

Kinetic theory

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1 Kinetic theory of ideal gas

We describe here the problem of motion of molecules in a gas, ignoring its rotational and vibration degrees of freedom, with energy:

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \quad (1)$$

we consider some assumption: 1) the molecules do not interact with each other most of the time (only through collision) and 2) the collision is not frequent. Through the collision, molecules exchange energy with each other, but every thing remain in equilibrium. We also assume the motion before and after the collision is independent, thus their kinetic energies are independent variables. With the above assumption, we can consider each molecules as an independent system connected to the heat reservoir at temperature T , where heat reservoir is "all other molecules in the gas"¹ and energy is exchanged with collisions².

Velocity distribution

The velocity distribution $g(\mathbf{v})$ is defined to the fraction of molecules with velocity \mathbf{v} (\mathbf{v} is the vector velocity while v is the absolute value).

$$g(\mathbf{v}) \propto e^{-mv^2/2k_B T} dv_x dv_y dv_z \quad (2)$$

$$\propto e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T} dv_x dv_y dv_z \quad (3)$$

$$= g(v_x)g(v_y)g(v_z) \quad (4)$$

we find the normalization factor for $g(v_x)$:

$$\int_{-\infty}^{\infty} e^{-mv_x^2/2k_B T} dv_x = \sqrt{\frac{2\pi k_B T}{m}} \quad (5)$$

$$g(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T} \quad (6)$$

with $g(v_i)$ normalized to 1, $g(v)$ from Eq.4 is then also normalized to 1. we can calculate the following values:

$$\begin{aligned} \langle v_x \rangle &= \int_{-\infty}^{\infty} v_x g(v_x) dv_x = 0 \\ \langle v_x^2 \rangle &= \int_{-\infty}^{\infty} v_x^2 g(v_x) dv_x = \frac{k_B T}{m} \end{aligned}$$

To find the distribution with respect to speed v instead of velocity \mathbf{v} , we consider the volume in velocity phase space corresponding to velocity v :

$$dV = 4\pi v^2 dv \quad (7)$$

which correspond to a thin spherical shell at radius v . The speed distribution function is then:

$$f(v)dv \propto v^2 dv e^{-mv^2/2k_B T} \quad (8)$$

¹Blundell, p48

²This point is not stated very clear in the book, but collision is the only way a gas molecule can interact with other molecules. The motion of the molecule after the collision is independent of their motion before the collision, therefore, the motion after the collision is entirely determined by the heat bath.

normalize $\int_0^\infty f(v)dv = 1$, we find the distribution function:

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (9)$$

which is known as the **Maxwell-Boltzmann distribution**. We can find the following expectation values:

$$\begin{aligned} \langle v \rangle &= \int_0^\infty v f(v) dv = \sqrt{\frac{8k_B T}{\pi m}} \\ \langle v^2 \rangle &= \int_0^\infty v^2 g(v) dv_x = \frac{3k_B T}{m} \\ v_{rms} &= \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \end{aligned} \quad (10)$$

where v_{rms} is the "root mean square" value. The mean kinetic energy of a gas molecule is then:

$$\langle E_k \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \quad (11)$$

Pressure

Since all molecules are equally likely to travel in any direction, the fraction of these whose velocity lie in solid angle $d\Omega$ is therefore $d\Omega/4\pi$. We consider the molecules traveling at angle between θ and $\theta + d\theta$ with some specific direction (z), the solid angle is given by:

$$d\Omega = 2\pi \sin \theta d\theta \quad (12)$$

So the fraction of molecules having speed between v and $v+dv$ and angel between θ and $\theta + d\theta$ with direction z is then:

$$f(v)dv \frac{2\pi \sin \theta d\theta}{4\pi} = \frac{1}{2} f(v)dv \sin \theta d\theta \quad (13)$$

In a time interval dt , a molecules with speed v travelling at an angle θ to the normal of the wall will hit the container wall if it is $vdt \cos \theta$ away from the wall. the number of such molecules (speed v at an angle θ) hitting the wall of area A is thus

$$A v dt \cos \theta n \cdot \frac{1}{2} f(v)dv \sin \theta d\theta \quad (14)$$

where the first part gives the total number of molecules in the volume $A v dt \cos \theta$ and the second part is the fraction of the molecule in the velocity and angle range.

