G25.2651: Statistical Mechanics

Notes for Lecture 1

Defining statistical mechanics: Statistical Mechanics provies the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

Why do we need Statistical Mechanics:

1. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory.

2. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions.

3. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

I. THE MICROSCOPIC LAWS OF MOTION

Consider a system of N classical particles. The particles a confined to a particular region of space by a "container" of volume V. The particles have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), ..., \mathbf{r}_N(t)$. The time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, ..., \mathbf{r}_N)$$

where $\mathbf{F}_1, ..., \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivaties, $\{\mathbf{r}_1(0), ..., \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), ..., \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

II. THE ENSEMBLE CONCEPT (HEURISTIC DEFINITION)

For a typical macroscopic system, the total number of particles $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we contented ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ Gbytes. The largest computers we have today have perhaps 10^3 Gbytes of memory, so we are off by 14 orders of magnitude just to specify 1 point in phase space.

Do we need all this detail? (Yes and No).

Yes – There are plenty of chemically interesting phenomena for which we really would like to know how individual atoms are moving as a process occurs. Experimental techniques such as ultrafast laser spectroscopy can resolve short time scale phenomena and, thus, obtain important insights into such motions. From a theoretical point of view, although we cannot follow 10^{23} particles, there is some hope that we could follow the motion of a system containing 10^4 or 10^5 particles, which might capture most of the features of true macroscopic matter. Thus, by solving Newton's equations of motion numerically on a computer, we have a kind of window into the microscopic world. This is the basis of what are known as *molecular dynamics calculations*.

No – Intuitively, we would expect that if we were to follow the evolution of a large number of systems all described by the same set of forces but having starting from different initial conditions, these systems would have essentially the same macroscopic characteristics, e.g. the same temperature, pressure, etc. even if the microscopic detailed evolution of each system in time would be very different. This idea suggests that the microscopic details are largely unimportant.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procecure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Ensemble: Consider a large number of systems each described by the same set of microscopic forces and sharing some common macroscopic property (e.g. the same total energy). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time. Thus, let A denote a macroscopic property and let a denote a microscopic function that is used to compute A. An example of A would be the temperature, and a would be the kinetic energy (a microscopic function of velocities). Then, A is obtained by calculating the value of a in each system of the ensemble and performing an average over all systems in the ensemble:

$$A = \frac{1}{\mathcal{N}} \sum_{\lambda=1}^{\mathcal{N}} a_\lambda$$

where $\mathcal{N}$ is the total number of members in the ensemble and a_λ is the value of a in the λth system.

The questions that naturally arise are:

1. How do we construct an ensemble?

2. How do we perform averages over an ensemble?

3. How many systems will an ensemble contain?

4. How do we distinguish time-independent from time-dependent properties in the ensemble picture?

Answering these questions will be our main objective in this course.

III. THE LAGRANGIAN FORMULATION OF CLASSICAL MECHANICS

In order to begin to make a connection between the microscopic and macroscopic worlds, we need to better understand the microscopic world and the laws that govern it. We will begin placing Newton's laws of motion in a formal framework which will be heavily used in our study of classical statistical mechanics.

First, we begin by restricting our discussion to systems for which the forces are purely *conservative*. Such forces are derivable from a potential energy function $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ by differentiation:

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

It is clear that such forces cannot contain dissipative or friction terms. An important property of systems whose forces are conservative is that they conserve the total energy

$$E = K + U = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2 + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

To see this, simply differentiate the energy with respect to time:

$$\frac{dE}{dt} = \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i + \sum_{i=1}^{N} \frac{\partial U}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i$$

$$= \sum_{i=1}^{N} \dot{\mathbf{r}}_i \cdot \mathbf{F}_i - \sum_{i=1}^{N} \mathbf{F}_i \cdot \dot{\mathbf{r}}_i$$

$$= 0$$

where, the second line, the facts that $\ddot{\mathbf{r}}_i = \mathbf{F}_i/m_i$ (Newton's law) and $\mathbf{F}_i = -\partial U/\partial \mathbf{r}_i$ (conservative force definition) have been used. This is known as the law of *conservation of energy*.

