

Thermodynamics

According to the laws of thermodynamics,

$$d E = d Q - d W$$

$$d E = T d S - P d V + \mu d N$$

Where E is the total internal energy, Q heat supplied to the system by the surroundings, and W is the work done by the system on the surroundings.

From these relations, we can calculate

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

In the thermodynamic limit, the extensive quantities like S , V , and N increase with the system size. The further assumption is E is a homogenous function of the extensive variables S , V , and N of degree 1.

Euler's function

Let's consider that $f(x,y,z, \dots)$ is a homogenous function. This implies,

$$x \left(\frac{\partial f}{\partial x} \right)_{y,z} + y \left(\frac{\partial f}{\partial y} \right)_{x,z} + z \left(\frac{\partial f}{\partial z} \right)_{x,y} = r f. \text{ Where } r \text{ is the degree of the function } f.$$

$$\text{In the energy representation, } E(S, V, N) = S \left(\frac{\partial E}{\partial S} \right)_{V,N} + V \left(\frac{\partial E}{\partial V} \right)_{S,N} + N \left(\frac{\partial E}{\partial N} \right)_{S,V}$$

We can also represent the same in the entropy representation, $S = (E, V, N)$. Using the relations for T , P and μ , the above relation modifies as

$$E = T S - P V + \mu N$$

This is called the Euler's relation in Thermodynamics. Using this relation, we can immediately get that

$$E - T S + P V = \mu N \text{ or } \mu = \frac{G}{N}$$

Where $G = E - T S + P V$ is the Gibbs free energy. Thus, chemical potential can be expressed as Gibbs free energy per particle.

Using the Euler's relation,

$$E = T S - P V + \mu N$$

$$d E = T d S - P d V + \mu d N + S d T - V d P + N d \mu$$

This implies,

$$S d T - V d P + N d \mu = 0$$

$$N d \mu = V d P - S d T$$

$$d\mu = \frac{V}{N} dP - \frac{S}{N} dT$$

$$d\mu = v dP - s dT$$

It is called the Gibbs-Duhem relation. Where v and s are specific volume and specific entropy, respectively.

Legendre transformation on $E(S, V, N)$ can give various relations, like for example,

$$\text{Enthalpy: } H(S, P, N) = E + P V$$

$$\text{Helmholtz free energy: } F(T, V, N) = E - T S$$

$$\text{Gibbs free energy: } G(T, P, N) = E - T S + P V$$

Field and state variables:

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

Field variables (intrinsic or independent): T, P, μ

State variables (extensive or dependent): S, V, N

For example, stress is an independent variable and the strain is a dependent variable.

Phase space

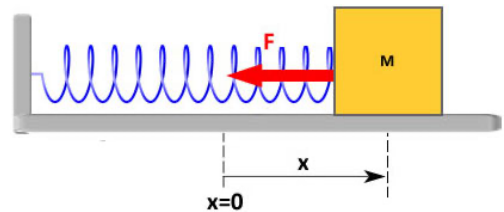
Consider a spring-mass, where k is the spring constant and m is the mass of the block. In the absence of air friction, one can write down the equation of motion by balancing the forces experienced by the block and its inertia.

Inertia of the block = forces acting on the block

$$m \ddot{x} + k x = 0$$

$$\ddot{x} + \frac{k}{m} x = 0$$

$$\ddot{x} + \omega_0^2 x = 0$$



The corresponding solution of the harmonic oscillator is $x(t) = A \cos(\omega_0 t + \phi)$

Where A and ϕ can be obtained by choosing proper initial conditions. $x(t)$ is a periodic function.

Since we neglected the friction in the force balance equation, there is no dissipation.