Pressure of a gas on its container can be calculated by $dP = Fdt$ where dP is the momentum change of the particle reflecting from the wall: $dP = 2mv \cos \theta$ (perpendicular to wall). Pressure is defined to be $p = F/A$, so that We integrate over all possible velocity and angle θ to obtain the expression of p :

$$p = \int_0^\infty dv \int_0^{\pi/2} d\theta (2mv \cos \theta) \left(v \cos \theta n \frac{1}{2} f(v) \sin \theta \right) \quad (15)$$

$$= \frac{1}{3} n m \langle v^2 \rangle \quad (16)$$

using the relationship $n = N/V$ and $\langle v^2 \rangle = 3k_B T/m$, we can obtain the ideal gas law:

$$pV = Nk_B T \quad (17)$$

Partial pressure

If we have a mixture of gases in equilibrium, the total pressure will be the sum of pressures of each component:

$$n = \sum_i n_i \quad (18)$$

$$p = \left(\sum_i n_i \right) k_B T = \sum_i p_i \quad (19)$$

where $n_i = N_i/V$

Effusion

Effusion is the process in which gas escape from a small hole³. we define the flux Φ as the number of molecules going through unit area per unit time, therefore, Φ has the unit of $m^{-2}s^{-1}$. we use the above result of particles hitting the wall to find flux:

$$\Phi = \int_0^\infty dv \int_0^{\pi/2} d\theta \left(v \cos \theta n \frac{1}{2} f(v) \sin \theta \right) \quad (20)$$

$$= \frac{1}{4} n \langle v \rangle \quad (21)$$

with the result:

$$\begin{aligned} n &= p/k_B T \\ \langle v \rangle &= \sqrt{\frac{8k_B T}{\pi m}} \\ \Phi &= \frac{p}{\sqrt{2\pi m k_B T}} \end{aligned} \quad (22)$$

Now, consider a we have a small hole (small enough that the gas escaping does not change the equilibrium distribution of gas near the hole), the number of molecules escaping through the hole is given as:

$$\Phi A = \frac{pA}{\sqrt{2\pi m k_B T}} \quad (23)$$

which is linear to pressure, inversely proportion to T and m .

It should be noted that the speed distribution of the gas through the hole is no longer the Maxwell-Boltzmann distribution, since the amount of gas that effuse through the hole depend on velocity v (in Eq.20), therefore the speed distribution of those that go through the hole as an extra factor v , compare to the speed distribution of gas molecules inside the box.

Average lifetime

We first considering a molecule moving at speed v with other molecules in the gas stationary. Within a time dt , the molecule sweep through an area $\sigma v dt$, where σ is the collision cross-section of the molecule. We denote $P(t)$ as the probability of this molecule travel without any collision up to time t . We have:

$$P(t + dt) = P(t) + \frac{dP}{dt} dt \quad (24)$$

$$P(t + dt) = P(t)(1 - n\sigma v dt) \quad (25)$$

with n the number density of gas and therefore $(1 - n\sigma v dt)$ gives the probability of having no other gas molecule in the volume the moving molecule is going to sweep over from time t to $t + dt$. Withe the above two equation, we obtain the result:

$$P(t) = e^{-n\sigma v t} \quad (26)$$

We have the boundary condition $P(0) = 1$ and $P(\infty) = 0$

The probability that the molecule collide in time interval from t to $t + dt$ is given by the probability that molecule does not collide at time t but do collide at time $t + dt$: $P(t) - P(t + dt)$ (since $P(t)$ decay with time, $dP(t) < 0$), we have:

$$-dP(t) = n\sigma v e^{-n\sigma v t} dt \quad (27)$$

We can calculate the mean scattering time:

$$\begin{aligned} \tau &= \int_0^\infty t n\sigma v e^{-n\sigma v t} dt \\ &= \frac{1}{n\sigma v} \int_0^\infty x e^{-x} dx \\ &= \frac{1}{n\sigma v} \end{aligned} \quad (28)$$

³Blundell, p64

where $x = n\sigma vt$ represent a change of variable.

