G25.2651: Statistical Mechanics

Notes for Lecture 2

I. THE LIOUVILLE OPERATOR AND THE POISSON BRACKET

From the last lecture, we saw that Liouville's equation could be cast in the form

$$\frac{\partial f}{\partial t} + \nabla_{\mathbf{x}} \cdot \dot{\mathbf{x}} f = 0$$

The Liouville equation is the foundation on which statistical mechanics rests. It will now be cast in a form that will be suggestive of a more general structure that has a definite quantum analog (to be revisited when we treat the quantum Liouville equation).

Define an operator

$$iL = \dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}}$$

known as the Liouville operator ($i = \sqrt{-1}$ – the i is there as a matter of convention and has the effect of making L a Hermitian operator). Then Liouville's equation can be written

$$\frac{\partial f}{\partial t} + iLf = 0$$

The Liouville operator also be expressed as

$$iL = \sum_{i=1}^{N} \left[\frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial H}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] \equiv \{..., H\}$$

where $\{A, B\}$ is known as the Poisson bracket between $A(\mathbf{x})$ and $B(\mathbf{x})$:

$$\{A, B\} = \sum_{i=1}^{N} \left[\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i} \right]$$

Thus, the Liouville equation can be written as

$$\frac{\partial f}{\partial t} + \{f, H\} = 0$$

The Liouville equation is a partial differential equation for the phase space probability distribution function. Thus, it specifies a general class of functions $f(\mathbf{x}, t)$ that satisfy it. In order to obtain a specific solution requires more input information, such as an initial condition on f, a boundary condition on f, and other control variables that characterize the ensemble.

II. PRESERVATION OF PHASE SPACE VOLUME AND LIOUVILLE'S THEOREM

Consider a phase space volume element $d\mathbf{x}_0$ at $t = 0$, containing a small collection of initial conditions on a set of trajectories. The trajectories evolve in time according to Hamilton's equations of motion, and at a time t later will be located in a new volume element $d\mathbf{x}_t$ as shown in the figure below:
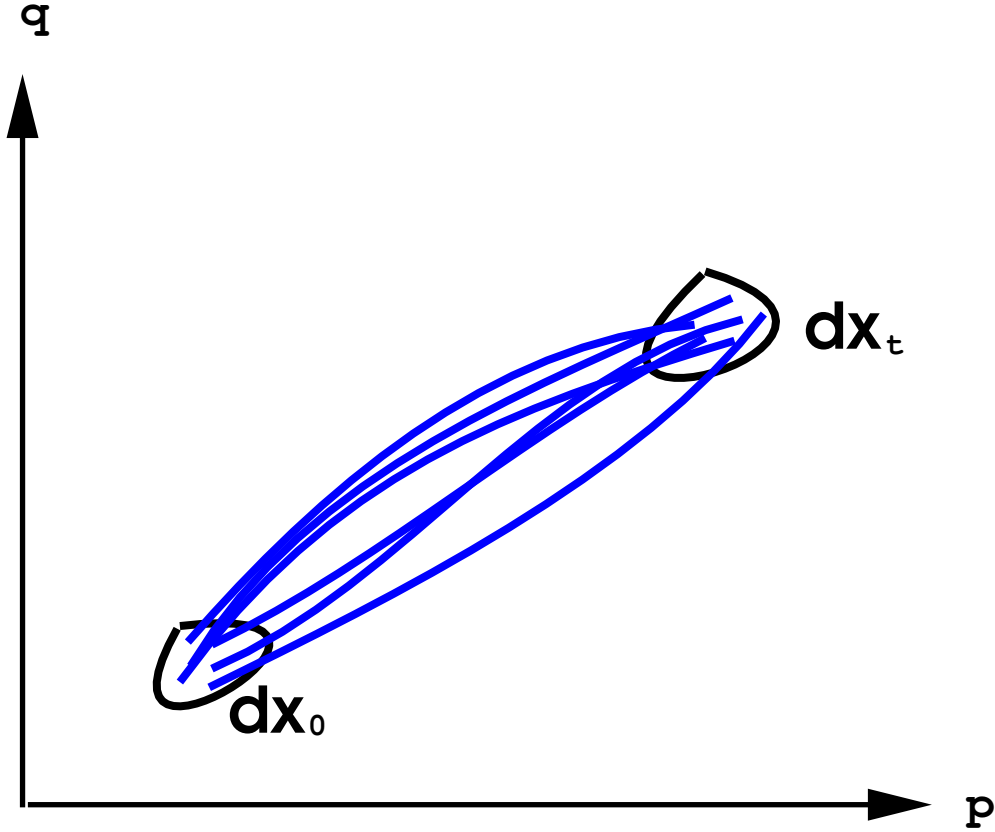
FIG. 1.

