

Introduction to the kinetic theory of non-equilibrium processes

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Abstract

In the presented lecture-course we attempt to make a brief introduction to the kinetic theory of non-equilibrium processes and link these processes with microscopic description of the gas-type or condensed (liquid-type) media. The well-know equations of hydrodynamics responsible for matter and energy transfer, such as Navier-Stokes, thermal conductivity, diffusion etc., will be rigourously constructed via kinetic approach fundamentally based on the Boltzmann kinetic equation. The lecture course requires elementary knowledge of probability theory, classical mechanics and concept of partial differential equations in mathematical physics.

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I. BOLTZMANN KINETIC EQUATION

A. Statistical distribution in the phase space. Probability density function

For macroscopic system, such as dense non-ideal gas or liquid, consisting of many particles the random distribution of its molecules (or atoms) can be described by the probability density function

$$f(x, y, z; p_x, p_y, p_z; t) \equiv f(\mathbf{r}, \mathbf{p}, t) \quad (1.1)$$

which has a meaning that the product

$$f(x, y, z; p_x, p_y, p_z; t) dx dy dz dp_x dp_y dp_z = f(\mathbf{r}, \mathbf{p}, t) d^3r d^3p \quad (1.2)$$

gives a number of molecules which spatial positions \mathbf{r} and linear momenta \mathbf{p} are respectively located inside the domains $(x, x + dx)$, $(y, y + dy)$, $(z, z + dz)$ and $(p_x, p_x + dp_x)$, $(p_y, p_y + dp_y)$, $(p_z, p_z + dp_z)$. Both the coordinates \mathbf{r} and $\mathbf{p} = m\mathbf{v}$ (where m is the molecule mass) considered together define a point in so called phase space of microscopic states of the molecule. The probability density function is normalized as follows

$$\int f(\mathbf{r}, \mathbf{p}, t) d^3r d^3p = N \quad (1.3)$$

where N is the total number of molecules. For macroscopic system this number is normally huge and as a consequence it lets us select the differential volume element in the phase space $d\gamma \equiv d^3r d^3p$ to be mesoscopically small but still containing a large number of molecules $dn = f d\gamma \gg 1$.

Once we know the statistical distribution in the phase space we can find any macroscopic parameters of the medium. For example the spatial density distribution $n(\mathbf{r}, t)$ is given by

$$n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{p}, t) d^3p \quad (1.4)$$

Other parameters can be similarly defined, but the tricky point is that the complicate internal dynamics of the medium allows us to introduce the closed equation only for probability density function and not for macroscopic parameters of the medium.

To derive such a basic equation let us start from a natural physical assumption that for macroscopic system the increment

$$f(\mathbf{r}, \mathbf{p}, t + dt) - f(\mathbf{r}, \mathbf{p}, t) = \frac{\partial f}{\partial t} dt \quad (1.5)$$

could be small [i. e. function f itself is slow-varied] during the interval dt when a significant number of molecules either entered or exited the volume $d\gamma$ as result of free motion or collision dynamics. Later on we will discuss the validity of this assumption.

At the first step we ignore collisions of the molecules and follow how f -function is changed due to free drifting of the particle through the volume $d\gamma$. Consider the box in normal position coordinate space together with the similar box in the momentum subspace as shown in the figure below and count the number of particles entering and exiting both the boxes during the time increment dt . The disbalance between the particles entering and exiting the

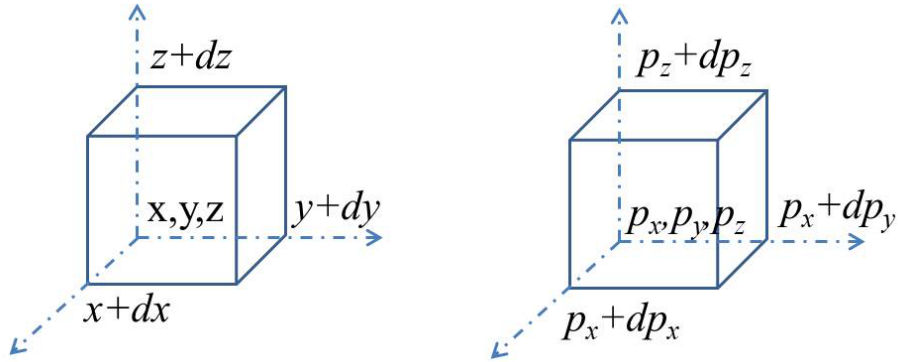


FIG. 1: An elementary volume of the phase space $d^3r d^3p = dx dy dz dp_x dp_y dp_z$ constructed near the point of the molecule microscopic state $(\mathbf{r}, \mathbf{p}) = (x, y, z; p_x, p_y, p_z)$.

left-hand box in x -direction during the time dt is given by

$$\begin{aligned} & f(x, y, z; \mathbf{p}; t) v_x dt dy dz d^3p - f(x + dx, y, z; \mathbf{p}; t) v_x dt dy dz d^3p \\ &= -\frac{\partial f}{\partial x} dx v_x dt dy dz d^3p = -v_x \frac{\partial f}{\partial x} d^3r d^3p dt \end{aligned} \quad (1.6)$$

where $v_x = p_x/m$ is the molecule velocity projected onto x -direction and m is the molecule mass. Similarly for the right-hand box with counting the particle disbalnce in p_x -direction we have

$$\begin{aligned} & f(\mathbf{r}; p_x, p_y, p_z; t) d^3r \dot{p}_x dt dp_y dp_z - f(\mathbf{r}; p_x + dp_x, p_y, p_z; t) d^3r \dot{p}_x dt dp_y dp_z \\ &= -\frac{\partial f}{\partial p_x} dp_x d^3r \dot{p}_x dt dp_y dp_z = -F_x \frac{\partial f}{\partial p_x} d^3r d^3p dt \end{aligned} \quad (1.7)$$

where in accordance with the second Newton's law $\dot{p}_x = F_x$ where F_x is external force acting on the particle. With taking into account all the three directions in coordinate and

momentum subspaces (i.e. all six coordinates in the entire phase space) we obtain the following disbalance for the number of particles in an elementary cell of the phase space

$$-\frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} d^3 r d^3 p dt - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} d^3 r d^3 p dt \quad (1.8)$$

But this is not complete contribution mediating the kinetic process as far as the molecules can enter or exit the momentum box shown in Fig 1 because of internal dynamics i.e. via collision process.

Each molecule located in the right-hand box can sharply change its momentum because of collision. The collision itself has negligible duration τ_c in comparison with increment dt such that $\tau_c \ll dt$. Thus for the rather dense gas we can expect a significant number of such events depleting the number of molecules in an elementary cell of the phase space

$$- b d^3 r d^3 p dt \quad (1.9)$$

The depletion is compensated by alternative gain process when the molecules income in the momentum volume of the phase space once one of the collision partners gets a kick of a linear momentum approximately equal to \mathbf{p}

$$a d^3 r d^3 p dt \quad (1.10)$$

Both the coefficients a (in-scattering term) and b (out-scattering term) are the subjects of calculation with precise tracking of the collision dynamics, which we do in the next sections.

