Concise introduction to statistical mechanics

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1 Foundations of statistical mechanics

In classical mechanics, the time-evolution of a system is described by Hamiltonian dynamics. If we want to describe the behavior of systems with a large number of degrees of freedom, such as an N-particle gas, it is convenient to consider its phase space. The phase space is an imagined space, where each degree of freedom has its own axis. Thus, the phase space of a three-dimensional N-particle gas has 3N axes to specify the coordinates of each particle (x, y, z), and 3N axes to specify the momentum of each particle (p_x, p_y, p_z). A specific point in the 6N-dimensional phase space corresponds to one unique microstate. Under Hamiltonian dynamics, this point moves around in the phase space, as the state of the system changes.

There are not many systems where we have access to the exact microstate. If you are given a container of gas, it would be impossible for you to determine the exact position and momentum of every particle in it. Thus, in the macroscopic world, we deal with macroscopic variables. In general, a macrostate of a system is defined by the properties which we can reliably measure. For a simple ideal gas, this is its temperature T, volume V and pressure p. For magnetic systems, we would include the magnetization M, and for liquids, the surface tension γ. All microstates that correspond to a given macrostate, constitutes a volume in phase space. Within this volume, we can assign a probability distribution to the points in the phase space. The exact distribution we assign depends on what information we have about the system, but the goal is that this probability distribution gives us the probability for the system to be in the corresponding microstate.

If we consider again the N-dimensional gas, a specific point in phase space is specified by 6N independent variables; the N three-dimensional momentum vectors $p_N = (p_1, \dots, p_N)$, and the N three-dimensional coordinate vectors $q_N = (q_1, \dots, q_N)$. If the state-vector $x_N = (p_N; q_N)$ is known at one time, it is known for all times, due to deterministic Hamiltonian evolution. Given the Hamiltonian $H_N \equiv H(x_N, t)$, we can find the time evolution of the system using Hamilton's equations,

$$\frac{dp_i}{dt} = -\frac{dH_N}{dq_i} \qquad \text{and} \qquad \frac{dq_i}{dt} = \frac{dH_N}{dp_i}. \tag{1}$$

The state-vector x_N traces out a trajectory in phase space, as it evolves in time. Since Hamiltonian dynamics defines a unique past and future for a given state x_N, it follows that the trajectory can not cross itself. If it could, then Hamiltonian evolution would be indeterministic. If we lack complete knowledge of the system, we have to consider x_N to be a stochastic variable, and associate a probability density, $\rho(x_N, t)$ to the phase space. The probability that the state is found in a volume element dx_N around x_N at time t, is then given by $\rho(x_N, t)dx_N$. Since the state must always lie somewhere in the phase space, the probability density has to be properly normalized:

$$\int_\Gamma \rho(x_N, t)dx_N = 1, \tag{2}$$

where $\int_\Gamma$ indicates integration over the full phase space. The probability to find the system in a region R is then given by

$$P(x_N \in R) = \int_R \rho(x_N, t)dx_N. \tag{3}$$

We can view this probability density in phase space as an incompressible fluid, that flows according to Hamiltonian dynamics. Therefore we can use fluid mechanics to find its equation of motion; the Liouville equation.

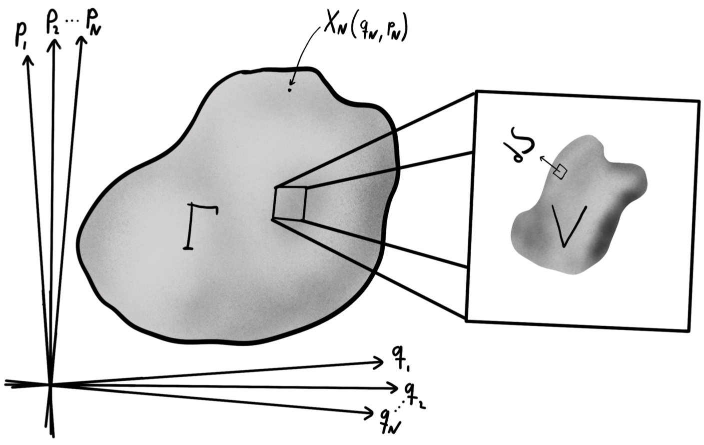

Figure 1: Representation of a 2Nd dimensional phase space, $\rho(x_N, t)$, where d is the spacial dimension of the system and N is the number of particles. The total phase space we consider is given by Γ, while a small volume element of that is V. The differential area-element normal to the surface of V is given by dS.