In the case of hard sphere approximation in a gas consist of molecules with equal radius, the collision cross-section is given as:

$$\sigma = \pi(r_1 + r_2)^2 = 4\pi a^2 \quad (29)$$

Mean free path of gas

With the previous result, we have, for the mean free path

$$\lambda = \langle v \rangle \tau = \langle v \rangle \frac{1}{n\sigma \langle v_r \rangle} \quad (30)$$

$\langle v \rangle$ is the average speed of gas molecules, where for the lifetime, instead of using v , we recognize that we should use relative speed v_r in a real system when all particles are in motion. It is not attempted to derive the value of $\langle v_r \rangle$ here (refer to Blundell, p73). But the final result is:

$$\lambda = \frac{1}{\sqrt{2}n\sigma} \quad (31)$$

2 Transport properties in Ideal gas

Viscosity

Viscosity η measures the resistance of a liquid (gas) to deform by shear stress. Suppose we sandwich fluid between two infinitely large plates. We fix the bottom plate and apply some force F to the top plate. The fluid between the bottom plate and the top plate will accelerate the fluid near it, then the momentum is passed down inside the liquid through internal interaction (collision).

Now, we wait for long enough time until the whole system is in equilibrium. The top plate will reach some final speed u and the fluid near the top plate will have the same macroscopic speed (condition of equilibrium). The bottom plate and the fluid near the bottom will be stationary (An external force is necessary to keep the bottom plate stationary). Therefore, a velocity gradient will be set up in the fluid between the two plates (in z direction). We define the viscosity by equation:

$$\tau_{shear} = \frac{F}{A} = \eta \frac{d\langle u_x \rangle}{dz} \quad (32)$$

With force F constantly applied on the top plate, we are inputting momentum Fdt per unit area in time dt . In equilibrium, this momentum will be transported completely to the bottom plate. Therefore, we have momentum flux through z direction (note that the momentum itself is along the plate, x direction, but the flux is along z):

$$\Pi_z = -F/A = -\eta \frac{d\langle u_x \rangle}{dz} \quad (33)$$

We have a negative sign because the momentum flow from high velocity area to low velocity area, which is opposite the velocity gradient.

We can calculate the momentum flux by considering the microscopic motion of gas molecules. We consider that the motion of free ideal gas superimposed with the collective drifting motion with velocity $\langle u_z \rangle$. A molecule travelling along z direction will change their momentum by collision with other molecules in the final position z_2 ($z_1 \rightarrow z_2$). The number of particles with velocity v travelling at an angle θ with z direction is $v \cos \theta n \cdot \frac{1}{2} f(v) dv \sin \theta d\theta$ per unit area A and time dt . How far they travel will be given by the mean free path λ . The momentum difference of a molecule just after collision at z_1 and just after collision at z_2 is given by:

$$-m \left(\frac{\partial \langle u_x \rangle}{\partial z} \right) \lambda \cos \theta \quad (34)$$

which is the momentum flux created by this single molecule. Summing over all molecules with different speed and angle, we have:

$$\Pi_z = \int_0^\infty dv \int_0^{\pi/2} d\theta v \cos \theta n \cdot \frac{1}{2} f(v) \sin \theta \cdot m \left(\frac{\partial \langle u_x \rangle}{\partial z} \right) \lambda \cos \theta \quad (35)$$

$$= -\frac{1}{3} nm \lambda \langle v \rangle \frac{\partial \langle u_x \rangle}{\partial z} \quad (36)$$

We obtain the viscosity:

$$\eta = \frac{1}{3}nm\lambda\langle v \rangle \quad (37)$$

Using the previous result $\lambda = (\sqrt{2}n\sigma)^{-1}$ and $\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$, we can also write:

$$\eta = \frac{2}{3\sigma} \left(\frac{mk_B T}{\pi} \right)^{1/2} \quad (38)$$

We have the following observations:

1. η is independent of pressure.
2. $\eta \propto T^{1/2}$.
3. For the above approximation of momentum transfer to be correct, we require $L \ll \lambda \ll d$, where d is the size of the molecule and L is the size scale of the container.