How is dx_0 related to dx_t? To answer this, consider a trajectory starting from a phase space vector x_0 in dx_0 and having a phase space vector x_t at time t in dx_t. Since the solution of Hamilton's equations depends on the choice of initial conditions, x_t depends on x_0:

$$x_0 = (\mathbf{p}_1(0), ..., \mathbf{p}_N(0), \mathbf{r}_1(0), ..., \mathbf{r}_N(0))$$
$$x_t = (\mathbf{p}_1(t), ..., \mathbf{p}_N(t), \mathbf{r}_1(t), ..., \mathbf{r}_N(t))$$
$$x_t^i = x_t^i(x_0^1, ..., x_0^{6N})$$

Thus, the phase space vector components can be viewed as a coordinate transformation on the phase space from $t = 0$ to time t. The phase space volume element then transforms according to

$$dx_t = J(x_t; x_0) dx_0$$

where $J(x_t; x_0)$ is the Jacobian of the transformation:

$$J(x_t; x_0) = \frac{\partial(x_t^1 \cdots x_t^n)}{\partial(x_0^1 \cdots x_0^n)}$$

where $n = 6N$. The precise form of the Jacobian can be determined as will be demonstrated below.

The Jacobian is the determinant of a matrix M,

$$J(x_t; x_0) = \det(M) = e^{\text{TrlnM}}$$

whose matrix elements are

$$M_{ij} = \frac{\partial x_t^i}{\partial x_0^j}$$

Taking the time derivative of the Jacobian, we therefore have

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$$\frac{dJ}{dt} = \mathrm{Tr}\left(\mathrm{M}^{-1}\frac{d\mathrm{M}}{dt}\right)e^{\mathrm{Tr\,ln\,M}}$$

$$= J\sum_{i=1}^{n}\sum_{j=1}^{n}\mathrm{M}_{ij}^{-1}\frac{d\mathrm{M}_{ji}}{dt}$$

The matrices M^{-1} and $d\mathrm{M}/dt$ can be seen to be given by

$$\mathrm{M}_{ij}^{-1} = \frac{\partial \mathrm{x}_0^i}{\partial \mathrm{x}_t^j}$$

$$\frac{d\mathrm{M}_{ji}}{dt} = \frac{\partial \dot{\mathrm{x}}_t^j}{\partial \mathrm{x}_0^i}$$

Substituting into the expression for dJ/dt gives

$$\frac{dJ}{dt} = J\sum_{i,j=1}^{n}\frac{\partial \mathrm{x}_0^i}{\partial \mathrm{x}_t^j}\frac{\partial \dot{\mathrm{x}}_t^j}{\partial \mathrm{x}_0^i}$$

$$= J\sum_{i,j,k=1}^{n}\frac{\partial \mathrm{x}_0^i}{\partial \mathrm{x}_t^j}\frac{\partial \dot{\mathrm{x}}_t^j}{\partial \mathrm{x}_t^k}\frac{\partial \mathrm{x}_t^k}{\partial \mathrm{x}_0^i}$$

where the chain rule has been introduced for the derivative $\partial \dot{\mathrm{x}}_t^j/\partial \mathrm{x}_0^i$. The sum over i can now be performed:

$$\sum_{i=1}^{n}\frac{\partial \mathrm{x}_0^i}{\partial \mathrm{x}_t^j}\frac{\partial \mathrm{x}_t^k}{\partial \mathrm{x}_0^i} = \sum_{i=1}^{n}\mathrm{M}_{ij}^{-1}\mathrm{M}_{ki} = \sum_{i=1}^{n}\mathrm{M}_{ki}\mathrm{M}_{ij}^{-1} = \delta_{kj}$$

