Kinetic theory of gases I

The Gibbs statistical mechanics is applicable to systems in thermodynamical equilibrium. In the subsequent lectures I will presented the second pillar of statistical mechanics – kinetic theory which can be applied to both equilibrium and non-equilibrium systems. The kinetic theory also aspires to explain unidirectional temporal evolution towards thermodynamical equilibrium.

The kinetic theory initiated by James Clerk Maxwell (1831-1879) and further developed by Ludwig Boltzmann (1844-1906) is a rich theory of various applications. My presentation, however, will be limited to dilute gases where atomic sizes are much smaller than inter-particle distances. Consequently gas particles are mostly non-interacting and there are interactions (collisions) of no more than two particles.

Distribution function

- The main object of kinetic theory is the distribution function $f(t,\mathbf{r},\mathbf{p})$ where $\mathbf{r}$ and $\mathbf{p}$ is the particle position and momentum and t denotes the time. The quantity

$$f(t,\mathbf{r},\mathbf{p})\,\frac{d^3r\,d^3p}{(2\pi)^3} \tag{1}$$

  tell us how many particles there are in the phase-space volume $\frac{d^3r\,d^3p}{(2\pi)^3}$ around $(\mathbf{r},\mathbf{p})$ at time t. The volume is infinitesimally small from a macroscopic point of view but it is microscopically so big that there are many gas particles in the volume. We note that there are 10^{19} atoms in cm^3 of the air in normal conditions.

- The integral

$$\int \frac{d^3r\,d^3p}{(2\pi)^3}\,f(t,\mathbf{r},\mathbf{p}) = N \tag{2}$$

  gives the total number of gas particles.

- The time-dependent particle density and flux are

$$\int \frac{d^3p}{(2\pi)^3}\,f(t,\mathbf{r},\mathbf{p}) = \rho(t,\mathbf{r}), \tag{3}$$

$$\int \frac{d^3p}{(2\pi)^3}\,\frac{\mathbf{p}}{m}\,f(t,\mathbf{r},\mathbf{p}) = \mathbf{j}(t,\mathbf{r}), \tag{4}$$

  where m and $\mathbf{v} \equiv \frac{\mathbf{p}}{m}$ are the particle mass and velocity, respectively.

- Since the gas is assumed to be dilute the energy of gas particles is mostly kinetic $\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}$ and the gas energy density equals

$$\int \frac{d^3p}{(2\pi)^3}\,\epsilon_{\mathbf{p}} f(t,\mathbf{r},\mathbf{p}) = \varepsilon(t,\mathbf{r}). \tag{5}$$

- If the gas is in the external field of potential forces, *e.g.* gravitational, and the particle potential energy is $v(\mathbf{r})$, the gas energy density is

$$\int \frac{d^3p}{(2\pi)^3}\,\big(\frac{\mathbf{p}^2}{2m} + v(\mathbf{r})\big) f(t,\mathbf{r},\mathbf{p}) = \varepsilon(t,\mathbf{r}). \tag{6}$$

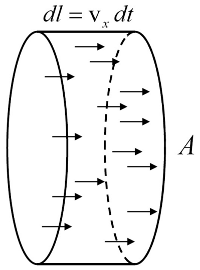

Figure 1: The pressure exerted on the surface A results from the particle collisions with the surface.

Gas in thermal equilibrium

Predictions of kinetic theory obviously agree with those of Gibbs mechanics in case of thermodynamical equilibrium. Nevertheless I will derive two simple already known formulas to show how the kinetic theory works.

- Keeping in mind the partition function of ideal gas, one guess that the equilibrium distribution function is proportional to $e^{-\frac{\epsilon_{\mathbf{p}}}{k_B T}}$. Choosing the normalization constant to satisfy Eq. (2), we get
$$f^{\rm eq}(\mathbf{p}) = \Big(\frac{2\pi}{mk_BT}\Big)^{3/2} \frac{N}{V}\, e^{-\frac{\mathbf{p}^2}{2mk_BT}}, \tag{7}$$
which is known as the Maxwell-Boltzmann distribution. Further on we will derive the distribution function (7) within the kinetic theory with no reference to the Gibbs statistical mechanics.

