto \frac{1}{N!} e^{N\mu/kT} \exp(-H(Q^N, P^N)/k_BT)$$

Not discussed in lecture

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Equilibrium statistical mechanics. The probability distribution of mechanical states in an equilibrium system, for specified N, V, T, is the canonical distribution function

$$P(Q^N, P^N) \propto \exp(-H(Q^N, P^N)/k_BT)$$

Dynamics for an isolated system. The equations of motion are

$$\begin{aligned} \dot{Q}_{i\alpha} &= \frac{\partial H(Q^N, P^N)}{\partial P_{i\alpha}} \\ \dot{P}_{i\alpha} &= -\frac{\partial H Q^N, P^N)}{\partial Q_{i\alpha}} \end{aligned}$$

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2.4 Dynamics

The general Hamiltonian equations of motion are:

$$\begin{aligned} \dot{Q}_{i\alpha} &= \frac{\partial H}{\partial P_{i\alpha}} \\ \dot{P}_{i\alpha} &= -\frac{\partial H}{\partial Q_{i\alpha}} \end{aligned}$$

2.5 External influences

The Hamiltonians discussed above are simply functions of the coordinates and momenta. Time does not appear in them. This is an appropriate form for the Hamiltonian of an isolated system of atoms or molecules.

But suppose the system is subject to some external influence, such as an external gravitational or electromagnetic field. Then the mechanics of the system are governed by the same type of Hamiltonian equations of motion. The only difference is that the external influence adds an additional term into the Hamiltonian.

$$H(Q^N, P^N, t) = T(Q^N, P^N) + V(Q^N) + H_{ext}(Q^N, P^N, t)$$

The specific form of the H_{ext} depends on the nature of the external influence. Construction of the form of H_{ext} requires an understanding of the physics of the interaction between the external influence and the system.

The new equations of motion are:

$$\begin{aligned} \dot{Q}_{i\alpha} &= \frac{\partial H(t)}{\partial P_{i\alpha}} \\ \dot{P}_{i\alpha} &= -\frac{\partial H(t)}{\partial Q_{i\alpha}} \end{aligned}$$

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The influence of the surroundings. E.g. an external gravitational or electric field.

$$H(Q^N, P^N, t) = T(Q^N, P^N) + V(Q^N) + H_{ext}(Q^N, P^N, t)$$

$$\begin{aligned}\dot{Q}_{i\alpha} &= \frac{\partial H(Q^N, P^N, t)}{\partial P_{i\alpha}} \\ \dot{P}_{i\alpha} &= -\frac{\partial H(Q^N, P^N, t)}{\partial Q_{i\alpha}}\end{aligned}$$

Distinguish between

- Fields that are independent of time → $H_{ext}(Q^N, P^N)$
- Fields (and H_{ext}) that are time dependent → $H_{ext}(Q^N, P^N, t)$

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It is worthwhile distinguishing between two different types of external fields.

- The first is fields that are independent of time. An example would be a gravitational field or a steady electric or magnetic field. If the field is independent of time, then it is possible that the system can come to equilibrium under the influence of that field. The standard formulas for the equilibrium distribution functions then apply, with the entire H, including the perturbation, appearing in the exponential.
- The second is fields that depend on time. Examples would be microwave radiation or visible light. In general, time dependent external fields perturb a system in such a way that it is not in equilibrium. They can feed energy into the system, leading to a rise in the temperature. A system whose properties are changing with time can not be in equilibrium. Thus, if a system is initially in equilibrium in the absence of an external field, and if a time dependent field is turned on, the system will be driven away from equilibrium. If the field is then turned off again, the system can return to equilibrium if given enough time.

2.6 Phase space and time evolution

The mechanical state of a system of N molecules at any particular time is specified by stating the values of the Q^N, P^N at that time. Each of the quantities is a real number. It is customary to regard this collection of numbers as the 'coordinates' of the system in 'phase space'. Phase space is a high dimensional space in which there is one dimension for each position variable and one dimension for each momentum variable. Thus for atomic liquids, if there are N particles there are $3N$ coordinates and $3N$ momenta and hence phase space is $6N$ dimensional. If you look at a system at any one time and make a list of the $6N$ positions and momenta and regard these as Cartesian coordinates for a $6N$ dimensional space, then the system at any one time corresponds to a point in phase space.