The energy of the simple harmonic oscillator is

$E = K.E + P.E$, where

$$K.E = \frac{1}{2} m v^2 = \frac{1}{2} m \omega_0^2 A^2 \sin^2(\omega_0 t + \phi) = \frac{1}{2} k A^2 \sin^2(\omega_0 t + \phi)$$

$$P.E = \frac{1}{2} k x^2 = \frac{1}{2} m \omega_0^2 A^2 \cos^2(\omega_0 t + \phi) = \frac{1}{2} k A^2 \cos^2(\omega_0 t + \phi)$$

$$E = K.E + P.E = \frac{1}{2} k A^2 = \frac{1}{2} m \omega_0^2 A^2$$

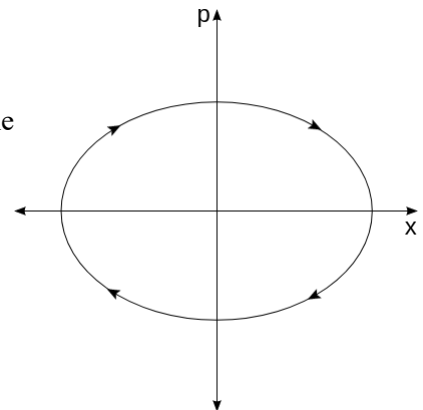
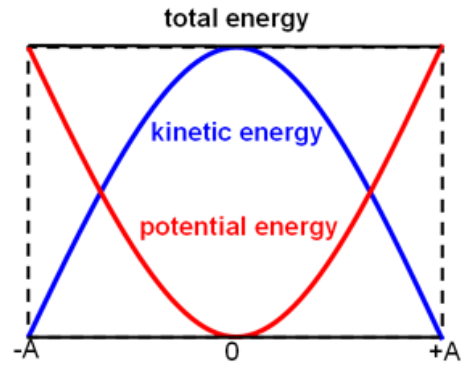
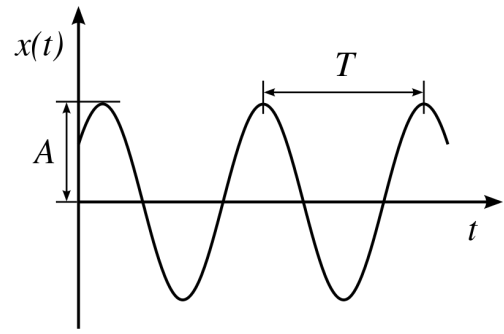
$$E = \frac{1}{2} k A^2 = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

$$\frac{p^2}{mkA^2} + \frac{x^2}{A^2} = 1$$

In one-dimension (1D), a particle has one position coordinate (x) and one momentum (p) coordinate.

Phase space spanned by the position and momentum coordinates.

- In one-dimension (1D), if the total energy is constant, then the dimension of the curve of constant energy is $2 - 1 = 1$
- In two-dimensions (2D), a particle have two position coordinates (x, y) and two momentum (p_x, p_y) coordinates. The phase space dimension is $2 + 2 = 4$. The dimension of the surface of constant energy is $4 - 1 = 3$
- Similarly, in 3D, a particle have three position coordinates (x, y, z) and three momentum (p_x, p_y, p_z) coordinates. The phase space dimension is $3 + 3 = 6$. The dimension of the surface of constant energy is $6 - 1 = 5$
- If there are N number of particles, then the phase space dimension will be $6N$.
- In addition, if there is restriction like for example, the total energy is constant, then the dimension of the surface of constant energy will be $6N - 1$.



Ergodic hypothesis

Consider a system of N particles, each with three degrees of freedom x, y, z . The system is described in Hamiltonian classical mechanics, by $6N$ canonical variables.

$$q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N}$$

Hamiltonian equations $\dot{p}_i = -\frac{\partial H}{\partial q_i}$; $\dot{q}_i = \frac{\partial H}{\partial p_i}$ where $i = 1, 2, \dots, 3N$

The phase space dimension of this system is $6N$. In general, the total energy will be conserved as the system moves. The condition $H[q_i, p_i] = E$ defines a $6N - 1$ dimensional surface in the phase space on which the system's trajectory is confined.