The entire balance for the particles in the elementary volume reads

$$\frac{\partial f}{\partial t} d^3 r d^3 p dt = -\frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} d^3 r d^3 p dt - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} d^3 r d^3 p dt + (a - b) d^3 r d^3 p dt \quad (1.11)$$

Canceling the phase volume $d\gamma = d^3 r d^3 p$ and the time increment dt we obtain

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\text{drift}} + \left(\frac{\partial f}{\partial t} \right)_{\text{col}} \quad (1.12)$$

where the drift and collision terms are respectively given by

$$\left(\frac{\partial f}{\partial t} \right)_{\text{drift}} = -\frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} \quad (1.13)$$

and

$$\left(\frac{\partial f}{\partial t} \right)_{\text{col}} = a - b \quad (1.14)$$

The balance relations (1.11) and (1.12) give us a precursor of the master equation mediating the entire dynamics of the density probability function.

We conclude this section by the following important remark. We can point out that incorporation of the drift term in the left-hand side of Eq. (1.2) leads

$$\frac{\partial f}{\partial t} - \left(\frac{\partial f}{\partial t} \right)_{\text{drift}} = \frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\mathcal{D}f}{\mathcal{D}t} \right) \quad (1.15)$$

and can be associated with complete time derivative if the molecular ensemble freely evolves and is only affected by external forces such that the probability density function is considered as composition function on time $f = f(\mathbf{r}, \mathbf{p}, t) = f(\mathbf{r}(t), \mathbf{p}(t), t)$. The fact that the probability density reveals an integral of motion for an ideal gas is expectable consequence of our discussion. Such a reduced equation would be time reversible and obey the Newton dynamics with saving entropy of the system. This observation emphasizes the physical difference between dynamical and kinetic description where the collision process induces an internal stochastic disturbance into the ideal dynamics and eventually makes the kinetic process irreversible in time.

B. The scattering cross-section

In this section we consider the basic parameter of the collision process namely the scattering cross-section. We follow the concept of classical mechanics and readdress the listeners to the textbooks in classical mechanics [L.D. Landau & E.M. Lifshitz "Mechanics"; H. Goldstein "Classical Mechanics"] for more details. To begin it is convenient to consider the simplest configuration when the low density flux of particles (molecules), conventionally called projectile particles, scatters by a repulsive potential centered at the origin of the coordinate frame. The process can be imaged by the diagram shown in Fig. 2. Each scattering trajectory in its incoming part can be parameterized by a transverse distance ρ from z -axis, which is coventionally defined as impact parameter of the collision. The outgoing part of the trajectory is deflected by the scattering angle θ . The impact parameter can be considered as function of the scattering angle and for a particular trajectory is expressed as $\rho = \rho(\theta, E)$. Because of energy conservation $E = E'$ the velocity and momentum of the particle preserve their value before and after collision - $|\mathbf{v}'| = |\mathbf{v}|$ and $|\mathbf{p}'| = |\mathbf{p}|$ - but change the direction. One of these quantities either initial energy $E = p^2/2m = mv^2/2$ or velocity $v = |\mathbf{v}|$ or

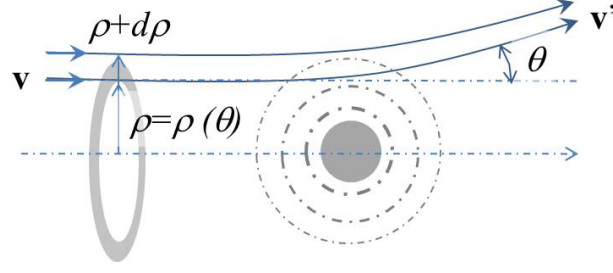


FIG. 2: The scattering process of a particle on a repulsive potential. As evident from the diagram the impact parameter ρ taken for a particular trajectory can be expressed as function of deflection angle θ and energy E : $\rho = \rho(\theta, E)$.

momentum $p = |\mathbf{p}|$ specifies the scattering trajectory.

Imagine that there is an ensemble of particles incident on the scattering center and outgoing in arbitrary directions. By detecting the particles scattered in a particular differential solid angle $d\Omega = 2\pi \sin \theta d\theta$ we can introduce the ratio

$$d\sigma(\theta, E) = \frac{d\nu}{I} \quad (1.16)$$

where $d\nu$ is the number of such particles detected per unit time and it is normalized by the density flux in the incident beam I . The quantity $d\sigma$ is known as differential cross-section and as evident from the diagram of Fig. 2 it is given by

$$d\sigma(\theta, E) = 2\pi \rho d\rho \quad (1.17)$$

or in extended form

$$\frac{d\sigma}{d\Omega} = \frac{\rho(\theta, E)}{\sin \theta} \left| \frac{d\rho}{d\theta} \right| \quad (1.18)$$

The last equation shows us that the cross-section can be found once we know the dependence $\rho = \rho(\theta, E)$. This requires to solve the equation of motion for the particle mediated by the scattering potential.

Consider now collision of two interacting molecules in a most typical situation when their interaction potential $U = U(\mathbf{r} - \mathbf{r}_1) = U(|\mathbf{r} - \mathbf{r}_1|)$ depends only on intermolecular separation. This process obeys the conservation laws of total momentum and energy

$$\begin{aligned} \mathbf{p} + \mathbf{p}_1 &= \mathbf{p}' + \mathbf{p}'_1 \\ \frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_1^2}{2m_1} &= \frac{\mathbf{p}'^2}{2m} + \frac{\mathbf{p}'_1^2}{2m_1} \end{aligned} \quad (1.19)$$

As a consequence the dynamics of such two-particle system is most naturally described in its center-of-momentum reference frame, where the problem transforms to the configuration of an effective single particle problem. The relative motion can be linked with dynamics of a single particle with reduced mass $\mu = m m_1 / (m + m_1)$ scattered by a potential center $U = U(r) = U(|\mathbf{r} - \mathbf{r}_1|)$. Indeed, in this frame two identical molecules with $m = m_1$ move symmetrically each other with the speed given by the half of the relative velocity $\mathbf{v}_0 = \mathbf{v} - \mathbf{v}_1$ as it is shown in Fig. 3. Each of the molecules moves along the scattering