Suppose a system at time t_0 is at some point in phase space. As time moves forward, the positions and momenta of the particles evolve continuously in time, and the system will move along a trajectory in phase space. An interesting thing about the trajectory is that it is completely determined by the starting point and by the Hamiltonian. The positions and momenta obey closed deterministic equations of motion.

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Phase space

A high dimensional Cartesian space.

The axes correspond to $Q_{i\alpha}$ and $P_{i\alpha}$ for all i and α.

(E.g. for N atoms, it is a $6N$ dimensional space.)

The mechanical state of the system at any time corresponds to a point in the phase space.

As time moves forward, the point moves around continuously and deterministically according to the Hamiltonian equations of motion.

The canonical distribution corresponds to a probability distribution in phase space.

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2.7 Conservation of energy when the Hamiltonian function is independent of time

Consider a single system evolving according to Hamilton's equation, with a Hamiltonian that has no explicit time dependence. The system traces out a path in phase space. Suppose that at each time (or at each point along the path) we evaluate the Hamiltonian at the current location of the system in phase space and plot the results for the system. We want to show that the graph is flat; i.e. that the value of the Hamiltonian at the system phase point is independent of time.

The proof is straightforward. The path of the phase point is $Q^N(t), P^N(t)$. So the time dependent value of the Hamiltonian along this path is $H(Q^N(t), P^N(t))$. The potential time dependence of this comes from the time dependence of the arguments, which is a consequence of the fact that the system is moving around in phase space.

Using the chain rule, we have

$$\frac{dH(Q^N(t), P^N(t))}{dt} = \sum_{i\alpha} \left(\frac{\partial H}{\partial Q_{i\alpha}} \dot{Q}_{i\alpha} + \frac{\partial H}{\partial P_{i\alpha}} \dot{P}_{i\alpha} \right)$$

where the partial derivatives should be evaluated at the point $Q^N(t), P^N(t)$ and everything is to be evaluated at the same time t.

Now evaluate $\dot{Q}_{i\alpha}$ and $\dot{P}_{i\alpha}$ using Hamilton's equations. We get

$$\frac{dH(Q^N(t), P^N(t))}{dt} = \sum_{i\alpha} \left(\frac{\partial H}{\partial Q_{i\alpha}} \frac{\partial H}{\partial P_{i\alpha}} + \frac{\partial H}{\partial P_{i\alpha}} \left(-\frac{\partial H}{\partial Q_{i\alpha}} \right) \right) = 0$$

When the Hamiltonian function has no explicit time dependence, the value of the function, evaluated along the trajectory of a system, is independent of time. For an isolated system, the Hamiltonian is the same thing as the mechanical energy of the system. This theorem states that energy is conserved for a system whose Hamiltonian is independent of time.

If the Hamiltonian has an explicit time dependence, the meaning of the time dependent term is somewhat problematic. In any case, under these conditions, the Hamiltonian of the system is not conserved.

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Consider

- an isolated system, or
- a system interacting with an external field that is independent of time

In either case, the Hamiltonian has no explicit time dependent.

Such system moves around in phase space in such a way that the value of its Hamiltonian does not change.

This is a statement of the **conservation of energy**.

The path of a point is $Q^N(t), P^N(t)$.

The value of the Hamiltonian at time t for the system is $H(Q^N(t), P^N(t))$.

$$\begin{aligned} \frac{dH(Q^N(t), P^N(t))}{dt} &= \sum_{i\alpha} \left(\frac{\partial H}{\partial Q_{i\alpha}} \dot{Q}_{i\alpha} + \frac{\partial H}{\partial P_{i\alpha}} \dot{P}_{i\alpha} \right) \\ = \quad \sum_{i\alpha} \left(\frac{\partial H}{\partial Q_{i\alpha}} \frac{\partial H}{\partial P_{i\alpha}} + \frac{\partial H}{\partial P_{i\alpha}} \left(- \frac{\partial H}{\partial Q_{i\alpha}} \right) \right) &= 0 \end{aligned}$$

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There is a geometric language that is often used to discuss this. Let's suppose that each molecule has r degrees of freedom. Then there are $2rN$ position and momentum variables for a system, and phase space has $2rN$ dimensions. At each point in phase space, the value of the (time independent) Hamiltonian is $H(Q^N, P^N)$. Suppose we pick an energy value E and then locate all points in phase space for which $H(Q^N, P^N) = E$. This is one equation with $2rN$ unknowns. Thus, the solutions lie on a $2rN - 1$ dimensional hypersurface in the $2rN$ dimensional space. Each such surface might be referred to as a constant energy surface or constant energy hypersurface.