- Substituting the function (7) into Eq. (5), one finds the gas energy density as
$$\varepsilon = \frac{3}{2}\, k_B T\, \frac{N}{V}. \tag{8}$$

- Let us now compute the pressure exerted on the wall of the surface A of the gas container. The pressure results from the collisions of gas particles which are assumed to be elastic. If the particle's momentum before the collision is $\mathbf{p} = (p_x, p_y, p_z)$ and the surface A is in the $yz-$plane, the momentum after the collision is $\mathbf{p}' = (-p_x, p_y, p_z)$. Therefore, the particle's momentum transferred to the wall is $2p_x$.

- One observes that particles with the velocity v_x, which hit the wall in the time interval dt, are, as shown in Fig. 1, in the volume $dV = Av_x dt$. Keeping in mind that the pressure p is a force perpendicular to the surface per unit area and that a force is a momentum transfer in unit time, one finds
$$\begin{aligned} p &= \int_0^\infty \frac{dp_x}{2\pi} \int_{-\infty}^\infty \frac{dp_y}{2\pi} \int_{-\infty}^\infty \frac{dp_z}{2\pi}\, \underbrace{Av_x dt}_{dV}\, \frac{2p_x}{Adt}\, f^{\rm eq}(\mathbf{p}) \qquad (9) \\ &= 2\Big(\frac{2\pi}{mk_BT}\Big)^{3/2} \frac{N}{V} \int_0^\infty \frac{dp_x}{2\pi}\, \frac{p_x^2}{m}\, e^{-\frac{p_x^2}{2mk_BT}} \Big(\int_{-\infty}^\infty \frac{dp_y}{2\pi}\, e^{-\frac{p_2^2}{2mk_BT}}\Big)^2 = k_B T\, \frac{N}{V}, \end{aligned}$$
where we have used the integral
$$\int_0^\infty dx\, x^2 e^{-x^2} = \frac{\sqrt{\pi}}{4}. \tag{10}$$
The integration over p_x in the expression (9) is only over positive momenta as we take into account only those particles which are approaching the wall.

Collisionless kinetic equation

We are going to derive the equation obeyed by the distribution function which is known as kinetic equation, transport equation or Boltzmann equation. Here we will ignore the inter-particle collisions but an external potential force will be taken into account.

- At the moment of time t the distribution function is $f(t,\mathbf{r},\mathbf{p})$. After a short interval of time dt the function becomes $f(t+dt,\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p})$, which is expanded in the Taylor series as
$$f(t+dt,\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p}) = f(t,\mathbf{r},\mathbf{p}) + \frac{\partial f(t,\mathbf{r},\mathbf{p})}{\partial t}\,dt + \nabla f(t,\mathbf{r},\mathbf{p})\cdot d\mathbf{r} + \nabla_p f(t,\mathbf{r},\mathbf{p})\cdot d\mathbf{p}, \tag{11}$$
where ∇_p is the momentum gradient.

- Since the inter-particle collisions are ignored but the external potential force $\mathbf{F}$ is taken into account we have
$$d\mathbf{r} = \mathbf{v}dt = \frac{\mathbf{p}}{m}dt, \qquad\qquad d\mathbf{p} = \mathbf{F}dt, \tag{12}$$
which substituted into Eq. (11) give
$$f(t+dt,\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p}) = f(t,\mathbf{r},\mathbf{p}) + \Big(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla + \mathbf{F}(\mathbf{r})\cdot\nabla_p\Big) f(t,\mathbf{r},\mathbf{p})\,dt. \tag{13}$$

- As the particles, which at t have been at $(\mathbf{r},\mathbf{p})$, have moved to $(\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p})$ after dt, the phase space density remains unchanged that is
$$f(t,\mathbf{r},\mathbf{p}) = f(t+dt,\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p}). \tag{14}$$

- Using Eq. (11) provides the collisionless kinetic equation or Vlasov equation
$$\Big(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla + \mathbf{F}(\mathbf{r})\cdot\nabla_p\Big) f(t,\mathbf{r},\mathbf{p}) = 0. \tag{15}$$

- If the external force $\mathbf{F}$ absent, a general solution of the collisionless kinetic equation is
$$f(t,\mathbf{r},\mathbf{p}) = h(\mathbf{r}-\mathbf{v}t,\mathbf{p}), \tag{16}$$
where $h(\mathbf{r},\mathbf{p})$ is an arbitrary function.

