

Physical kinetics seminar

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The first chapter in Soto's book deals with introductory concepts in kinetic theory.

1.1 Velocity distribution function

Distribution function is a ubiquitous and widely applicable concept in kinetic theory.

For now, we will consider gas of a single species. More the relevant concept is the velocity distribution function.

We assume that the gas occupies a volume V , that is, subdivided into smaller volumes. These smaller volumes are such that they are small enough to be homogeneous, that is, the average quantities, like velocities, are the same throughout the subvolume. On the other hand, the subvolumes should be large enough to hold a large number of molecules, so that statistical averaging procedures can be used.

In this book, particle velocities are denoted by \vec{c} , with \bar{v} being the average velocity.

We now define the velocity distribution function $f(\vec{r}, \vec{c}, t)$ with

$$f(\vec{r}, \vec{c}, t) d^3r d^3c$$

being the average number of molecules in volume d^3r around \vec{r} with velocities in d^3c around \vec{c} at time t .

We will later use this function to describe transport phenomena and relaxation of out-of-equilibrium systems.

If we had several species of molecules, then we would have several distribution functions $f_i(\vec{r}, \vec{c}, t)$, defined in an analogous way.

For now we will stick with single species of particles.

We will later treat d^3r d^3c as differentials, but physically they should be of mesoscopic size.

We know that a mole of gas with $N_A = 6.022 \cdot 10^{23}$ molecules occupies a volume of 22.4 litres at standard conditions. From this we can calculate that such a small subvolume of $1 \mu\text{m}^3$ will have $2.4 \cdot 10^8$ particles.

A comment on our use of averaging. If we took even smaller subvolumes, the number of particles in there would change very rapidly, because the particles would enter, leave and collide with each other. By averaging in somewhat larger subvolumes, we smooth out this erratic behaviour. This kind of procedure is called coarse-graining.

1. 2. The Maxwell-Boltzmann distribution function

Let us consider particles in thermal equilibrium without any external fields. The velocity distribution function f depends on neither time nor spatial position. From statistical mechanics we know that it is given by the Maxwell-Boltzmann distribution:

$$f(\vec{v}) = n f_{MB}(\vec{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{mv^2}{2k_B T} \right)$$

Here n is the particle number density.

The distribution of speeds is given by

$$\phi_{MB}(c) = \int_0^\infty f(c) c^2 dc = \int_0^\infty dc \int_0^\pi \sin \theta d\theta c^2 f(c) = 4\pi n \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} c^2 \exp \left(-\frac{mc^2}{2k_B T} \right)$$

From here we can obtain the most probable speed

$$c_{mp} = \sqrt{\frac{2k_B T}{m}}$$

the average speed

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

and the average square speed

$$\langle v^2 \rangle = \frac{3k_B T}{m}$$

1.3 Densities and fluxes

From the distribution function we can obtain the particle density by integrating over the velocities

$$n(\vec{r}, t) = \int f(\vec{r}, \vec{c}, t) d^3 c$$

We can consider any quantity φ that depends on single particle velocity. Examples can be the kinetic energy $\varphi = \frac{mc^2}{2}$ or mass $\varphi = m$.

The local average of this quantity is defined as:

$$\langle \varphi \rangle (\vec{r}, t) = \frac{1}{n(\vec{r}, t)} \int \varphi(\vec{c}) f(\vec{r}, \vec{c}, t) d^3 c$$

The local density of this quantity is defined by

$$\beta \varphi(\vec{r}, t) = n(\vec{r}, t) \langle \varphi \rangle (\vec{r}, t)$$

With these definitions we can introduce the velocity field

$$\vec{v}(\vec{r}, t) = \frac{1}{n(\vec{r}, t)} \int \vec{c} f(\vec{r}, \vec{c}, t) d^3 c$$

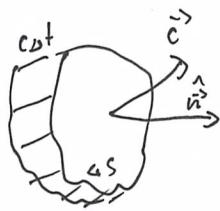
Note that if we have the Maxwell - Boltzmann distribution with $e^{-\frac{mc^2}{2k_B T}}$, the velocity field will be zero everywhere. This can be changed by $\vec{c} \rightarrow (\vec{c} - \vec{v})$.