Thus,

$$\frac{dJ}{dt} = J\sum_{j,k=1}^{n}\delta_{jk}\frac{\partial \dot{\mathrm{x}}_t^j}{\partial \mathrm{x}_t^k}$$

$$= J\sum_{j=1}^{n}\frac{\partial \dot{\mathrm{x}}_t^j}{\mathrm{x}_t^j} = J\nabla_{\mathrm{x}}\cdot\dot{\mathrm{x}}$$

or

$$\frac{dJ}{dt} = J\nabla_{\mathrm{x}}\cdot\dot{\mathrm{x}}$$

The initial condition on this differential equation is $J(0) \equiv J(\mathrm{x}_0;\mathrm{x}_0) = 1$. Moreover, for a Hamiltonian system $\nabla_{\mathrm{x}}\cdot\dot{\mathrm{x}} = 0$. This says that $dJ/dt = 0$ and $J(0) = 1$. Thus, $J(\mathrm{x}_t;\mathrm{x}_0) = 1$. If this is true, then the phase space volume element transforms according to

$$d\mathrm{x}_0 = d\mathrm{x}_t$$

which is another conservation law. This conservation law states that the phase space volume occupied by a collection of systems evolving according to Hamilton's equations of motion will be preserved in time. This is one statement of Liouville's theorem.

Combining this with the fact that $df/dt = 0$, we have a conservation law for the phase space probability:

$$f(\mathrm{x}_0,0)d\mathrm{x}_0 = f(\mathrm{x}_t,t)d\mathrm{x}_t$$

which is an equivalent statement of Liouville's theorem.

III. LIOUVILLE'S THEOREM FOR NON-HAMILTONIAN SYSTEMS

The equations of motion of a system can be cast in the generic form

$$\dot{x} = \xi(x)$$

where, for a Hamiltonian system, the vector function ξ would be

$$\xi(x) = \left(-\frac{\partial H}{\partial \mathbf{r}_1}, ..., -\frac{\partial H}{\partial \mathbf{r}_N}, \frac{\partial H}{\partial \mathbf{p}_1}, ..., \frac{\partial H}{\partial \mathbf{p}_N} \right)$$

and the incompressibility condition would be a condition on ξ:

$$\nabla_x \cdot \dot{x} = \nabla_x \cdot \xi = 0$$

A non-Hamiltonian system, described by a general vector funciton ξ, will not, in general, satisfy the incompressibility condition. That is:

$$\nabla_x \cdot \dot{x} = \nabla_x \cdot \xi \neq 0$$

Non-Hamiltonian dynamical systems are often used to describe open systems, i.e., systems in contact with heat reservoirs or mechanical pistons or particle reservoirs. They are also often used to describe driven systems or systems in contact with external fields.

The fact that the compressibility does not vanish has interesting consequences for the structure of the phase space. The Jacobian, which satisfies

$$\frac{dJ}{dt} = J\nabla_x \cdot \dot{x}$$

will no longer be 1 for all time. Defining $\kappa = \nabla_x \cdot \dot{x}$, the general solution for the Jacobian can be written as

$$J(x_t; x_0) = J(x_0; x_0) \exp\left(\int_0^t ds\kappa(x_s) \right)$$

Note that $J(x_0; x_0) = 1$ as before. Also, note that $\kappa = d\ln J/dt$. Thus, κ can be expressed as the total time derivative of some function, which we will denote W, i.e., $\kappa = \dot{W}$. Then, the Jacobian becomes

$$J(x_t; x_0) = \exp\left(\int_0^t ds\dot{W}(x_s) \right)$$

$$= \exp\left(W(x_t) - W(x_0) \right)$$

Thus, the volume element in phase space now transforms according to

$$dx_t = \exp\left(W(x_t) - W(x_0) \right) dx_0$$

which can be arranged to read as a conservation law:

$$e^{-W(x_t)} dx_t = e^{-W(x_0)} dx_0$$

Thus, we have a conservation law for a modified volume element, involving a "metric factor" $\exp(-W(x))$. Introducing the suggestive notation $\sqrt{g} = \exp(-W(x))$, the conservation law reads $\sqrt{g(x_t}dx_t = \sqrt{g(x_0}dx_0$. This is a generalized version of Liouville's theorem. Furthermore, a generalized Liouville equation for non-Hamiltonian systems can be derived which incorporates this metric factor. The derivation is beyond the scope of this course, however, the result is

$$\partial(f\sqrt{g}) + \nabla_x \cdot (\dot{x}f\sqrt{g}) = 0$$

We have called this equation, the *generalized Liouville equation* Finally, noting that $\sqrt{g}$ satisfies the same equation as J, i.e.,

$$\frac{d\sqrt{g}}{dt} = \kappa\sqrt{g}$$

the presence of $\sqrt{g}$ in the generalized Liouville equation can be eliminated, resulting in

$$\frac{\partial f}{\partial t} + \dot{\mathrm{x}} \cdot \nabla_{\mathrm{x}} f = \frac{df}{dt} = 0$$

which is the ordinary Liouville equation from before. Thus, we have derived a modified version of Liouville's theorem and have shown that it leads to a conservation law for f equivalent to the Hamiltonian case. This, then, supports the generality of the Liouville equation for both Hamiltonian and non-Hamiltonian based ensembles, an important fact considering that this equation is the foundation of statistical mechanics.

IV. EQUILIBRIUM ENSEMBLES

An equilibrium ensemble is one for which there is no explicit time-dependence in the phase space distribution function, $\partial f / \partial t = 0$. In this case, Liouville's equation reduces to

$$\{f, H\} = 0$$

which implies that $f(\mathrm{x})$ must be a pure function of the Hamiltonian

$$f(\mathrm{x}) = F(H(\mathrm{x}))$$

The specific form that $F(H(\mathrm{x}))$ has depends on the specific details of the ensemble.

The integral over the phase space distribution function plays a special role in statistical mechanics:

$$\mathcal{F} = \int d\mathrm{x} F(H(\mathrm{x})) \tag{1}$$

It is known as the partition function and is equal to the number of members in the ensemble. That is, it is equal to the number of microstates that all give rise to a given set of macroscopic observables. Thus, it is the quantity from which all thermodynamic properties are derived.

If a measurement of a macroscopic observable $A(\mathrm{x})$ is made, then the value obtained will be the ensemble average:

$$\langle A \rangle = \frac{1}{\mathcal{F}} \int d\mathrm{x} A(\mathrm{x}) F(H(\mathrm{x})) \tag{2}$$

Eqs. (1) and (2) are the central results of ensemble theory, since they determine all thermodynamic and other observable quantities.

A. Introduction to the Microcanonical Ensemble

The microcanonical ensemble is built upon the so called postulate of equal *a priori* probabilities:

Postulate of equal a priori probabilities: For an isolated macroscopic system in equilibrium, all microscopic states corresponding to the same set of macroscopic observables are equally probable.

1. Basic definitions and thermodynamics

Consider a thought experiment in which N particles are placed in a container of volume V and allowed to evolve according to Hamilton's equations of motion. The total energy $E = H(\mathrm{x})$ is conserved. Moreover, the number of particles N and volume V are considered to be fixed. This constitutes a set of three thermodynamic variables N, V, E that characterize the ensemble and can be varied to alter the conditions of the experiment.

The evolution of this system in time generates a trajectory that samples the constant energy hypersurface $H(\mathrm{x}) = E$. All points on this surface correspond to the same set of macroscopic observables. Thus, by the postulate of equal a priori probabilities, the corresponding ensemble, called the *microcanonical ensemble*, should have a distribution function $F(H(\mathrm{x}))$ that reflects the fact that all points on the constant energy hypersurface are equally probable. Such a distribution function need only reflect the fact that energy is conserved and can be written as

$$F(H(\mathrm{x})) = \delta(H(\mathrm{x}) - E)$$

where $\delta(x)$ is the Dirac delta function. The delta function has the property that

$$\int_{-\infty}^{\infty} \delta(x - a)f(x)dx = f(a)$$

for any function $f(x)$.