Constant energy hypersurfaces will not be discussed in lecture.

For example, suppose we have $N = 1$ and $r = 1$. We have one molecule with one degree of freedom. Therefore we have one position and one momentum variable and hence a two dimensional phase space. Solving the equation $H(Q, P) = E$ gives a curved line in the two dimensional space. This is a contour line of constant E. If the system were a harmonic oscillator, the Hamiltonian would be

$$H(Q, P) = \frac{P^2}{2m} + \frac{kQ^2}{2}$$

where k is the force constant for the oscillator. Then the lines of constant energy are ellipses in the two dimensional phase space.

Thus, for a specific starting point in phase space, there is in general a constant energy hypersurface that passes through that point. As time moves forward and the system moves in phase space, it always stays on the same constant energy hypersurface on which it started.

2.8 Time evolution of the Hamiltonian when it has an explicit time dependence

This subsection will not be discussed in lecture.

Suppose the Hamiltonian has an explicit time dependence, due to the presence of some time dependent external mechanical influence on the system. As a system moves along in phase space, the value of the Hamiltonian evaluated at the location of the system is $H(Q^N(t), P^N(t), t)$. It has an additional source of time dependence. Thus we have

$$\frac{dH(Q^N(t), P^N(t), t)}{dt} = \sum_{i\alpha} \left(\frac{\partial H}{\partial Q_{i\alpha}} \dot{Q}_{i\alpha} + \frac{\partial H}{\partial P_{i\alpha}} \dot{P}_{i\alpha} \right) + \frac{\partial H}{\partial t}$$

When we evaluate the first term on the right, the two contributions cancel as above. We get

$$\frac{dH(Q^N(t), P^N(t), t)}{dt} = \frac{\partial H(Q^N(t), P^N(t), t)}{\partial t} = \frac{\partial H_{ext}(Q^N(t), P^N(t), t)}{\partial t}$$

The net result is that when a system is subject to a time dependent external field, its energy is not constant but varies with time as a result of the work done on it by the external field.[2]

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[2] Incidentally, the definition of energy for a system that has a time dependent Hamiltonian is somewhat ambiguous. The ambiguity arises because it is unclear whether the H_{ext} should be regarded as a contribution to the energy of the system or to the energy of the surroundings. H_{ext} is associated with the interaction of the system with the surroundings and is not unambiguously associated solely with either one. Nevertheless, it is safe to say that if the system is subject to a time dependent Hamiltonian, its energy changes with time, as long as we are not too specific about what energy is meant.

2.9 Liouville equation

Let us consider an ensemble of systems all of which have the same N. An ensemble, you recall, is a collection of systems all prepared according to some well defined prescription. The ensemble might be an equilibrium ensemble or a nonequilibrium ensemble.

At time t_0, when the ensemble was prepared, the state of each system is Q^N, P^N. These are random variables governed by a probability distribution function. To avoid confusion with the P^N, we shall use the symbol f for this probability distribution function. Thus it is $f(Q^N, P^N)$.

Let us define a time dependent probability distribution $f(Q^N, P^N, t)$. At each time t it gives the probability distribution of $Q^N(t), P^N(t)$.

A useful picture is the following one. Suppose you consider phase space, and at time 0 put a point in phase space associated with each of the systems in the ensemble. We get a dense cloud of points in phase space. The original probability distribution $f(Q^N, P^N, 0)$ represents the normalized density of that cloud. As time moves forward, each system moves in phase space; thus each point in the original picture moves; thus the density as a function of location may change. $f(Q^N, P^N, t)$ represents the normalized density at time t.