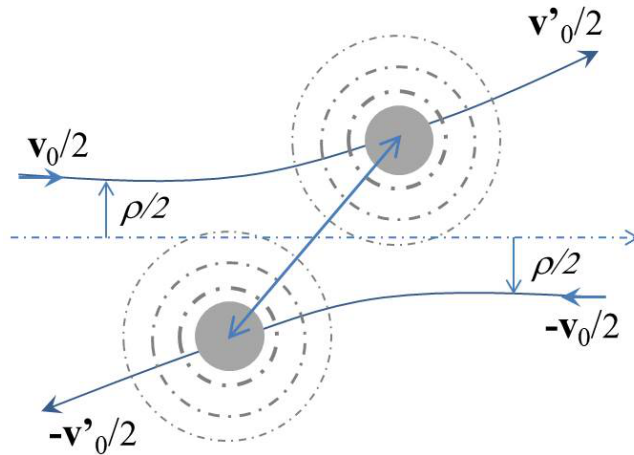


FIG. 3: Two particles collision observed in their center-of-momentum reference frame.

trajectories similarly as shown in Fig 2 for the single particle scattering on a potential center. Since $v_0 = |\mathbf{v}_0| = |\mathbf{v}'_0|$ for statistical ensemble of the scattering events we can introduce the differential cross-section similarly to Eq. (1.16)

$$d\sigma(\Omega, v_0) = \frac{d\nu}{IN_{\text{tar}}} \quad (1.20)$$

where I is the density flux associated with the particles with momentum \mathbf{p} (conventionally named projectiles) incident with the relative speed v_0 onto other particles with momentum \mathbf{p}_1 (conventionally named targets) and N_{tar} is the number of targets. Then $d\nu$ gives us the number of projectiles scattered per unit time in direction $\Omega = \theta, \phi$ into a differential solid angle $d\Omega = \sin\theta d\theta d\phi$ defined in respect to the center-of-momentum reference frame. As far as $d\nu$ is enlarged with both the numbers of projectiles and targets the cross-section is defined as internal characteristic of an elementary scattering event.

If the above scattering process is considered in an arbitrary [laboratory] frame then the differential cross-section would be also defined by Eq. (1.20), but with the detection angle

directed along the linear momenta of the scattered molecules (projectiles) in the laboratory frame. Since we consider the same scattering events $d\nu$, only observed in different reference frames, it is crucially important to recognize that the value of the cross-section should be the same in both the frames as well. For proper mathematical relation one has to express the scattering angle as function of $\mathbf{p}, \mathbf{p}_1, \mathbf{p}', \mathbf{p}'_1$ such that

$$d\sigma(\Omega, v_0) = d\sigma(\Omega(\mathbf{p}' - \mathbf{p}'_1), |\mathbf{p} - \mathbf{p}_1|/m) \equiv d\sigma(\mathbf{p}, \mathbf{p}_1 \rightarrow \mathbf{p}', \mathbf{p}'_1) \quad (1.21)$$

This technical problem can be easily resolved by applying the simple kinematic transformations between the frames.

In the case of the disordered atomic gas there is a naturally created statistical ensemble of colliding molecules. The positions of both the projectiles and targets occupy the same differential volume element reproduced by the left-hand box in Fig. 1. But at the same time the projectiles and targets belong to different momentum cells reproduced by the right-hand box. For the in-scattering process, described by term a in (1.14), the projectiles are located outside the selected box before collisions and get in this box after the collisions. So that we have an ensemble of scattering events with initial momenta $\mathbf{p}', \mathbf{p}'_1$ transferred to the final momenta \mathbf{p}, \mathbf{p}_1 . In contrast for the out-scattering process, described by term b in (1.14), the projectiles are located inside the selected box before collisions and get off this box after the collisions. So that we have an ensemble of scattering events with initial momenta \mathbf{p}, \mathbf{p}_1 transferred to the final momenta $\mathbf{p}', \mathbf{p}'_1$. As follows from the above derivation and supporting discussion, both the processes should have identical cross-section so we can further accept the following symmetry relation

$$d\sigma(\mathbf{p}, \mathbf{p}_1 \rightarrow \mathbf{p}', \mathbf{p}'_1) = d\sigma(\mathbf{p}', \mathbf{p}'_1 \rightarrow \mathbf{p}, \mathbf{p}_1) \quad (1.22)$$

This intuitively clear assumption can be rigorously proven with applying the time reversibility arguments for microscopic dynamics in a two-particle system, for more details see [L.D. Landau & E.M. Lifshitz "Mechanics"; H. Goldstein "Classical Mechanics"].

C. Boltzmann equation

Firstly, let us consider the out-scattering process. The number of target particles located in an elementary volume of the phase space $d^3r d^3p_1$ can be evaluated as

$$N_{\text{tar}} = f(\mathbf{r}, \mathbf{p}_1, t) d^3p_1 d^3r \quad (1.23)$$

Recall that for mesoscopically scaled differential volume this number is expected to be sufficiently large. The density flux of the projectile particles located in the volume $d\gamma \equiv d^3r d^3p$ is given by

$$I = v_0 f(\mathbf{r}, \mathbf{p}, t) d^3p \quad (1.24)$$

where $v_0 = |\mathbf{p} - \mathbf{p}_1|/m$. Then from Eq. (1.20) we can estimate the number of scattering events per unit time which take the projectiles away from the volume $d\gamma$

$$d\nu = d\sigma(\Omega, v_0) v_0 f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t) d^3p d^3p_1 d^3r \quad (1.25)$$

Let us integrate this expression over d^3p_1 and over scattering angle $d\Omega$ (defined in respect to the central-of-momentum reference frame!). Then in accordance with the concept and definitions of balance relation (1.11) we arrive

$$b d^3r d^3p = \int \int d\sigma(\Omega, v_0) v_0 f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t) d^3p_1 d^3r d^3p \quad (1.26)$$

which gives us the off-scattering contribution to the collision term in equation (1.12).

For the in-scattering process the number of target particles located in an elementary volume of the phase space $d^3r d^3p'_1$ can be evaluated as

$$N'_{\text{tar}} = f(\mathbf{r}, \mathbf{p}'_1, t) d^3p'_1 d^3r \quad (1.27)$$

The density flux of the projectile particles located in the volume $d^3r d^3p'$ is given by

$$I' = v'_0 f(\mathbf{r}, \mathbf{p}', t) d^3p' \quad (1.28)$$

where $v'_0 = |\mathbf{p}' - \mathbf{p}'_1|/m$. Then from Eq. (1.20) we can estimate the number of scattering events per unit time, which deliver the projectiles into the volume $d\gamma \equiv d^3r d^3p$

$$d\nu' = d\sigma(\Omega', v'_0) v'_0 f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) d^3p' d^3p'_1 d^3r \quad (1.29)$$

where the cross-section $d\sigma(\Omega', v'_0)$ serves the reversed scattering process $\mathbf{p}', \mathbf{p}'_1 \rightarrow \mathbf{p}, \mathbf{p}_1$, see comment in the end of the previous section. As far as the momenta $\mathbf{p}', \mathbf{p}'_1$ and \mathbf{p}, \mathbf{p}_1 belong to one specific trajectory selected by a certain impact parameter we can construct the functions $\mathbf{p}'_1 = \mathbf{p}'(\mathbf{p}, \mathbf{p}_1)$; $\mathbf{p}' = \mathbf{p}'(\mathbf{p}, \mathbf{p}_1)$ and transform the measure in the above differential relation $d^3p' d^3p'_1 \Rightarrow d^3p d^3p_1$. In accordance with the statement of the Liouville's theorem of classical mechanics this differential measure transform is scaled by unit Jacobian. With making use

of the symmetry relation (1.22) and taking into account that for relative velocity $v'_0 = v_0$ we can rewrite (1.29) in the following form

$$dv' = d\sigma(\Omega, v_0) v_0 f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) d^3p d^3p_1 d^3r \quad (1.30)$$