Thermal conductivity

We define the heat flux in the z direction

$$J_z = -\kappa \left(\frac{\partial T}{\partial z} \right) \quad (39)$$

$$\mathbf{J} = -\kappa \nabla T \quad (40)$$

The gas molecules carrier heat through their kinetic energy, which depend on temperature T via $\langle E_k \rangle = 3k_B T/2$. Defining heat capacity of a molecule as C , we can calculate the total heat flux:

$$J_z = \int_0^\infty dv \int_0^{\pi/2} d\theta v \cos \theta n \frac{1}{2} f(v) \sin \theta \cdot -C \left(\frac{\partial T}{\partial z} \right) \lambda \cos \theta \quad (41)$$

$$= -\frac{1}{3}nC\lambda\langle v \rangle \frac{\partial T}{\partial z} \quad (42)$$

Using $C_V = nC$, the thermal conductivity of gas is therefore

$$\kappa = \frac{1}{3}C_V\lambda\langle v \rangle \quad (43)$$

We observe that Eq.42 is very similar to Eq.36, and we have:

$$\frac{\kappa}{\eta} = \frac{C}{m} \quad (44)$$

Particle Diffusion

We consider a gas of molecules in which some of them is labelled, if those labelled molecules are initially confined in certain area and the confinement is removed, they will start to diffuse (Self-diffuse). Suppose that the diffusion is along z direction and we use $n^*(z)$ to denote the density of those labelled particles, we can define the diffusion coefficient:

$$\Phi_z = -D \left(\frac{\partial n^*}{\partial z} \right) \quad (45)$$

Following the above microscopic picture, we have:

$$\Phi_z = \int_0^\infty dv \int_0^{\pi/2} d\theta v \cos \theta \frac{1}{2} f(v) \sin \theta \cdot - \left(\frac{\partial n^*}{\partial z} \right) \lambda \cos \theta \quad (46)$$

$$= -\frac{1}{3}\lambda\langle v \rangle \frac{\partial T}{\partial z} \quad (47)$$

giving the self-diffusion coefficient

$$D = \frac{1}{3}\langle v \rangle \quad (48)$$

We have the following relationship:

1. $D \propto T^{3/2}$
2. $D\rho = \eta$, where ρ is the density $\rho = nm$

Heat diffusion equation

Given the heat flux $J = -\kappa \nabla T$, the total heat flow out of a closed surface S is $\int_S J \cdot dS$. This value should equal to the loss of total thermal energy $\int_V CTdV$, where C here is the volume heat capacity. We have the Result:

$$\int_S J \cdot dS = \int_V \nabla \cdot J dV = -\frac{\partial}{\partial t} \int_V CTdV \quad (49)$$

where we obtain the first equality through divergence theorem. We have

$$\nabla \cdot J = -C \frac{\partial T}{\partial t} \quad (50)$$

$$\frac{\partial T}{\partial t} = D \nabla^2 T \quad (51)$$

with $D = \kappa/C$ is the thermal diffusivity. Eq.51 is called **Thermal diffusion equation**.

In a steady state, we have $\partial T/\partial t = 0$ so that the diffusion equation is reduced to

$$\nabla^2 T = 0 \quad (52)$$

Suppose we have a gas between two hot plates separate with a distance L , one maintained at temperature T_1 and the other at $T_2 < T_1$. By integrating the equation $\partial^2 T/\partial x^2 = 0$ twice (note that this equation imply a linear temperature distribution) and using the boundary condition, we have:

$$T = \frac{(T_2 - T_1)x}{L} + T_1 \quad (53)$$

The heat flux is given by:

$$J = -\kappa \left(\frac{\partial T}{\partial x} \right) = \frac{\kappa}{L} (T_1 - T_2) \quad (54)$$

The value κ/L is called **thermal conductance**.

If heat is generated at a rate H per unit volume, the divergence of J will be:

$$\nabla \cdot J = -C \frac{\partial T}{\partial t} + H \quad (55)$$

and the thermal diffusion equation will be modified to be:

$$\frac{\partial T}{\partial t} = D \nabla^2 T + \frac{H}{C} \quad (56)$$

Thermal diffusion equation in 1D

We want to solve the equation:

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} \quad (57)$$

to obtain the temperature profile.