Averaging over the microcanonical distribution function is equivalent to computing the time average in our thought experiment. The microcanonical partition function $\Omega(N, V, E)$ is given by

$$\Omega(N, V, E) = C_N \int d\mathrm{x}\ \delta(H(\mathrm{x}) - E)$$

In Cartesian coordinates, this is equivalent to

$$\Omega(N, V, E) = C_N \int d^n\mathbf{p} \int_{D(V)} d^N\mathbf{r}\delta(H(\mathbf{p}, \mathbf{r}) - E)$$

where C_N is a constant of proportionality. It is given by

$$C_N = \frac{E_0}{N!h^{3N}}$$

Here h is a constant with units Energy·Time, and E_0 is a constant having units of energy. The extra factor of E_0 is needed because the δ function has units of inverse energy. Such a constant has no effect at all on any properties). Thus, $\Omega(N, V, E)$ is dimensionless. The origin of C_N is quantum mechanical in nature (h turns out to be Planck's constant) and must be put into the classical expression by hand. Later, we will explore the effects of this constant on thermodynamic properties of the ideal gas.

The microcanonical partition function function measures the number of microstates available to a system which evolves on the constant energy hypersurface. Boltzmann identified this quantity as the entropy, S of the system, which, for the microcanonical ensemble is a natural function of N, V and E:

$$S = S(N, V, E)$$

Thus, Boltzmann's relation between $\Omega(N, V, E)$, the number of microstates and $S(N, V, E)$ is

$$S(N, V, E) = k \ln \Omega(N, V, E)$$

where k is Boltzmann's constant $1/k = 315773.218$ Kelvin/Hartree. The importance of Boltzmann's relation is that it establishes a connection between the thermodynamic properties of a system and its microscopic details.

Recall the standard thermodynamic definition of entropy:

$$S = \int \frac{dQ}{T}$$

where an amount of heat dQ is assumed to be absorbed *reversibly*, i.e., along a thermodynamic path, by the system. The first law of thermodynamics states that the energy, E of the system is given by the sum of the heat absorbed by the system and the work done on the system in a thermodynamic process:

$$E = Q + W$$

If the thermodynamic transformation of the system is carried *reversibly*, i.e., along a thermodynamic path, then the first law will be valid for the *differential* change in energy, dE due to absorption of a differential amount of heat, dQ_{rev} and a differential amount of work, dW done on the system:

$$dE = dQ + dW$$

The work done on the system can be in the form of compression/expansion work at constant pressure, P, leading to a change, dV in the volume and/or the insertion/deletion of particles from the system at constant chemical potential, μ, leading to a change dN in the particle number. Thus, in general

$$dW = -PdV + \mu dN$$

(The above relation for the work is true only for a one-component system. If there are M types of particles present, then the second term must be generalized according to $\sum_{k=1}^{M} \mu_k dN_k$). Then, using the fact that $dQ = TdS$, we have

$$dE = TdS - PdV + \mu dN$$

or

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

But since $S = S(N, V, E)$ is a natural function of N, V, and E, the differential, dS is also given by

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

Comparing these two expressions, we see that

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}$$

$$-\left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{\mu}{T}$$

Finally, using Boltzmann's relation between the entropy S and the partition function Ω, we obtain a prescription for obtaining the thermodynamic properties of the system starting from a microscopic, particle-based description of the system:

$$\frac{1}{T} = k \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V}$$

$$\frac{P}{T} = k \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E}$$

$$\frac{\mu}{T} = -k \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E}$$

Of course, the ultimate test of Boltzmann's relation between entropy and the partition function is that the above relations correctly generate the known thermodynamic properties of a given system, e.g. the equation of state. We will soon see several examples in which this is, indeed, the case.