For conservative systems, there is an elegant formulation of classical mechanics known as the *Lagrangian* formulation. The *Lagrangian* function, L, for a system is defined to be the difference between the kinetic and potential energies expressed as a function of positions and velocities. In order to make the nomenclature more compact, we shall introduce a shorthand for the complete set of positions in an N-particle system: $\mathbf{r} \equiv \mathbf{r}_1, ..., \mathbf{r}_N$ and for the velocities: $\dot{\mathbf{r}} \equiv \dot{\mathbf{r}}_1, ..., \dot{\mathbf{r}}_N$. Then, the Lagrangian is defined as follows:

$$L(\mathbf{r}, \dot{\mathbf{r}}) = K - U = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 - U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

In terms of the Lagrangian, the classical equations of motion are given by the so called *Euler-Lagrange* equation:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial L}{\partial \mathbf{r}_i} = 0$$

The equations that result from application of the Euler-Lagrange equation to a particular Lagrangian are known as the *equations of motion*. The solution of the equations of motion for a given initial condition is known as a *trajectory* of the system. The Euler-Lagrange equation results from what is known as an *action principle*. We shall defer further discussion of the action principle until we study the Feynman path integral formulation of quantum statistical mechanics in terms of which the action principle emerges very naturally. For now, we accept the Euler-Lagrange equation as a definition.

The Euler-Lagrange formulation is completely equivalent to Newton's second law. In order to see this, note that

$$\frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i \dot{\mathbf{r}}_i$$

$$\frac{\partial L}{\partial \mathbf{r}_i} = -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i$$

Therefore,

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial L}{\partial \mathbf{r}_i} = m_i \ddot{\mathbf{r}}_i - \mathbf{F}_i = 0$$

which is just Newton's equation of motion.

An important property of the Lagrangian formulation is that it can be used to obtain the equations of motion of a system in *any set of coordinates*, not just the standard Cartesian coordinates, via the Euler-Lagrange equation (see problem set #1).

IV. THE HAMILTONIAN FORMULATION OF CLASSICAL MECHANICS

The Lagrangian formulation of mechanics will be useful later when we study the Feynman path integral. For our purposes now, the Lagrangian formulation is an important springboard from which to develop another useful formulation of classical mechanics known as the *Hamiltonian* formulation. The Hamiltonian of a system is defined to be the sum of the kinetic and potential energies expressed as a function of positions and their *conjugate momenta*. What are conjugate momenta?

Recall from elementary physics that momentum of a particle, $\mathbf{p}_i$, is defined in terms of its velocity $\dot{\mathbf{r}}_i$ by

$$\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$$

In fact, the more general definition of conjugate momentum, valid for any set of coordinates, is given in terms of the Lagrangian:

$$\mathbf{p}_i = \frac{\partial L}{\partial \dot{\mathbf{r}}_i}$$

Note that these two definitions are equivalent for Cartesian variables.

In terms of Cartesian momenta, the kinetic energy is given by

$$K = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}$$

Then, the Hamiltonian, which is defined to be the sum, $K + U$, expressed as a function of positions and momenta, will be given by

$$H(\mathbf{p}, \mathbf{r}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N) = H(\mathbf{p}, \mathbf{r})$$

where $\mathbf{p} \equiv \mathbf{p}_1, ..., \mathbf{p}_N$. In terms of the Hamiltonian, the equations of motion of a system are given by *Hamilton's equations*:

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} \qquad\qquad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i}$$

The solution of Hamilton's equations of motion will yield a trajectory in terms of positions and momenta as functions of time. Again, Hamilton's equations can be easily shown to be equivalent to Newton's equations, and, like the Lagrangian formulation, Hamilton's equations can be used to determine the equations of motion of a system in any set of coordinates.