Thus the in-scattering term can be expressed similarly to Eq. (1.26) for out-scattering term

$$a d^3r d^3p = \iint d\sigma(\Omega, v_0) v_0 f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) d^3p_1 d^3r d^3p \quad (1.31)$$

where linear momenta \mathbf{p}' , \mathbf{p}'_1 are assumed to be explicitly defined by \mathbf{p} , \mathbf{p}_1 for each scattering trajectory specified by differential cross section (impact parameter of the collision).

Both the contribution can be incorporated in one term of the symbolic collision time derivative (1.14)

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \iint d^3p_1 d\sigma(\Omega, v_0) v_0 [f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t)] \quad (1.32)$$

and it is known in the kinetic theory as collision integral. With substituting it into the balance relation (1.12) we obtain a closed master equation for the probability density function known as Boltzmann kinetic equation

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \iint d^3p_1 d\sigma(\Omega, v_0) v_0 [f' f'_1 - f f_1] \quad (1.33)$$

where we denoted $f \equiv f(\mathbf{r}, \mathbf{p}, t)$, $f_1 \equiv f(\mathbf{r}, \mathbf{p}_1, t)$, $f' \equiv f(\mathbf{r}, \mathbf{p}', t)$, $f'_1 \equiv f(\mathbf{r}, \mathbf{p}'_1, t)$. This equation was derived by famous Austrian theoretician **Ludwig Boltzmann** in 1872 and it entirely opens a family of so called kinetic master equations driving the macroscopic processes of mass/matter transfer, energy transfer, thermal conductivity, hydrodynamics and many other non-equilibrium phenomena associated with as classical as quantum self-consistent description of the macroscopic behavior of matter.

The external force \mathbf{F} can be associated either with gravity

$$\mathbf{F} = m\mathbf{g} = -mg \mathbf{e}_z \quad (1.34)$$

where $\mathbf{g} = -g \mathbf{e}_z$ is the gravitational acceleration directed opposite to z-axis, or with the Lorentz force of electromagnetic action on charged particles

$$\mathbf{F} = e\mathbf{E} + \frac{e}{mc} [\mathbf{p} \times \mathbf{B}] \quad (1.35)$$



FIG. 4: **Ludwig Boltzmann**, 1844-1906, University of Vienna, Austria, Germany

where e denotes the charge of the particle (normally of an electron or an ion in plasma) and $\mathbf{E} = \mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B} = \mathbf{B}(\mathbf{r}, t)$ are respectively electric and magnetic fields in the medium considered at the point of the particle position.

The derived equation is not fundamental physical equation and its applicability is restricted by the following assumptions concerning the spatial and temporal behavior of the probability density function. As clear from our discussion the elementary mesoscopic volume in position space d^3r cannot be considered as infinitely small and vanishing since its minimal scale δr is limited by a distance of interatomic interaction $O(1)a_0$, where $a_0 \sim 0.5 \cdot 10^{-8} \text{ cm}$ is the Bohr radius estimating a typical size of atoms or atomic particles, or small molecules. We have assumed by default that the spatial inhomogeneity of the probability density function $f = f(\mathbf{r}, \mathbf{p}, t)$ is weak and $|\nabla(\ln f)\delta\mathbf{r}| \ll 1$. Any suggested solution of the kinetic equation should satisfy this condition. Furthermore, when considering the dependence of function $f(\mathbf{r}, \mathbf{p}, t)$ on time we have to expect it as slow-varying during the collision time τ_c so that $|\partial(\ln f)/\partial t \tau_c| \ll 1$. Otherwise it would be impossible to think about collision as a shot-type event with negligible duration. The time increment dt should not be considered as infinitely short and its minimal scale δt could be taken as sufficiently longer than τ_c . It would be also valuable to justify that the internal correlations as well as the complex collisions with three or more partners, which we have ignored in our derivation, only negligibly affected the considered kinetic evolution of the probability density function. But that makes very



FIG. 5: **Andrey Markov**, 1856-1922, St-Petersburg University, Russian Empire/USSR.

subtle issue addressed to the theory of stochastic processes, which we avoid to discuss here. We readdress the listeners to the general probability theory of stochastic processes where the solution of Boltzmann equation is qualified as an example of so called Markovian-type stochastic processes often met in statistical physics. Hopefully all the above pointed restrictions are not so robust and most of the classical disordered systems existing in either gas or liquid phases can be described via relevant solutions of the Boltzmann equation.

From mathematical point of view the Boltzmann equation is a non-linear integro-differential equation, and its solution would be quite difficult to construct in general case. The differential part of this equation contains the partial derivative of the first order that makes specific problem with the boundary conditions. Nevertheless, as we show in the next lectures, the equation accepts approximate but physically clear transformation scheme to the set of macroscopic equations fairly described by the standard approaches of mathematical physics.

D. Equilibrium state. Maxwell-Boltzmann distribution

Let us consider equation (1.31) in a particular case when (i) there is no external force $\mathbf{F} = 0$, (ii) gas is spatially homogeneous $\partial f/\partial \mathbf{r} = 0$, and (iii) it exists in steady state conditions $\partial f/\partial t = 0$. Then the kinetic equation transforms to

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \iint d^3 p_1 d\sigma(\Omega, v_0) v_0 [f' f'_1 - f f_1] \equiv S(\mathbf{p}) = 0 \quad (1.36)$$

The function $f = f(\mathbf{p})$ now is only function of momentum and the collision integral is parameterized by arbitrary linear momentum \mathbf{p} as well. Then this equation can be fulfilled only if its integrand vanishes, so we get

$$f(\mathbf{p}') f(\mathbf{p}'_1) = f(\mathbf{p}) f(\mathbf{p}_1) \quad (1.37)$$

Take logarithm of this equation

$$\ln f(\mathbf{p}') + \ln f(\mathbf{p}'_1) = \ln f(\mathbf{p}) + \ln f(\mathbf{p}_1) \quad (1.38)$$

One can see that $\ln f$ should be expressed via those functions of the collision process which sum conserves before and after collision i.e. via so named additive integrals of motion. There is only limited number of such integrals namely number of particles, linear momentum and energy. So we get

$$\begin{aligned} \ln f(\mathbf{p}) &= \text{Const} + \beta \mathbf{u} \cdot \mathbf{p} - \beta \frac{\mathbf{p}^2}{2m} \\ &= \text{Const}' - \frac{\beta}{2m} [\mathbf{p} - m\mathbf{u}]^2 \end{aligned} \quad (1.39)$$

where $\text{Const} = \text{Const}' - \beta m \mathbf{u}^2/2$, \mathbf{u} and β are arbitrary constants.