Since this equation is a second order linear partial equation, we can look for wave-like solutions

$$T(x, t) \propto \exp(i(kx - \omega t)) \quad (58)$$

with $k = 2\pi/\lambda$ and $\omega = 2\pi/f$ the wave vector and angular frequency. Solution is given by:

$$-i\omega = -Dk^2 \quad (59)$$

$$k = \pm(1+i)\sqrt{\frac{\omega}{2D}} \quad (60)$$

Noting that with $k = -(1+i)\sqrt{\frac{\omega}{2D}}$, $T \rightarrow \infty$ as $x \rightarrow \infty$. Therefore, the solution for the temperature profile can be written as a summation of frequency:

$$T(x, t) = \sum_{\omega} A(\omega) \exp(-i\omega t) \exp((i-1)\sqrt{\frac{\omega}{2D}}x) \quad (61)$$

As an application, consider solving the 1D problem of heat diffusion into the earth ground. The boundary profile is given by

$$T(0, t) = T_0 + \Delta T \cos(\Omega t) = T_0 + \frac{\Delta T}{2} e^{i\Omega t} + \frac{\Delta T}{2} e^{-i\Omega t} \quad (62)$$

where the period is given by the alternation of day and night.

Requiring Eq.61 to give the boundary condition Eq.62, we obtain the solution:

$$T(x, t) = T_0 + \Delta T e^{-x/\delta} \cos(\Omega t - \frac{x}{\delta}) \quad (63)$$

where $\delta = \sqrt{2D/\Omega}$ is called the skin depth, and temperature fall off exponentially as $e^{-x/\delta}$.

Newton's law of cooling

Newton's law of cooling states that the heat loss of a surface is proportional to the area of the surface multiplied by the temperature difference. The heat flux is given by:

$$J = h\Delta T \quad (64)$$

with h the heat transfer coefficient of the surface. As an example, suppose a cup of tea at temperature T_{hot} is placed in a room at temperature T_{air} and the heat loss is through the surface area A . Suppose the air temperature near the surface is maintained at T_{air} with convection, we have:

$$-C \frac{\partial T}{\partial t} = JA = hA(T - T_{air}) \quad (65)$$

$T(t)$ is the temperature of the tea. We have the solution

$$T(t) = T_{air} + (T_{hot} - T_{air})e^{-\lambda t} \quad (66)$$

with $\lambda = Ah/C$

Prandtl number

Apart from thermal diffusion, convection also play a part in the heat transfer in solid and gas. Convection will dominate if momentum diffusion dominates. We can thus compare the magnitude of the two mechanism by

$$\sigma_p = \frac{v}{D} = \frac{\eta c_p}{\kappa} \quad (67)$$

where $v = \eta/\rho$ is the kinematic viscosity and D is the thermal diffusivity $D = \kappa/(\rho c_p)$ (c_p is the specific heat). This value of called **Prandtl number**. For $\sigma_p \gg 1$, the convection is the dominant mode of heat transport. For gas, σ_p can be found to be 2/3 with the previous results. For liquid, $\sigma_p \gg 1$.

3 Sound velocity in gas

In fluids, only longitudinal wave (compression) can be transitted. Transverse wave cannot be transitted since gas cannot transmit shear. Speed of sound for a fluid can be derived from the **continuity equation** and **Euler equation**. The continuity equation for a fluid is:

$$\int_S \rho \mathbf{u} dS = \int_V \nabla \cdot (\rho \mathbf{u}) dV = -\frac{\partial}{\partial t} \int_V \rho dV \quad (68)$$

$$\nabla \cdot (\rho \mathbf{u}) = -\frac{\partial \rho}{\partial t} \quad (69)$$

where ρ is the local fluid density, S is the surface area of a volume element V and \mathbf{u} is the local fluid velocity. The first term in Eq.68 is the flux through the surface, the second term is obtained by divergence theorem. In 1D, the equation is reduced to:

$$\frac{\partial(\rho u)}{\partial x} = -\frac{\partial \rho}{\partial t} \quad (70)$$