Consider a small volume element V with surface area S,at a fixed point in phase space, as shown in Fig. 1. The total probability is conserved, so any change in the probability to find the state in this volume,

$$\frac{d}{dt}P(x_N \in V) = \frac{\partial}{\partial t}\int_V \rho(x_N, t)dx_N, \tag{4}$$

is also given by the flow of probability through it,

$$\frac{d}{dt}P(x_N \in V) = -\oint_S \rho(x_N,t)\dot{x}_N \cdot dS. \tag{5}$$

Here $\dot{x}_N$ is the velocity of the state-vector, and dS is the area-element normal to the surface S. We can now use Gauss's theorem, which transforms the surface integral to a volume integral, to obtain

$$\frac{\partial}{\partial t}\int_V \rho(x_N,t)dx_N = -\int_V \boldsymbol{\nabla}_{x_N} \cdot [\rho(x_N,t)\ \dot{x}_N]\, dx_N, \tag{6}$$

where $\boldsymbol{\nabla}_{x_N} = (\partial_{q_1}, \ldots \partial_{q_N}, \partial_{p_1}, \ldots, \partial_{p_N})$ is the gradient with respect to all the phase space variables. Since the volume area V is independent of time, we can take the time-derivative inside the integral on the left side. The arguments of the integral therefore have to be the same, giving us

$$\frac{\partial}{\partial t}\rho(x_N,t) + \boldsymbol{\nabla}_{x_N} \cdot [\rho(x_N,t)\dot{x}_N] = 0. \tag{7}$$

We can calculate the divergence term to get

$$\boldsymbol{\nabla}_{x_N} \cdot [\rho(x_N,t)\dot{x}_N] = \dot{x}_N \cdot \boldsymbol{\nabla}_{x_N}\rho(x_N,t) + \rho(x_N,t)\boldsymbol{\nabla}_{x_N} \cdot \dot{x}_N,$$

and if we now use Hamilton's equations (Eq. 1), we see that

$$\boldsymbol{\nabla}_{x_N} \cdot \dot{x}_N = \sum_{i=1}^{N}\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) = \sum_{i=1}^{N}\left(\frac{\partial^2 H_N}{\partial q_i \partial p_i} - \frac{\partial^2 H_N}{\partial p_i \partial q_i}\right) = 0. \tag{8}$$

From Eq. (7) we therefore get

$$\frac{\partial}{\partial t}\rho(x_N,t) + \dot{x}_N \cdot \boldsymbol{\nabla}_{x_N}\rho(x_N,t) = 0 \tag{9}$$

Since the total time derivative is defined as

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{x}_N\boldsymbol{\nabla}_{x_N}, \tag{10}$$

we see that if we pick a specific point in phase space x_N, and follow its trajectory as the phase space evolves it time, the probability density in the neighborhood of that point remains constant:

$$\frac{d}{dt}\rho(x_N,t) = 0. \tag{11}$$

We can further rewrite Eq. (9) into a more familiar form by using Hamilton's equation.

$$\begin{aligned}\frac{\partial}{\partial t}\rho(x_N,t) &= -\dot{x}_N \cdot \boldsymbol{\nabla}_{x_N}\rho(x_N,t)\\ &= -\sum_{i=1}^{N}\left(\frac{\partial \dot{q}_i}{\partial t}\frac{\partial}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial t}\frac{\partial}{\partial p_i}\right)\rho(x_N,t)\\ &= -\sum_{i=1}^{N}\left(\frac{\partial H_N}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H_N}{\partial q_i}\frac{\partial}{\partial p_i}\right)\rho(x_N,t). \end{aligned} \tag{12}$$

This equation is known as Liouville's equation, and it is often written using the Poisson bracket notation:

$$\frac{\partial}{\partial t}\rho(x_N, t) = -\left\{\rho(x_N, t), H_N\right\}. \tag{13}$$