Recalling the normalization condition (1.3) we arrive to the following probability density distribution for equilibrium gas

$$f(\mathbf{p}) = f_0(\mathbf{p}) = \frac{n_0}{(2\pi mT)^{3/2}} \exp \left[-\frac{(\mathbf{p} - m\mathbf{u})^2}{2mT} \right] \quad (1.40)$$

where $n_0 = N/V$ is the density of N -molecules distributed in the volume V , $T = \beta^{-1}$ is the gas temperature, \mathbf{u} is an average speed of the sample considered as a bulk object. It may seem surprising but, as follows from our derivation, the obtained Maxwell distribution is valid for any non-ideal gas. However the tricky point is that this observation gives us only

miserable support towards finding the thermodynamic properties of the gas or fluid and does not help us in constructing a macroscopic equation of state, thermal capacity etc. It is also important to point out that temperature T contributes in the derived solution (1.40) as external parameter associated with environment.[1]

In a more general situation when the molecules interact with a stationary external force having potential $\mathbf{F} = -\nabla U(\mathbf{r})$ (which can be either gravity or electric field) the steady state solution of the kinetic equation is given by the Maxwell-Boltzmann distribution

$$f = f_0(\mathbf{r}, \mathbf{p}) = \frac{n_0}{(2\pi mT)^{3/2}} \exp \left[-\frac{\mathbf{p}^2}{2mT} - \frac{U(\mathbf{r})}{T} \right] \quad (1.41)$$

Evidently we have to set $\mathbf{u} = 0$ for such a configuration and associate n_0 with the gas density at the point where $U(\mathbf{r}) = 0$. In the case of gravity the Maxwell-Boltzmann distribution leads to the well-known barometric formula for the pressure of a natural mixture of N_2 and O_2 molecules (air-gas) in the atmosphere.

E. Low of increasing entropy. Boltzmann H-theorem

The entropy balance is a fundamental signature of irreversibility of non-equilibrium processes driven by internal randomizing interactions in the macroscopic system. So we can expect that the derived equation (1.33) should confirm the law of increasing entropy in an isolated system. For the sake of simplicity consider again the situation in a particular case when (i) there is no external force $\mathbf{F} = 0$, and (ii) the gas is spatially homogeneous $\partial f / \partial \mathbf{r} = 0$.

The entropy is introduced as a functional of the probability density function, which is defined as follows

$$S[f] = - \iint d^3r d^3p f(\mathbf{r}, \mathbf{p}, t) \ln f(\mathbf{r}, \mathbf{p}, t) = S(t) \quad (1.42)$$

The functional approaches its maximum for the equilibrium distribution if the following conditions are fulfilled

$$\begin{aligned} \iint d^3r d^3p f(\mathbf{r}, \mathbf{p}, t) &= N \\ \iint d^3r d^3p \frac{\mathbf{p}^2}{2m} f(\mathbf{r}, \mathbf{p}, t) &= \bar{\epsilon}N = \bar{E} \end{aligned} \quad (1.43)$$

[1] Here we follow the system of units with Boltzmann constant $k_B = 1$ so that absolute temperature T is measured in energy units.

where $\bar{\epsilon}$ is an average kinetic energy of the molecule and \bar{E} is the total energy of the system. It can be straightforwardly verified that

$$S_{\max} = S[f_0] \quad (1.44)$$

where $f = f_0(\mathbf{p})$ is given by Eq. (1.40) considered in the internal reference frame of the sample with $\mathbf{u} = 0$. The temperature T would appear as Lagrange multiplier $\beta = T^{-1}$ associated with the second conditions presented in Eq. (1.43). The maximum of the entropy indicates that the system has attained a most chaotic distribution in its phase space.

The internal kinetic evolution of an isolated system is always accompanied by entropy increase. In order to prove this statement let us consider the time derivative

$$\frac{dS}{dt} = - \int \int d^3r d^3p \left[\frac{\partial f}{\partial t} \ln f + \frac{\partial f}{\partial t} \right] \quad (1.45)$$

For spatially homogeneous configuration we can omit the integral over \mathbf{r} as unimportant external factor, and then substitute the time derivative from the Boltzmann equation

$$\frac{dS}{dt} \propto - \int \int \int d^3p d^3p_1 d\sigma(\Omega, v_0) v_0 [f' f'_1 - f f_1] (\ln f + 1) \quad (1.46)$$

The integral in the right-hand side is closed over all the momentum variables and scattering directions. With making use - (i) of equivalence between the momenta \mathbf{p} and \mathbf{p}_1 in respect to the variable change $\mathbf{p} \leftrightarrow \mathbf{p}_1$; (ii) of the reversibility of the scattering process in respect to the extended change of internal variables $\mathbf{p}, \mathbf{p}_1 \leftrightarrow \mathbf{p}', \mathbf{p}'_1$, see Eq. (1.22); and (iii) of the Liouville's theorem $d^3p' d^3p'_1 = d^3p d^3p_1$ - we can transform (1.44) to the following form

$$\frac{dS}{dt} \propto - \int \int \int d^3p d^3p_1 d\sigma(\Omega, v_0) v_0 [f' f'_1 - f f_1] (\ln f f_1 - \ln f' f'_1) \quad (1.47)$$

As one can see for either case $f' f'_1 > f f_1$ or $f' f'_1 < f f_1$ we always have

$$\frac{dS}{dt} > 0 \quad (1.48)$$

Historically this consequence of the kinetic equation has been pointed out by Ludwig Boltzmann for another function $H(t) = -S(t)$, so it is known in the statistical theory as Boltzmann H -theorem.