Now we want to introduce the temperature field by the equipartition theorem, but we must remember that temperature is determined by fluctuations about the average velocity:

$$\frac{3}{2} k_B T(\vec{r}, t) = \left\langle \frac{n(\vec{c} - \vec{v})^2}{2} \right\rangle$$

Moving particles transfer their properties from one spatial location to another. With each quantity φ we can associate its flux \vec{j}_φ , which tells us how much of the quantity is transferred. Strictly speaking, the flux vector measures the amount of stuff transferred through the unit area during the unit time.

Let's say we have a surface



In time Δt a molecule will reach the surface if it is in volume $\Delta V = \frac{4}{3} \pi r^3 \Delta t$

The number of molecules with specific velocities that will cross this surface is

$$\Delta N = f(\vec{r}, \vec{c}, t) \vec{c} \cdot \hat{n} \Delta t \Delta S d^3 c$$

If each molecule carries quantity $\varphi(\vec{c})$, then the quantity that is transferred through ΔS during Δt is

$$\Delta \varphi = \Delta t \Delta S \int f(\vec{r}, \vec{c}, t) \varphi(\vec{c}) \vec{c} \cdot \hat{n} d^3 c$$

We define the flux by the relation

$$\Delta \varphi = \vec{J}_\varphi \cdot \hat{n} \Delta t \Delta S$$

Thus

$$\vec{J}_\varphi(\vec{r}, t) = \int f(\vec{r}, \vec{c}, t) \varphi(\vec{c}) \vec{c} d^3 c$$

Note that we keep the sign of \vec{c} , which is logical.

Now we define some relevant fluxes. The mass flux is

$$\vec{J}_m = m n(\vec{r}, t) \vec{c}(\vec{c}, t)$$

The kinetic energy flux is

$$\vec{J}_e(\vec{r}, t) = \frac{m}{2} \int f(\vec{r}, \vec{c}, t) c^2 \vec{c} d^3 c$$

Defining flux for momentum gives us some pause, as it is a vectorial quantity.

We can consider a Cartesian component of momentum, $\varphi = mc_i$. Its flux is a vector

$$\vec{J}_{c_i} = m \int f(\vec{r}, \vec{c}, t) c_i \vec{c} d^3 c$$

If we take a component of this vector, we obtain a quantity with two indices, suggesting that we have a tensor. It is indeed the case:

$$\tilde{P}_{ik} = m \int f(\vec{r}, \vec{c}, t) c_i c_k d^3 c$$

Obviously, this tensor is symmetric. Its interpretation is that $\tilde{P}_{ik} n_k$ is the total momentum in the direction i that crosses a unitary surface oriented along the k direction per unit time.

1.3.1 Stress tensor and energy flux

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From expressions of kinetic energy and momentum fluxes we see that they have a contribution if the gas has some net velocity. These contributions are called convective. We can subtract them by defining quantities

$$q_i = \frac{m}{2} \int f(\vec{r}, \vec{c}, t) (\vec{c} - \vec{v})^2 (c_i - v_i) d^3 c$$

$$\rho_{ih} = m \int f(\vec{r}, \vec{c}, t) (c_i - v_i) (c_a - v_a) d^3 c$$

They measure the fluxes of energy and momentum in a frame that is comoving with the gas. They have contributions only due to fluctuations around the mean velocity.

Now let us consider a volume of the gas enclosed by a boundary S , which is comoving with the gas.

The rate of change of mass in the volume (positive change meaning mass entering the volume) is

$$\frac{dM}{dt} = - \iint_S f(\vec{r}, \vec{c}, t) m (\vec{c} - \vec{v}) \cdot d\vec{s} d^3 c$$

By definition of the velocity field, this is zero.

The momentum entering the volume per unit time is

$$\frac{dp_i}{dt} = - \iint_S f(\vec{c}) m c_i (\vec{c} - \vec{v}) \cdot d\vec{s} d^3 c$$

Here we can change $c_i \rightarrow c_i - v_i$ because the subtracted term will average out to zero.

$$\frac{dp_i}{dt} = - \iint_S f(\vec{c}) m (c_i - v_i) (\vec{c} - \vec{v}) d\vec{s} d^3 c = - \iint_S \rho_{ih} dS_a$$

We can say that $-\rho_{ih} dS_a$ is the force acting on the volume, because the mass inside doesn't change. Then it follows from Newton's third law that $\rho_{ih} dS_a$ is the force that is exerted by the gas on the exterior through the surface $d\vec{s}$. We therefore call ρ_{ih} the stress tensor.