If one wanted to compute the measured value of some quantity, averaged over an interval of time τ . It is defined as

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} f[q_i(t), p_i(t)] dt$$

In general, for large N , we expect the trajectory to be some horrible complicated curve on the constant energy surface, that we have no way of computing directly.

To compute $\langle f \rangle$ we therefore need to make an assumption. The ergodic hypothesis says: during any time interval τ , sufficiently long, the location of the system in the phase space $\{q_i(t), p_i(t)\}$ is **equally likely** to be anywhere on the surface of constant energy E . Therefore,

$$\langle f \rangle = \int dq_i dp_i f(q_i, p_i) \rho(q_i, p_i)$$

$$\text{Where } \rho(q_i, p_i) = C \delta(H[q_i, p_i] - E)$$

C is the normalizing factor such that $\int dq_i dp_i \rho(q_i, p_i) = 1$

Here ρ is called the probability density or the density matrix.

With the above form, ρ is called the micro-canonical ensemble.

The ergodic hypothesis cannot be in general proven. But the existence of Thermodynamics, as an empirically constant theory, suggests it may be true.

Liouville's theorem

Liouville's theorem applies only to Hamiltonian systems. The Hamiltonian is allowed to vary with time, and there are no restrictions regarding how strongly the degrees of freedom are coupled. Liouville's theorem states that: *The density of states in an ensemble of many identical states with different initial conditions is constant along every trajectory in phase space.*

It states that if one constructs an ensemble of paths, the probability density along the trajectory remains constant.

Probability density must obey a local conservation equation.

$$0 = \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} \text{ where } \nabla \cdot \mathbf{J} = \sum_{n=1}^N \left(\frac{\partial(\rho \dot{q}_n)}{\partial q_n} + \frac{\partial(\rho \dot{p}_n)}{\partial p_n} \right)$$

Where \mathbf{J} is the flux or the probability current, that tells how the points (density) flow in the phase space.

$$\nabla \cdot \mathbf{J} = \sum_{n=1}^N \left(\dot{q}_n \frac{\partial \rho}{\partial q_n} + \dot{p}_n \frac{\partial \rho}{\partial p_n} \right) + \rho \sum_{n=1}^N \left(\frac{\partial \dot{q}_n}{\partial q_n} + \frac{\partial \dot{p}_n}{\partial p_n} \right)$$

The second term on the RHS vanishes because our variables obey Hamilton's equations of motion:

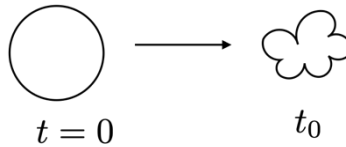
$$\sum_{n=1}^N \left(\frac{\partial \dot{q}_n}{\partial q_n} + \frac{\partial \dot{p}_n}{\partial p_n} \right) = \sum_{n=1}^N \left(\frac{\partial^2 H}{\partial q_n \partial p_n} - \frac{\partial^2 H}{\partial p_n \partial q_n} \right) = 0,$$

Finally, we get

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial x_i} \frac{dx_i}{dt} = 0$$

$\frac{d\rho}{dt}$ is called the convective derivative. It is how ρ changes in time if one moves along with “particles”.

$\frac{d\rho}{dt} = 0$ implies, density in phase space is constant in time as it flows like an incompressible fluid.



Equilibrium requires a stronger condition, namely $\frac{\partial \rho}{\partial t} = 0$, so that ensemble averages will not vary in time.

$\frac{\partial \rho}{\partial t} = 0$ implies, $[\rho, H] = 0$. This means, $\rho(q_i, p_i)$ depends on q_i, p_i only via the function $H[q_i, p_i]$, i.e., $\rho = \rho(H[q_i, p_i])$, and it must be constant on constant energy surfaces, if ρ is to describe the equilibrium.

For example, $\rho(q_i, p_i) \sim \delta(H[q_i, p_i] - E)$, which represents the microcanonical ensemble.

Another example, $\rho(q_i, p_i) \sim e^{-H[q_i, p_i]/k_B T}$, which represents the canonical ensemble.