We conclude this section by the following remark concerning validity of the obtained result. Of course, we can consider (1.47), (1.48) only as faithful justification but not complete and rigorous statistical prove for the law of increasing entropy. This complicated problem

needs much deeper insight, see our above comments concerning validity of the Boltzmann equation itself. The definition of the entropy functional, given by (1.42), completely ignores the correlations among the molecules and cannot be accepted for the systems considered near the critical points (i.e. near the points of phase transitions). In those cases the macroscopic behavior becomes extremely sensitive to quite subtle features of the interparticle interactions and the entire system gets ability for self-organization. The correct definition of the entropy should be based on a many particle probability density function determining the probability to observe the system in a certain point of its complete multi-dimension phase space. For further discussion we readdress the listeners to the special literature on statistical physics and thermodynamics [Radu Balescu, *Equilibrium and nonequilibrium statistical mechanics* (John Willey and Sons, Inc. 1975)].

Control exercises

Ex.1) Consider collision of two solid balls in their center-of-momentum reference frame. Find the differential cross-section and verify that this type of scattering is isotropic in that frame. Would this scattering process be isotropic in a laboratory reference frame? For this example approve the validity of the Liouville's theorem: $d^3p' d^3p'_1 = d^3p d^3p_1$

Ex.2) Generalize the Boltzmann equation for a gas mixture consisting of different chemical components.

Ex.3) Verify the solution (1.41) of the Boltzmann equation obtained in spatially inhomogeneous steady state conditions. Could we introduce the similar solution in the presence of magnetic field?

Ex.4) Consider atomic gas in an equilibrium conditions with the probability density function given by the Maxwell-Boltzmann distribution. Find the mean value for the velocity of a molecule and for the relative velocity for a pair of the molecules.

Ex.5) Approve that the entropy functional has a maximum given by Eq. (1.44) under conditions (1.43). What is physical meaning of the Lagrange multiplier for the condition expressed by the first line of (1.43)?

Ex.6) Derive Eq. (1.47) from Eq. (1.46).

II. MACROSCOPIC DESCRIPTION OF MATTER, MOTION AND ENERGY TRANSFER

In this part of our course we link the developed microscopic kinetic approach with a hydrodynamic approach, in-demanded for various applications and for description of the condensed disordered matter such as non-ideal gas or liquid. We will see that under the frame of the Boltzmann kinetic approach the well-known macroscopic equations of matter, motion and energy transfer can be connected with certain properties of the collision integral.

A. The important properties of the collision integral

Consider the collision integral as function of external variables

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \iint d^3p_1 d\sigma(\Omega, v_0) v_0 [f(\mathbf{r}, \mathbf{p}', t) f(\mathbf{r}, \mathbf{p}'_1, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_1, t)] = S(\mathbf{r}, \mathbf{p}, t) \quad (2.1)$$

Let us construct the following integral

$$\begin{aligned} G &= G(\mathbf{r}, t) \equiv \int d^3p \varphi(\mathbf{p}) S(\mathbf{r}, \mathbf{p}, t) \\ &= \iiint d^3p d^3p_1 d\sigma(\Omega, v_0) v_0 \varphi(\mathbf{p}) [f' f'_1 - f f_1] \end{aligned} \quad (2.2)$$

where $\varphi(\mathbf{p})$ is an arbitrary function of the molecule's linear momentum, which we will specify below. The constructed integral accumulates the complete set of the trajectories (parameterized by particles' momenta and impact parameters) so we have $\mathbf{p}'_1 = \mathbf{p}'(\mathbf{p}, \mathbf{p}_1)$; $\mathbf{p}' = \mathbf{p}'(\mathbf{p}, \mathbf{p}_1)$ for each contributing trajectory. We can formally redefine the internal variables $\mathbf{p}, \mathbf{p}_1 \leftrightarrow \mathbf{p}', \mathbf{p}'_1$ and express the integral (2.2) as follows

$$G = \iiint d^3p' d^3p'_1 d\sigma'(\Omega', v'_0) v'_0 \varphi(\mathbf{p}') [f f_1 - f' f'_1] \quad (2.3)$$

In accordance with Eq. (1.22) the collision $\mathbf{p}, \mathbf{p}_1 \rightarrow \mathbf{p}', \mathbf{p}'_1$ and $\mathbf{p}', \mathbf{p}'_1 \rightarrow \mathbf{p}, \mathbf{p}_1$ are provided by the same impact parameters (i.e. the same differential cross-sections). Making use of the Liouville's theorem: $d^3p' d^3p'_1 = d^3p d^3p_1$ and of conservation of the relative velocity we can make the following compilation of (2.2) and (2.3)

$$G = \frac{1}{2} \iiint d^3p d^3p_1 d\sigma(\Omega, v_0) v_0 [\varphi(\mathbf{p}) - \varphi(\mathbf{p}')] [f' f'_1 - f f_1] \quad (2.4)$$

This integrates all the momenta of projectiles (\mathbf{p}) and targets (\mathbf{p}_1) over all the scattering directions, so we can ignore conventional difference between these definitions for the differential cross-section. Once we change variables $\mathbf{p} \Leftrightarrow \mathbf{p}_1$ we obtain the following relation

$$G = \frac{1}{4} \iiint d^3p d^3p_1 d\sigma(\Omega, v_0) v_0 [\varphi(\mathbf{p}) + \varphi(\mathbf{p}_1) - \varphi(\mathbf{p}') - \varphi(\mathbf{p}'_1)] [f' f'_1 - f f_1] \quad (2.5)$$

Let us make the following three specific choices of function $\varphi = \varphi(\mathbf{p})$

$$\begin{aligned} \varphi(\mathbf{p}) &= 1 \\ \varphi(\mathbf{p}) &\Rightarrow \mathbf{p} \\ \varphi(\mathbf{p}) &= \frac{\mathbf{p}^2}{2m} \end{aligned} \quad (2.6)$$

Then we get $G = G(\mathbf{r}, t) \equiv 0$, which can be interpreted as macroscopic manifestation of the microscopic conservation laws associated with the two-particle collision. Indeed, the obtained result can be written in a symbolic balance form expressed in terms of the collision-type time derivative so that

$$\int d^3p \left(\frac{\partial f}{\partial t} \right)_{\text{col}} = \frac{\partial}{\partial t} n(\mathbf{r}, t) \Big|_{\text{col}} = 0 \quad (2.7)$$

means conservation of the density of the molecules (i. e. number of particles located in an elementary spatial volume). Next integral

$$\int d^3p \mathbf{p} \left(\frac{\partial f}{\partial t} \right)_{\text{col}} = \frac{\partial}{\partial t} [\langle \mathbf{p} \rangle n(\mathbf{r}, t)] \Big|_{\text{col}} = 0 \quad (2.8)$$

means conservation of the local density of momentum and

$$\int d^3p \frac{\mathbf{p}^2}{2m} \left(\frac{\partial f}{\partial t} \right)_{\text{col}} = \frac{\partial}{\partial t} \left[\left\langle \frac{\mathbf{p}^2}{2m} \right\rangle n(\mathbf{r}, t) \right] \Big|_{\text{col}} = 0 \quad (2.9)$$

means conservation of the local density of energy. In other words for any elementary volume in the coordinate space, considered at a certain moment of time, the total number of particles, total linear momentum and kinetic energy are unchanged in result of collision process.