- To check that the function (16) solves Eq. (15) one introduce the variable $\mathbf{s} \equiv \mathbf{r} - \mathbf{v}t$ and computes
$$\Big(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\Big) f(t,\mathbf{r},\mathbf{p}) = \Big(\frac{\partial s^i}{\partial t} + v^j\frac{\partial s^i}{\partial r^j}\Big)\frac{\partial h(\mathbf{s},\mathbf{p})}{\partial s^i} = \Big(-v^i + v^i\Big)\frac{\partial h(\mathbf{s},\mathbf{p})}{\partial s^i} = 0. \tag{17}$$

Gas expansion into vacuum

Let us consider a gas in the thermal equilibrium kept in a container. At a moment of time t_0 the walls of the container are removed and the gas expands into vacuum. How does the process proceed?

- To simplify the problem instead of the container there is a Gaussian distribution of gas density. The initial distribution function is
$$f(t=0,\mathbf{r},\mathbf{p}) = \frac{N}{(\sqrt{2\pi}L_0)^3}\Big(\frac{2\pi}{mk_BT}\Big)^{3/2} e^{-\frac{\mathbf{r}^2}{2L_0^2}}\, e^{-\frac{\mathbf{p}^2}{2mk_BT}} = \frac{N}{(mk_BTL_0^2)^{3/2}}\, e^{-\frac{\mathbf{r}^2}{2L_0^2}}\, e^{-\frac{\mathbf{p}^2}{2mk_BT}}, \tag{18}$$
where L_0 is the container size.

- Knowing the general solution (16), the distribution function for $t \geq 0$ is written as
$$f(t,\mathbf{r},\mathbf{p}) = \frac{N}{(mk_BTL_0^2)^{3/2}}\, e^{-\frac{(\mathbf{r}-\mathbf{v}t)^2}{2L_0^2}}\, e^{-\frac{\mathbf{p}^2}{2mk_BT}}. \tag{19}$$

- Taking the position integral of the function (19) we find the momentum distribution
$$\int d^3r\, f(t,\mathbf{r},\mathbf{p}) = \Big(\frac{2\pi}{mk_BT}\Big)^{3/2} e^{-\frac{\mathbf{p}^2}{2mk_BT}}, \tag{20}$$
which, as expected, does not change in time.

- Taking the integral over momentum we find the density distribution
$$\rho(t,\mathbf{r}) = \Big(\frac{m}{2\pi(mL_0^2 + k_BT\,t^2)}\Big)^{3/2} N\, \exp\Big(-\frac{m\,\mathbf{r}^2}{2(mL_0^2 + k_BT\,t^2)}\Big), \tag{21}$$
which evolves with time.

- One checks that the density (21) integrated over $\mathbf{r}$ gives N, as it should.

- Using the formula (21) one shows how the gas expands. The dispersion of the region, where the gas particles are present, is
$$L(t) \equiv \sqrt{\langle \mathbf{r}^2\rangle - \langle \mathbf{r}\rangle^2} = \sqrt{L_0^2 + \frac{k_BT}{m}\, t^2} = \sqrt{L_0^2 + \frac{1}{3}\, v_T^2 t^2}, \tag{22}$$
where we have introduced the quantity $v_T = \sqrt{\frac{3k_BT}{m}}$ which is the *average velocity* or *thermal velocity* defined through the equality
$$\frac{1}{2}\, m\, v_T^2 = \frac{3}{2}\, k_BT. \tag{23}$$
As seen, the higher gas temperature the faster expansion.