The Hamiltonian and Lagrangian formulations possess an interesting connection. The Hamiltonian can be directly obtained from the Lagrangian by a transformation known as a *Legendre transform*. We will say more about Legendre transforms in a later lecture. For now, note that the connection is given by

$$H(\mathbf{p}, \mathbf{r}) = \sum_{i=1}^{N} \mathbf{p}_i \cdot \dot{\mathbf{r}}_i - L(\mathbf{r}, \dot{\mathbf{r}})$$

which, when the fact that $\dot{\mathbf{r}}_i = \mathbf{p}_i / m_i$ is used, becomes

$$H(\mathbf{p}, \mathbf{r}) = \sum_{i=1}^{N} \mathbf{p}_i \cdot \frac{\mathbf{p}_i}{m_i} - \sum_{i=1}^{N} \frac{1}{2} m_i \left(\frac{\mathbf{p}_i}{m_i} \right)^2 + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

Because a system described by conservative forces conserves the total energy, it follows that Hamilton's equations of motion conserve the total Hamiltonian. Hamilton's equations of motion conserve the Hamiltonian

$$H(\mathbf{p}(t), \mathbf{r}(t)) = H(\mathbf{p}(0), \mathbf{r}(0)) = E$$

Proof: $H = \text{const} \Rightarrow dH/dt = 0$

$$\frac{dH}{dt} = \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \frac{\partial H}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right)$$

$$= \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{r}_i} \cdot \frac{\partial H}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial H}{\partial \mathbf{r}_i} \right) = 0$$

QED. This, then, provides another expression of the law of conservation of energy.

V. PHASE SPACE

We construct a cartesian space in which each of the $6N$ coordinates and momenta is assigned to one of $6N$ mutually orthogonal axes. Phase space is, therefore, a $6N$ dimensional space. A point in this space is specified by giving a particular set of values for the $6N$ coordinates and momenta. Denote such a point by

$$\mathbf{x} = (\mathbf{p}_1, ..., \mathbf{p}_N, \mathbf{r}_1, ..., \mathbf{r}_N)$$

x is a $6N$ dimensional vector. Thus, the time evolution or trajectory of a system as specified by Hamilton's equations of motion, can be expressed by giving the phase space vector, x as a function of time.

The law of conservation of energy, expressed as a condition on the phase space vector:

$$H(\mathbf{x}(t)) = \text{const} = E$$

defines a $6N - 1$ dimensional hypersurface in phase space on which the trajectory must remain.

A. Classical microscopic states or microstates and ensembles

A *microscopic state* or *microstate* of a classical system is a specification of the complete set of positions and momenta of the system at any given time. In the language of phase space vectors, it is a specification of the complete phase space vector of a system at any instant in time. For a conservative system, any valid microstate must lie on the constant energy hypersurface, $H(\mathbf{x}) = E$. Hence, specifying a microstate of a classical system is equivalent to specifying a point on the constant energy hypersurface.

The concept of classical microstates now allows us to give a more formal definition of an ensemble.

An ensemble is a collection of systems sharing one or more macroscopic characteristics but each being in a unique microstate. The complete ensemble is specified by giving *all* systems or microstates consistent with the common macroscopic characteristics of the ensemble.

The idea of ensemble averaging can also be expressed in terms of an average over all such microstates (which comprise the ensemble). A given macroscopic property, A, and its microscopic function $a = a(\mathbf{x})$, which is a function of the positions and momenta of a system, i.e. the phase space vector, are related by

$$A = \langle a \rangle_{\text{ensemble}} = \frac{1}{\mathcal{N}} \sum_{\lambda=1}^{\mathcal{N}} a(\mathbf{x}_\lambda)$$

where $\mathbf{x}_\lambda$ is the microstate of the λth member of the ensemble.