The Liouville equation is the differential equation that determines the time evolution of $f(Q^N, P^N, t)$. We now want to derive this equation. This function obeys a closed equation because its value at any time determines where the systems are and the motion of each system in phase space is determined by where it is. Thus the cloud of points has a definite flow associated with it, and $\partial f(Q^N, P^N, t)/\partial t$ is determined by $f(Q^N, P^N, t)$.

The derivation will not be discussed in detail in the lecture.

To derive this equation, let's first consider a mechanical problem with one degree of freedom. So we have $f(Q, P)$, and phase space is two dimensional and can easily be represented as a plane.

Consider a little rectangle of dimension dQ in the Q direction and dP in the P direction whose center is at Q, P. Imagine a cloud of points in and around this rectangle. We want to calculate the rate at which the density of points inside this rectangle is changing. The velocity of any point is uniquely determined by its location. The right edge is centered at $(Q + dQ/2, P)$.

The density of the cloud there is $f(Q + dQ/2, P, t)$. The rate at which these points are moving into the rectangle is given by $-\dot{Q}(Q + dQ/2, P, t)$. Thus the flow of points into the rectangle along this edge is

$$\left(-\dot{Q}(Q + dQ/2, P, t)\right)\left(f(Q + dQ/2, P, t)\right)(dP)$$

The first two factors represent the flux (flow per unit length per unit time) and the last factor represents the length of the side. The minus sign takes into account the fact that positive values of $\dot{Q}$ correspond to moving out of the rectangle and not into it. Similarly, for the left edge, the rate at which points are moving into the rectangle is

$$\left(\dot{Q}(Q - dQ/2, P, t)\right)\left(f(Q - dQ/2, P, t)\right)(dP)$$

The sum of these two is

$$\begin{aligned} & -\left(\dot{Q}(Q + dQ/2, P, t) f(Q + dQ/2, P, t) - \dot{Q}(Q - dQ/2, P, t) f(Q - dQ/2, P, t)\right) dP \\ = & \ -\frac{\partial}{\partial Q}\left(\dot{Q}(Q, P, t) f(Q, P, t)\right) dQdP \end{aligned}$$

This is the net rate at which systems in the cloud are flowing in at the left and right. The corresponding calculation for the top and bottom gives a similar result

$$-\frac{\partial}{\partial P}\left(\dot{P}(Q, P, t) f(Q, P, t)\right) dQdP$$

But the total rate at which the contents of the rectangle are changing with time is also equal to

$$\frac{\partial f(Q, P, t)}{\partial t} dQdP$$

It follows that

$$\frac{\partial f(Q, P, t)}{\partial t} = -\frac{\partial}{\partial Q}\left(\dot{Q}(Q, P, t) f(Q, P, t)\right) - \frac{\partial}{\partial P}\left(\dot{P}(Q, P, t) f(Q, P, t)\right)$$

Now use Hamilton's equations.

$$\frac{\partial f(Q, P, t)}{\partial t} = -\frac{\partial}{\partial Q}\left(\frac{\partial H(Q, P, t)}{\partial P} f(Q, P, t)\right) + \frac{\partial}{\partial P}\left(\frac{\partial H(Q, P, t)}{\partial Q} f(Q, P, t)\right)$$

When we calculate the partial derivative, the second derivatives of H cancel. The only terms that survive are those in which the partial derivatives act on the f.

$$\frac{\partial f(Q,P,t)}{\partial t} = -\frac{\partial H(Q,P,t)}{\partial P}\frac{\partial f(Q,P,t)}{\partial Q} + \frac{\partial H(Q,P,t)}{\partial Q}\frac{\partial f(Q,P,t)}{\partial P}$$

This is the Liouville equation for a system with one degree of freedom.

Note that all the functions that appear are to be evaluated at the same point in phase space, namely Q, P. With the understanding that this is the case, we can write an abbreviated version off this equation as

$$\frac{\partial f(Q,P,t)}{\partial t} = -\frac{\partial H(t)}{\partial P}\frac{\partial f(t)}{\partial Q} + \frac{\partial H(t)}{\partial Q}\frac{\partial f(t)}{\partial P}$$

End of the derivation not discussed in lecture.