The Euler equation, on the other hand, determines the dynamics of a fluid, as:

$$-\frac{1}{\rho}\nabla p = \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} \quad (71)$$

$$-\frac{1}{\rho}\frac{\partial p}{\partial x} = \frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} \quad (72)$$

To obtain the velocity of sound in fluid in 1D, we expand the continuity equation and divide both side by ρ :

$$\frac{u}{\rho}\frac{\partial \rho}{\partial x} + \frac{\partial u}{\partial x} = -\frac{1}{\rho}\frac{\partial \rho}{\partial t} \quad (73)$$

$$\frac{\partial u}{\partial x} = -\frac{1}{\rho}\frac{\partial \rho}{\partial t} \quad (74)$$

where we ignored the first term since it is second order ($u d\rho$). We also discard the second order term in the Euler equation and obtain:

$$-\frac{1}{\rho}\frac{\partial p}{\partial x} = \frac{\partial u}{\partial t} \quad (75)$$

$$-\frac{1}{\rho^2}\left(\rho\frac{\partial p}{\partial \rho}\right)\frac{\partial \rho}{\partial x} = \frac{\partial u}{\partial t} \quad (76)$$

$$-\frac{B}{\rho^2}\frac{\partial \rho}{\partial x} = \frac{\partial u}{\partial t} \quad (77)$$

where we used the definition of the Bulk modulus:

$$B = -V\frac{\partial p}{\partial V} = \rho\frac{\partial p}{\partial \rho} \quad (78)$$

$$\text{Using } d\rho = Md\left(\frac{1}{V}\right) = -M\frac{dV}{V^2} = -\rho\frac{dV}{V} \quad (79)$$

Now, using the result:

$$\frac{\partial u}{\partial x} = -\frac{1}{\rho}\frac{\partial \rho}{\partial t} \quad (80)$$

$$\frac{\partial u}{\partial t} = -\frac{B}{\rho^2}\frac{\partial \rho}{\partial x} \quad (81)$$

and partial differentiate with respect to t and x , we can remove u :

$$-\frac{\partial^2 \rho}{\partial t^2} = -\frac{B}{\rho}\frac{\partial^2 \rho}{\partial x^2} \quad (82)$$

which is a wave equation and the solution is given by:

$$\rho \approx e^{i(kx - \omega t)} \quad (83)$$

with propogating velocity:

$$v_s = \frac{\omega}{k} = \sqrt{\frac{B}{\rho}} \quad (84)$$

Sound velocity under isothermal and adiabatic conditions

The difference between isothermal and adiabatic condition is whether temperature or entropy (no relaxation process) is fixed during the transmission of the sound wave. In isothermal condition, we have:

$$B_T = -V\left(\frac{\partial p}{\partial V}\right)_T = p \quad (85)$$

so that the sound velocity is:

$$v_s = \sqrt{\frac{B_T}{\rho}} = \sqrt{\frac{nm\langle v^2 \rangle}{3\rho}} = \sqrt{\frac{\langle v^2 \rangle}{3}} \quad (86)$$

which coincide with the mean molecular speed in a given direction.

In the adiabatic condition, the gas obey:

$$\frac{dp}{p} = -\gamma \frac{dV}{V} \quad (87)$$

The adiabatic bulk modulus is then:

$$B_S = -V \left(\frac{\partial p}{\partial V} \right)_S = \gamma p \quad (88)$$

and the speed of sound is given by:

$$v_s = \sqrt{\frac{\gamma \langle v^2 \rangle}{3}} \quad (89)$$

Since sound wave is passed by compressing and decompressing the fluid and as the fluid is compressed, their temperature will increase. Therefore, The isothermal process is realized if there are enough time for thermal equilibration to take place. In the real case, the compression process is generally fast and the sound waves are almost always adiabatic.

4 Brownian motion and fluctuations

Appendix A: Time average and ensemble average

Definition

In a system with random fluctuations, one can only discuss the averaged quantity of a single system over a certain time (space) interval or averaged quantity of many identical systems at certain time instance (spatial positions). The former is called **time average** and the later is called **ensemble average**.