However, recall the original problem of determining the microscopic detailed motion of each individual particle in a system. In reality, measurements are made only on a single system and all the microscopic detailed motion is present. However, what one observes is still an average, but it is an average over time of the detailed motion, an average that also washes out the microscopic details. Thus, the time average and the ensemble average should be equivalent, i.e.

$$A = \langle a \rangle_{\text{ensemble}} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt\; a(\mathrm{x}(t))$$

This statement is known as the *ergodic hypothesis*. A system that is ergodic is one for which, given an infinite amount of time, it will visit all possible microscopic states available to it (for Hamiltonian dynamics, this means it will visit all points on the constant energy hypersurface). No one has yet been able to prove that a particular system is truly ergodic, hence the above statement cannot be more than a supposition. However, it states that *if* a system is ergodic, then the ensemble average of a property $A(\mathrm{x})$ can be equated to a time average of the property over an ergodic trajectory.

VI. PHASE SPACE DISTRIBUTION FUNCTIONS AND LIOUVILLE'S THEOREM

Given an ensemble with many members, each member having a different phase space vector x corresponding to a different microstate, we need a way of describing how the phase space vectors of the members in the ensemble will be distributed in the phase space. That is, if we choose to observe one particular member in the ensemble, what is the probability that its phase space vector will be in a small volume $d\mathrm{x}$ around a point x in the phase space at time t. This probability will be denoted

$$f(\mathrm{x}, t) d\mathrm{x}$$

where $f(\mathrm{x}, t)$ is known as the *phase space probability density* or *phase space distribution function*. It's properties are as follows:

$$f(\mathrm{x}, t) \geq 0$$
$$\int d\mathrm{x} f(\mathrm{x}, t) = \text{Number of members in the ensemble}$$

Liouville's Theorem: The total number of systems in the ensemble is a constant. What restrictions does this place on $f(\mathrm{x}, t)$? For a given volume Ω in phase space, this condition requires that the rate of decrease of the number of systems from this region is equal to the flux of systems into the volume. Let $\hat{\mathbf{n}}$ be the unit normal vector to the surface of this region.

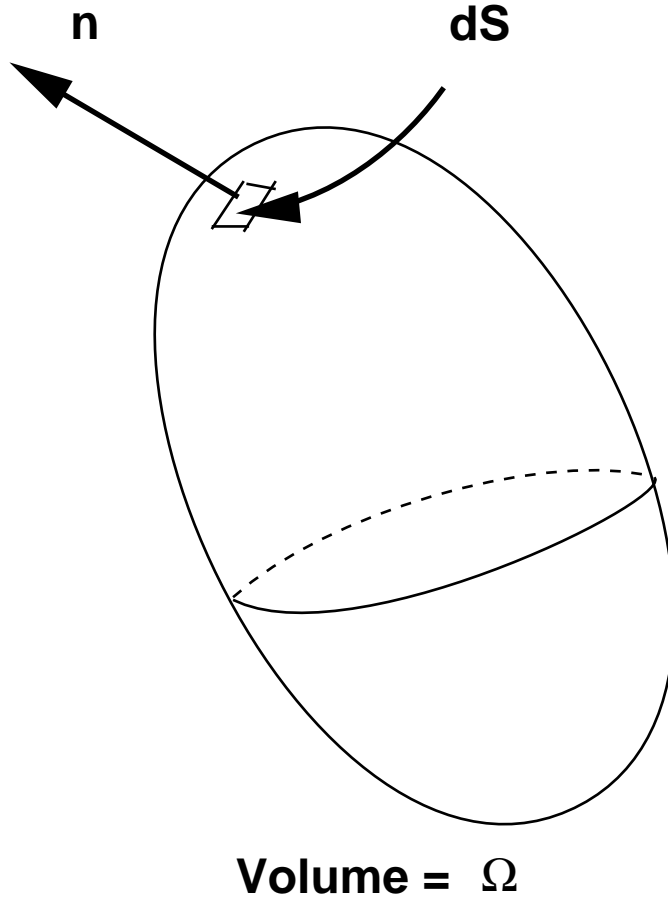**n**   **dS**

Volume = Ω

FIG. 1.