B. Cross-over from the kinetic to hydrodynamic approach

The probability density function itself contains excessive information about momentum distribution, which is not so necessarily to know for description of the macroscopic hydrodynamic processes. The results of previous section encourage us to convert the kinetic equation

to the set of equations expressed directly for the parameters of the local density, flow velocity, and energy density, associated with the chaotic motion, inside the continuous medium.

Let us integrate the Boltzmann equation over the momentum \mathbf{p} . Then for the first term in the left-hand side of (1.33) we get

$$\int d^3p \frac{\partial f}{\partial t} = \frac{\partial}{\partial t} \int d^3p f(\mathbf{r}, \mathbf{p}, t) = \frac{\partial}{\partial t} n(\mathbf{r}, t) \quad (2.10)$$

The second term can be similarly transformed

$$\int d^3p \frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} = \frac{\partial}{\partial \mathbf{r}} \int d^3p \mathbf{v} f(\mathbf{r}, \mathbf{p}, t) = \frac{\partial}{\partial \mathbf{r}} [n(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)] \quad (2.11)$$

where

$$\mathbf{u}(\mathbf{r}, t) = \frac{\int d^3p \mathbf{v} f(\mathbf{r}, \mathbf{p}, t)}{\int d^3p f(\mathbf{r}, \mathbf{p}, t)} = \frac{1}{n(\mathbf{r}, t)} \int d^3p \mathbf{v} f(\mathbf{r}, \mathbf{p}, t) \quad (2.12)$$

is the flow velocity. The last term in the left-hand side vanishes after its integration over the momentum variable. Indeed if $\mathbf{F} = \mathbf{F}(\mathbf{r}, t)$ we straightforwardly obtain

$$\begin{aligned} \int d^3p \mathbf{F}(\mathbf{r}, t) \frac{\partial f}{\partial \mathbf{p}} &= \mathbf{F} \int d^3p \frac{\partial f}{\partial \mathbf{p}} = F_x \iint dp_y dp_z \int_{-\infty}^{\infty} dp_x \frac{\partial f}{\partial p_x} + \dots \\ &= F_x \iint dp_y dp_z f \Big|_{p_x \rightarrow -\infty}^{p_x \rightarrow \infty} + \dots = 0 \end{aligned} \quad (2.13)$$

where ellipses denote other projections. For magnetic component of the Lorentz force it is convenient to apply tensor notations so it is similarly transformed as

$$\int d^3p \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \frac{e}{mc} \iiint d^3p \epsilon_{ijk} p_j B_k \frac{\partial f}{\partial p_i} = \frac{e}{mc} \iint d^2p \epsilon_{ijk} p_j B_k f \Big|_{p_i \rightarrow -\infty}^{p_i \rightarrow \infty} = 0 \quad (2.14)$$

where we made use that $i \neq j$ in the Levi-Cevita symbol $\epsilon_{ijk} = \pm 1$ (where the (\pm) -sign is determined by either "even" or "odd" parity for the number of transpositions required to order the indices from $1, 2, 3 \rightarrow i, j, k$).

With having in mind Eq. (2.7) we obtain the well known continuity equation always valid for any continuous medium and reproducing the conservation law of matter itself

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \text{div} [\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)] = 0 \quad (2.15)$$

where we introduced the local [volumetric] mass density $\rho(\mathbf{r}, t) = m n(\mathbf{r}, t)$ as more common parameter in the hydrodynamic description of a continuous matter.

With multiplying Boltzmann equation on the momentum \mathbf{p} we can attempt to derive the equation of motion for the flow velocity $\mathbf{u}(\mathbf{r}, t)$. The first term in the left-hand side of (1.33) is transformed as follows

$$\int d^3p \mathbf{p} \frac{\partial f}{\partial t} = \frac{\partial}{\partial t} \int d^3p \mathbf{p} f(\mathbf{r}, \mathbf{p}, t) = \frac{\partial}{\partial t} [\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)] \quad (2.16)$$

For the transformation of the second term it is convenient to use tensor notations

$$\begin{aligned} \iiint d^3p p_i \left(\frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} \right) &= \iiint d^3p p_i \frac{p_j}{m} \frac{\partial f}{\partial x_j} = m \frac{\partial}{\partial x_j} \iiint d^3p v_i v_j f \\ &= \frac{\partial}{\partial x_j} [P_{ij} + u_i u_j \rho] \end{aligned} \quad (2.17)$$

where we denoted

$$P_{ij} = P_{ij}(\mathbf{r}, t) = m \iiint d^3p [v_i - u_i(\mathbf{r}, t)] [v_j - u_j(\mathbf{r}, t)] f(\mathbf{r}, \mathbf{p}, t) \quad (2.18)$$

and it introduces so named momentum flux tensor, which evaluates the transfer of either i -th or j -th momentum component of the chaotic motion transported in either j -th or i -th directions. This tensor is evidently symmetric $P_{ij} = P_{ji}$ and the random molecule velocity is centered here at the mean value of the local flow velocity.

The last term in the left-hand side of the kinetic equation can be independently transformed for the external forces of different types. If $\mathbf{F} = \mathbf{F}(\mathbf{r}, t)$ we get

$$\begin{aligned} \iiint d^3p p_i \left(\mathbf{F} \frac{\partial f}{\partial \mathbf{p}} \right) &= \iiint d^3p p_i F_j \frac{\partial f}{\partial p_j} = F_j \int \int d^2p p_i f \Big|_{p_j \rightarrow -\infty}^{p_j \rightarrow \infty} - F_j \iiint d^3p \frac{\partial p_i}{\partial p_j} f \\ &= -F_i n \equiv -\mathcal{F}_i \end{aligned} \quad (2.19)$$

where $\mathcal{F}(\mathbf{r}, t) = \mathbf{F}(\mathbf{r}, t) n(\mathbf{r}, t)$ is a volumetric density of the external force. For the magnetic component of the Lorentz force we get

$$\begin{aligned} \iiint d^3p p_i \frac{e}{mc} [\mathbf{p} \times \mathbf{B}]_j \frac{\partial f}{\partial p_j} &= \dots - \frac{e}{mc} \int \int \int d^3p [\mathbf{p} \times \mathbf{B}]_i f = -\frac{e}{c} [n \mathbf{u} \times \mathbf{B}]_i \\ &= -\frac{1}{c} [\mathbf{j} \times \mathbf{B}]_i \equiv -\mathcal{F}_i \end{aligned} \quad (2.20)$$

where ellipses denote the vanishing partial integral with the f -function taken at $p_j \rightarrow \pm\infty$. Here we introduced the current density vector for the charged particles in plasma $\mathbf{j} =$