Let's consider N systems which have time dependent observable $x^i(t)$, where i index the system. We can define the following averages:

First-order time average:

$$\overline{x^i(t)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} x^i(t) dt \quad (90)$$

Second-order time average:

$$\overline{x^i(t)^2} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} (x^i(t))^2 dt \quad (91)$$

Autocorrelation function:

$$\phi_x^i(\tau) = \overline{x^i(t)x^i(t+\tau)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} x^i(t)x^i(t+\tau) dt \quad (92)$$

First-order ensemble average:

$$\langle x(t_1) \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N x^i(t_1) = \int_{-\infty}^{\infty} x_1 p_1(x_1, t_1) dx_1 \quad (93)$$

Second-order ensemble average:

$$\langle x(t_1)^2 \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N (x^i(t_1))^2 = \int_{-\infty}^{\infty} (x_1(t))^2 p_1(x_1, t_1) dx_1 \quad (94)$$

Covariance:

$$\langle x(t_1)x(t_2) \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N x^i(t_1)x^i(t_2) = \int_{-\infty}^{\infty} x_1 x_2 p_2(x_1, t_1; x_2, t_2) dx_1 dx_2 \quad (95)$$

where for esemble average, t_1 and t_2 refer to a certain time. $p(x, t)$ is the probability density function so that $p_1(x_1, t_1)dx_1$ is the first-order probability that x is found between x_1 and x_1+dx_1 at time t_1 . $p_2(x_1, t_1; x_2, t_2)dx_1 dx_2$ is the probability that x is between x_1 and x_1+dx_1 at time t_1 and between x_2 and x_2+dx_2 at a different time t_2 .

Statistically stationary and nonstationary process

A "process" refers to the trajectory of a system as it evolve through time. If the statistics of the process of a system do not change in time, we call such process stationary. The ensemble average of system with stationary process are identical to its time average. Such process is called **ergodic**. When a process is ergodic, any one system can represent the entire ensemble.

We make the following definition: *A stochastic process is stationary of order k if the k-th order joint probability density function satisfies:*

$$P(\alpha_1, t_1; \dots; \alpha_k, t_k) = P(\alpha_1, t_1 + \epsilon; \dots; \alpha_k, t_k + \epsilon) \quad (96)$$

for all ϵ , where α denote some observables. For example, if $P_1(x, t_1) = P_1(x, t_1 + \epsilon)$, the process is stationary of order 1. if $P_2(x_1, t_1; x_2, t_2) = P_2(x_1, t_1 + \epsilon; x_2, t_2 + \epsilon)$, the process is stationary of order 2.

A process of the system is called "strictly stationary" if it is stationary for any order. A process is called "wide-sense stationary" if its mean value is constant and its autocorrelation function depends only on $\tau = t_2 - t_1$.

/subsection*Ergodicity

Ergodicity can also have different levels: We call a process "ergodic in the mean" if

$$\overline{x(t)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} x(t) dt = \langle x(t) \rangle \quad (97)$$

since $\overline{x(t)}$ is independent of time, $\langle x(t) \rangle$ is also independent of time. which is ensured by the probability density function requirement of stationary process $P_1(x, t_1) = P_1(x, t_1 + \epsilon)$. A process is called ergodic in the autocorrelation if

$$\phi_x(\tau) = \overline{x(t)x(t+\tau)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} x(t)x(t+\tau)dt = \langle x(t)x(t+\tau) \rangle \quad (98)$$

As an example, consider some observable of a system that can be written as a function of time by $x(t) = \sin(\omega t + \theta)$. θ is a random variable distributed over $0 < \theta < 2\pi$. This process is ergodic in both mean and autocorrelation. The time average $\overline{x(t)}$ is 0, the ensemble average at any time is also 0, averaged over system with different choice of θ . Eq.98 is also satisfied since both $\overline{x(t)x(t+\tau)}$ and $\langle x(t)x(t+\tau) \rangle$ vanish, since x depend on time through a sin function and can increase or decrease after a time interval τ (time average) and from the choice of θ , both case average to 0. However, if we limit the variable θ to other distribution, this process will no longer be ergodic.