The flux through the small surface area element, dS is just $\hat{\mathbf{n}} \cdot \dot{\mathrm{x}} f(\mathrm{x}, t) dS$. Then the total flux out of volume is obtained by integrating this over the entire surface that encloses Ω:

$$\int dS \hat{\mathbf{n}} \cdot \dot{\mathrm{x}} f(\mathrm{x}, t)) = \int_{\Omega} \nabla_{\mathrm{x}} \cdot (\dot{\mathrm{x}} f(\mathrm{x}, t))$$

which follows from the divergence theorem. ∇_{x} is the $6N$ dimensional gradient on the phase space

$$\nabla_{\mathrm{x}} = \left(\frac{\partial}{\partial \mathbf{p}_1}, ..., \frac{\partial}{\partial \mathbf{p}_N}, \frac{\partial}{\partial \mathbf{r}_1}, ..., \frac{\partial}{\partial \mathbf{r}_N} \right)$$

$$= (\nabla_{\mathbf{p}_1}, ..., \nabla_{\mathbf{p}_N}, \nabla_{\mathbf{r}_1}, ..., \nabla_{\mathbf{r}_N})$$

On the other hand, the rate of decrease in the number of systems out of the volume is

$$-\frac{d}{dt} \int_{\Omega} d\mathrm{x} f(\mathrm{x}, t) = -\int_{\Omega} d\mathrm{x} \frac{\partial}{\partial t} f(\mathrm{x}, t)$$

Equating these two quantities gives

$$\int_{\Omega} d\mathrm{x} \nabla_{\mathrm{x}} \cdot (\dot{\mathrm{x}} f(\mathrm{x}, t)) = -\int_{\Omega} d\mathrm{x} \frac{\partial}{\partial t} f(\mathrm{x}, t)$$

But this result must hold for any arbitrary choice of the volume Ω, which we may also allow to shrink to 0 so that the result holds locally, and we obtain the local result:

$$\frac{\partial}{\partial t} f(\mathrm{x}, t) + \nabla_{\mathrm{x}} \cdot (\dot{\mathrm{x}} f(\mathrm{x}, t)) = 0$$

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But

$$\nabla_{\mathrm{x}} \cdot (\dot{\mathrm{x}} f(\mathrm{x}, t)) = \dot{\mathrm{x}} \cdot \nabla_{\mathrm{x}} f(\mathrm{x}, t) + f(\mathrm{x}, t) \nabla_{\mathrm{x}} \cdot \dot{\mathrm{x}}$$

This equation resembles an equation for a "hydrodynamic" flow in the phase space, with $f(\mathrm{x}, t)$ playing the role of a density. The quantity $\nabla_{\mathrm{x}} \cdot \dot{\mathrm{x}}$, being the divergence of a velocity field, is known as the phase space compressibility, and it does not, for a general dynamical system, vanish. Let us see what the phase space compressibility for a Hamiltonian system is:

$$\nabla_{\mathrm{x}} \cdot \dot{\mathrm{x}} = \sum_{i=1}^{N} [\nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i]$$

However, by Hamilton's equations:

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

Thus, the compressibility is given by

$$\nabla_{\mathrm{x}} \cdot \dot{\mathrm{x}} = \sum_{i=1}^{N} [-\nabla_{\mathbf{p}_i} \cdot \nabla_{\mathbf{r}_i} H + \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{p}_i} H] = 0$$

Thus, Hamiltonian systems are incompressible in the phase space, and the equation for $f(\mathrm{x}, t)$ becomes

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

which is Liouville's equation, and it implies that $f(\mathrm{x}, t)$ is a conserved quantity when x is identified as the phase space vector of a particular Hamiltonian system. That is, $f(\mathrm{x}_t, t)$ will be conserved along a particular trajectory of a Hamiltonian system. However, if we view x is a *fixed* spatial label in the phase space, then the Liouville equation specifies how a phase space distribution function $f(\mathrm{x}, t)$ evolves in time from an initial distribution $f(\mathrm{x}, 0)$.