It is the equation of motion for the probability density in phase space, and from it we can solve any dynamical Hamiltonian system, given that we know the initial probability density $\rho(x_N, 0)$. A probability density that does not depend on time, $\partial_t \rho(x_N, t) = 0$, is associated with a system at equilibrium. The condition that makes both Liouville's equation and the stationary probability density compatible is clearly

$$\{\rho(x_N, t), H_N\} = 0. \tag{14}$$

Once choice of $\rho(x_N, t)$ that satisfies this equation is one that does not depend on x_N. In other words

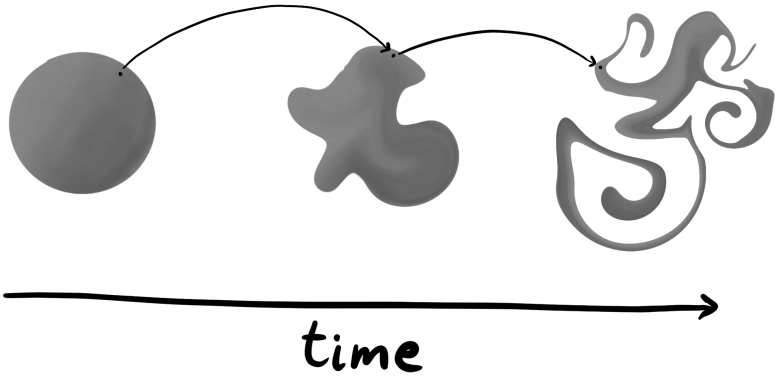

Figure 2: Illustration of the Hamiltonian flow of a phase space density according to Liouville's theorem.

$$\rho(x_N, t) = \text{const.} \tag{15}$$

In general, the Hamiltonian flow of the phase space density makes an initially smooth phase space density quickly evolve into an extremely complicated structure, with tendrils going in all directions in phase space. An illustration of this is shown in Fig. 2, where an initially spherical phase space density evolves into a complicated structure. However, no matter how complicated the structure becomes, its total volume remains the same.

2 Ensemble theory

Ensemble theory is the foundation that all of statistical mechanics is built upon. The probability density $\rho(x_N, t)$ can be interpreted as an ensemble of microstates belonging to the same macrostate. If we imagine we have M identical copies of a three-dimensional ideal gas (6N dimensional phase space), each member of the ensemble is a vector pointing to a point in the phase space. The density of these representative points in phase space is then given by $M\rho(x_N, t)$.

The ensemble average of a function $f(x_N)$ is defined as

$$\langle f \rangle_\Gamma = \frac{\int_\Gamma f(x_N)\ \rho(x_N, t)\ dx_N}{\int_\Gamma \rho(x_N, t)\ dx_N}, \tag{16}$$

where the integration extends over the full phase space Γ. In general f can be an explicit function of time $f = f(x_N, t)$, which makes the ensemble average time-dependent as well. The ensemble is stationary if

$$\frac{\partial}{\partial t}\rho(x_N, t) = 0, \tag{17}$$

and for such an ensemble the average value of any function f will be time independent. Stationary ensembles correspond to equilibrium distributions, and the condition that ensures that a system is both in equilibrium and obeys Hamiltonian dynamics can be found by combining Eq. (17) and Eq. (13) to obtain

$$\{\rho(x_N, t), H_N\} = 0. \tag{18}$$

A final thing we need in order to define the different ensembles, is the concept of ergodicity. We can define the time average of a function $f(x_N)$ as

$$\langle f \rangle_T = \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} f(x_N)\ dt. \tag{19}$$

The ergodic hypothesis states that for a given equilibrium macro state, the time spent by the system in some region of phase space is proportional to the volume of the region. This implies that all corresponding micro states are equally probable of a long period of time, which makes the ensemble average equal to the time average

$$\langle f \rangle_\Gamma = \langle f \rangle_T\,. \tag{20}$$

The exact time scale where the ergodic hypothesis becomes valid depends on the macroscopic system in question. For some system the time it takes to explore the full phase space can be so large that the equilibrium state exhibit ergodicity breaking. We also see that the probability to find a macro state in some specific region of phase space, is proportional to the area of the region.