Similarly, we can analyze the energy flux through the comoving surface:

$$\frac{dE}{dt} = - \iint_S f(\vec{c}) \frac{mc^2}{2} (\vec{c} \cdot \vec{v}) \cdot d\vec{s} d^3 c$$

We can express c^2 as

$$c^2 = (\vec{c} \cdot \vec{v})^2 + 2(\vec{c} \cdot \vec{v}) \cdot \vec{v} + v^2$$

Then

$$\begin{aligned} \frac{dE}{dt} &= - \iint_S f(\vec{c}) \frac{mc^2}{2} (\vec{c} \cdot \vec{v})^2 (\vec{c} \cdot \vec{v}) \cdot d\vec{s} d^3 c - \\ &\quad - \iint_S f(\vec{c}) \frac{m}{2} \cdot 2(\vec{c} \cdot \vec{v}) \cdot \vec{v} (\vec{c} \cdot \vec{v}) d\vec{s} d^3 c \\ &\quad - \iint_S f(\vec{c}) \frac{m}{2} v^2 (\vec{c} \cdot \vec{v}) \cdot d\vec{s} d^3 c = \\ &= - \iint_S \vec{q}_v \cdot d\vec{s} - \iint_S P_{ih} v_i dS_h = 0 \end{aligned}$$

The first term is the heat flux through the surface and the second is the mechanical power of external gas (integral of $-\vec{v} \cdot d\vec{F}$). Therefore, \vec{q}_v should be interpreted as thermodynamic heat flux, as what we have is basically the first law of thermodynamics.

We can relate the fluxes in the lab frame and in the comoving frame

$$\begin{aligned} \tilde{P}_{ih} &= m \iint f(\vec{v}, \vec{c}, t) (c_i - v_i)(c_h - v_h) d^3 c + m \iint f(\vec{v}, \vec{c}, t) v_i v_h d^3 c = \\ &= P_{ih} + m n v_i v_h \end{aligned}$$

So here we add to the stress tensor the convective term.

$$\begin{aligned} \gamma_{ei} &= \frac{m}{2} \iint f(\vec{v}, \vec{c}, t) c^2 c_i d^3 c = \frac{m}{2} \iint f(\vec{v}, \vec{c}, t) (\vec{c} \cdot \vec{v})^2 \frac{-v_i + v_e}{c_i} d^3 c + \\ &\quad + m \iint f(\vec{v}, \vec{c}, t) (\vec{c} \cdot \vec{v}) \vec{v} \cdot \vec{c}_i d^3 c + \frac{m}{2} \iint f(\vec{v}, \vec{c}, t) v^2 c_i d^3 c = \\ &= q_{ei} + n \frac{3}{2} k_B T v_i + P_{ih} v_h + n \frac{mv^2}{2} v_i = \\ &= n \left(\frac{mv^2}{2} + \frac{3}{2} k_B T \right) v_i + P_{ih} v_h + q_{ei} \end{aligned}$$

The first term here is convective transport, the total kinetic energy transported by the fluid. Second term is mechanical power. Third is heat flow

1.3.2 Stress tensor and heat flux in equilibrium

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The expression for the heat flux vanishes for equilibrium, when the velocity distribution function is Maxwellian, because we have odd function under the integral sign.

Similarly, the stress tensor will have only diagonal and equal values, thus it will be isotropic. Clearly,

$$\rho_{ii} = n \frac{1}{3} \langle m (\vec{c} - \vec{v})^2 \rangle = n \frac{1}{3} 3k_B T = nk_B T$$

Thus

$$\rho_{ih} = \alpha_h n k_B T \sigma_{ij}$$

We obtain the ideal gas law.

The force the gas exerts can be interpreted as pressure.

Ideal gas law is valid only for small densities.

When talking about fluxes we neglected possible momentum transfer through the surface:



We define scalar pressure by $p = \frac{1}{3} \rho_{ii}$

Then the ideal gas law will hold under any non-equilibrium conditions.

1.3.3 Flux distribution

What is the velocity distribution of particles that cross a surface?

Only particles in volume $\Delta V = \vec{v} \cdot \vec{n} \Delta S$ will cross.

The distribution of particles crossing the surface is then

$$f_{\text{flux}}(\vec{c}) = f(\vec{c}) \vec{c} \cdot \vec{n}$$

This is flux distribution, which is anisotropic.