The general equation is of the same form and can be derived in the same way, but it is a little complicated because of the higher dimensionality of the phase space. The result is

$$\frac{\partial f(Q^N,P^N,t)}{\partial t} = \sum_{i\alpha}\left(\frac{\partial H(t)}{\partial Q_{i\alpha}}\frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial H(t)}{\partial P_{i\alpha}}\frac{\partial f(t)}{\partial Q_{i\alpha}}\right)$$

Here it is to be understood that everything is to be evaluated at the same point Q^N, P^N in phase space.

This is the general form of the Liouville equation. It describes the time evolution of the cloud of probability associated with an ensemble of systems all of which have the same N. It is applicable to systems with a Hamiltonian that is either time dependent or time independent.

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Liouville equation

Consider a probability density in phase space at one instant of time, say $t = 0$.

Call it $f(Q^N, P^N, 0)$. *The cloud analogy.*

As time moves forward, the probability density may change because each system evolves in time. The time evolution of the probability density is determined by the underlying mechanics.

The probability density obeys a time evolution equation called the Liouville equation.

$$\begin{aligned}&\frac{\partial f(Q^N, P^N, t)}{\partial t}\\ &\quad = \sum_{i\alpha}\left(\frac{\partial H(Q^N, P^N, t)}{\partial Q_{i\alpha}}\frac{\partial f(Q^N, P^N, (t)}{\partial P_{i\alpha}} - \frac{\partial H(Q^N, P^N, t)}{\partial P_{i\alpha}}\frac{\partial f(Q^N, P^N, t)}{\partial Q_{i\alpha}}\right)\end{aligned}$$

Here it is to be understood that everything is to be evaluated at the same point Q^N, P^N in phase space.

This is the general form of the Liouville equation.

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2.10 Liouville equation applied to the canonical ensemble with time independent Hamiltonian

Consider an equilibrium canonical ensemble with a time independent Hamiltonian $H(Q^N, P^N)$. Its initial density is

$$f(Q^N, P^N, t_0) = C \exp\left(-H(Q^N, P^N)/k_B T\right)$$

As time moves forward, each system in the ensemble will move in phase space. What happens to the shape of the cloud of probability?

Let's calculate the initial time derivative of f. Note that

$$\frac{\partial f(Q^N, P^N, t_0)}{\partial Q_{i\alpha}} = -\frac{1}{k_B T}\frac{\partial H(Q^N, P^N)}{\partial Q_{i\alpha}} f(Q^N, P^N, t_0)$$

$$\frac{\partial f(Q^N, P^N, t_0)}{\partial P_{i\alpha}} = -\frac{1}{k_B T}\frac{\partial H(Q^N, P^N)}{\partial P_{i\alpha}} f(Q^N, P^N, t_0)$$

When these are substituted into the Liouville equation, we get

$$\frac{\partial f(Q^N, P^N, t_0)}{\partial t} = 0$$

Thus, initially the cloud will not change shape anywhere in phase space.

In fact, the cloud never changes shape. It is straightforward to show that

$$f(Q^N, P^N, t) = C \exp\Big(-H(Q^N, P^N)/k_B T\Big) = f(Q^N, P^N, t_0)$$

is a (time independent) solution of the Liouville equation whose initial value is the canonical distribution.

The net result is that although each system in the ensemble moves around in phase space, the overall cloud of points does not change shape. This actually makes sense for an equilibrium ensemble. If the probability distribution function changed with time, then the systems in the ensemble would shift around from region of phase space to another as time evolved. This should lead to ensemble averages, which correspond to measureable properties, changing with time. But in equilibrium the measurable properties do not change with time.

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Suppose we have

- a system with a time independent Hamiltonian $H(Q^N, P^N)$
- a probability distribution in phase space at time t_0 that is a canonical distribution

$$f(Q^N, P^N, t_0) = C \exp\Big(-H(Q^N, P^N)/k_B T\Big)$$

What is the probability distribution at later times?

It is straightforward to solve the Liouville equation for this initial condition and find that

$$f(Q^N, P^N, t) = C \exp\Big(-H(Q^N, P^N)/k_B T\Big) \quad \text{for all } t \geq t_0$$

The distribution is independent of time, even though every system in the distribution is changing with time.

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