2.1 The microcanonical ensemble

The simplest ergodic stationary state, is given by a Hamiltonian of constant energy $H(x_N) = E$. This equation defines a hypersurface in the phase space. For a gas with 6N dimensional phase space, the energy hypersurface spans 6N-1 dimension. From theorem Eq. (14), we see that the probability density compatible with this Hamiltonian is one that is constant everywhere on the hypersurface. And from the ergodic theorem, we know that the probability to find the system in a region R in phase space, is proportional to the area of that region, which we can normalize using the total area of the hypersurface

$$P(x_N \in R) = \frac{\int_R\ \delta\left(H(x_N) - E\right) dx_N}{\int_\Gamma\ \delta\left(H(x_N) - E\right) dx_N} = \frac{\Omega(R)}{\Omega(E)}. \tag{21}$$

Here $\Omega(R)$ is the area of the region R, while $\Omega(E)$ is the area of the full energy hypersurface. We can then write down the normalized probability distribution of the energy surface as

$$\rho(x_N, E) = \begin{cases} \frac{1}{\Omega(E)}, & \text{for } H(x_N) = E \\ 0, & \text{otherwise.} \end{cases} \tag{22}$$

This probability distribution constitutes the microcanonical ensemble, and represents a closed system with constant energy, where we equal a priori probabilities for the possible micro states.

2.2 The canonical ensemble

Most thermodynamic systems do not have an exactly fixed energy. Even a closed system at equilibrium will exchange heat with its environment, in such a way that the energy of the system fluctuates around a mean value. To find the equilibrium distribution of such and ensemble we maximize the Gibbs entropy,

$$S = -k_B \int dx_N \ \rho(x_N) \ \log \rho(x_N). \tag{23}$$

This is identical to the Shannon entropy (derived in chapter **??**), with $K = k_B$. Since the maximization is constrained by the normalized probability and the average energy,

$$\int_\Gamma dx_N \rho(x_N) = 1, \qquad \int_\Gamma dx_N \rho(x_N) H_N = \langle E \rangle , \tag{24}$$

we use the method of Lagrange multipliers to obtain

$$\lambda_1 - k_B + \lambda_2 H_N - k_B \log \rho(x_N) = 0, \tag{25}$$

where $\lambda_{1/2}$ are the Lagrange multipliers. This gives us

$$\rho(x_N) = \exp\left(\frac{\lambda_1}{k_B} - 1 + \frac{\lambda_2}{k_B} H_N\right). \tag{26}$$

To determine the Lagrange multipliers we first use the normalized probability condition and obtain

$$\int_\Gamma \exp\left(\frac{\lambda_2}{k_B} H_N\right) = \exp\left(1 - \frac{\lambda_1}{k_B}\right). \tag{27}$$

Next, we take Eq. (25), multiply it by $\rho(x_N)$ and integrate over Γ. This leaves us with

$$-k_B \int_\Gamma dx_N e^{\left(\frac{\lambda_2}{k_B} H_N\right)} + \lambda_2 \langle E \rangle + S = 0. \tag{28}$$

Comparing this equation to the definition of the Helmholtz free energy $F - U + TS = 0$, we see that $\lambda_2 = -1/T = -\beta$. Putting it all back into Eq. (26) we finally obtain the probability density for the canonical ensemble;

$$\rho(x_N) = \frac{e^{-\beta H_N}}{\int_\Gamma dx_N \ e^{-\beta H_N}} = \frac{e^{-\beta H_N}}{Z_\Gamma}. \tag{29}$$

The function Z_Γ is the canonical partition function, and can be considered a normalization constant for the probability density $\rho(x_N)$.

2.3 The grand canonical ensemble

The grand canonical ensemble is derived in an almost identical way as above, only now we maximize the entropy with an additional constraint, on the average number of particles $\int N\rho(x_N)\, dx_N = \langle N \rangle$. The probability density in the grand canonical ensemble becomes

$$\rho(x_N) = \frac{e^{-\beta(H_N-\mu N)}}{\int_\Gamma dx_N \; e^{-\beta(H_N-\mu N)}}, \tag{30}$$

where μ is the chemical potential.