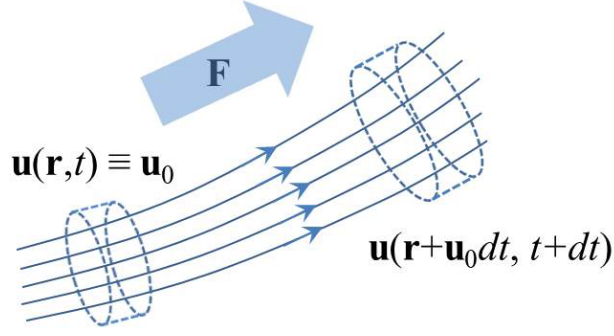


FIG. 6: An elementary fluid volume (indicated in dashed) is shown as drifting with the flow, interacting with environment (with the molecules from other proximal volumes), and driven by the external force \mathbf{F} . The dynamics of the process is described by the convective time derivative $D/Dt \equiv \partial/\partial t + \mathbf{u}\nabla$, which contributes to the respective equation of motion based on the second Newton's law.

$\mathbf{j}(\mathbf{r}, t) = e n(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)$. So \mathcal{F} has the same above given meaning of a volumetric density of the magnetic component of the Lorentz force.

Eventually in accordance with (2.8) we obtain the following macroscopic equation of motion

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j} [P_{ij} + u_i u_j \rho] = \mathcal{F}_i \quad (2.21)$$

which with the aid of continuity equation (2.15) can be transformed to

$$\frac{\partial}{\partial t} u_i(\mathbf{r}, t) + [\mathbf{u}(\mathbf{r}, t) \cdot \nabla] u_i(\mathbf{r}, t) = -\frac{1}{\rho(\mathbf{r}, t)} \frac{\partial}{\partial x_j} P_{ij}(\mathbf{r}, t) + \frac{1}{\rho(\mathbf{r}, t)} \mathcal{F}_i(\mathbf{r}, t) \quad (2.22)$$

In the derived equation its left-hand side performs acceleration of an elementary fluid volume drifting with the flow so that the total convective time derivative consists of both the partial time derivative and drift terms. The physical meaning of the convective derivative is clarified in Fig. 6.

Equation (2.22) describes the mechanical motion of an elementary fluid volume affected by the second Newton's law. The acceleration of the volume is mediated by two physical processes. First is an external force given by the last term in the right-hand side of the equation. The first term reveals the precursor of viscosity and describes the interfere between the different fluid volumes. As one can see here the microscopic nature of viscosity is connected with the mixing of the molecules from proximal volumes of a fluid flow. This

friction-type force can exist only in the non-equilibrium regime in a medium disturbed by external action and is characterized by the momentum flux tensor (2.18).

Let us introduce the mean value of kinetic energy associated with the chaotic motion of the molecules

$$\int d^3p \frac{m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2}{2} f(\mathbf{r}, \mathbf{p}, t) \equiv n(\mathbf{r}, t)W(\mathbf{r}, t) \equiv \rho(\mathbf{r}, t)U(\mathbf{r}, t) \quad (2.23)$$

where $W(\mathbf{r}, t)$ is the average energy density of chaotic motion normalized to unit volume and $U(\mathbf{r}, t)$ is the same density but normalized to unit mass. With addressing to the problem of non-equilibrium thermodynamics the introduced quantity $U(\mathbf{r}, t)$ is normally called as thermal energy or thermal internal energy of the medium and it contributes to the equation of heat transfer, to the entropy balance and to the temperature distribution in a Boltzmann gas.

With multiplying Boltzmann equation on $m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2/2$ and integrating it over the momentum \mathbf{p} we can attempt to derive the equation of heat transfer. Then the first term in the left-hand side of the Boltzmann equation (1.33) is transformed as follows

$$\int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} \frac{\partial f}{\partial t} = \frac{\partial}{\partial t} \int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} f + m \frac{\partial \mathbf{u}}{\partial t} \int d^3p [\mathbf{v} - \mathbf{u}] f = \frac{\partial}{\partial t} [\rho U] \quad (2.24)$$

where the last integral vanishes because of $\langle \mathbf{v} \rangle = \mathbf{u}$. The second term is transformed as

$$\begin{aligned} \int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} \mathbf{v} \frac{\partial f}{\partial \mathbf{r}} &= \frac{\partial}{\partial \mathbf{r}} \int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} \mathbf{v} f + m \frac{\partial u_i}{\partial x_j} \int d^3p [v_i - u_i] v_j f \\ &= \text{div}[\mathbf{J} + \mathbf{u} \rho U] + \frac{\partial u_i}{\partial x_j} P_{ij} \end{aligned} \quad (2.25)$$

where

$$\mathbf{J} = \mathbf{J}(\mathbf{r}, t) = \int d^3p \frac{m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2}{2} [\mathbf{v} - \mathbf{u}(\mathbf{r}, t)] f(\mathbf{r}, \mathbf{p}, t) \quad (2.26)$$

is the so named heat flux or heat flux density and the momentum flux tensor was earlier introduced by Eq. (2.18). The third term in the left-hand side of the Boltzmann equation vanishes since the integral

$$\int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = 0 \quad (2.27)$$

for the external force of any type. We leave this statement as to be proven by the listeners and just point out here its physical evidence. Indeed the external force can only mediate the mechanical motion of the gas, as shown in Fig. 6, and cannot affect the internal chaotic motion inside the medium.

In accordance with (2.9) we obtain the following equation of the heat transfer

$$\frac{\partial}{\partial t}[\rho U] + \text{div}[\mathbf{J} + \mathbf{u} \rho U] + \frac{\partial u_i}{\partial x_j} P_{ij} = 0 \quad (2.28)$$

which with the aid of continuity equation (2.15) can be transformed to

$$\frac{\partial}{\partial t} U(\mathbf{r}, t) + [\mathbf{u}(\mathbf{r}, t) \cdot \nabla] U(\mathbf{r}, t) = -\frac{1}{\rho(\mathbf{r}, t)} P_{ij}(\mathbf{r}, t) \frac{\partial}{\partial x_j} u_i(\mathbf{r}, t) - \frac{1}{\rho(\mathbf{r}, t)} \text{div}[\mathbf{J}(\mathbf{r}, t)] \quad (2.29)$$

where in the left-hand side we have constructed the same convective time derivative as in equation of motion (2.22). As one can see the internal thermal energy of the medium is balanced by two processes: (i) the dissipation of the kinetic energy of the regular motion, which is expressed by the first term in the right-hand side; (ii) and by the heat transfer between different parts of the medium, which is expressed by the second term in the right-hand side.

Although the derived equations have quite natural physical interpretation they mostly useless for practical implementations. That is because these equations are not closed and contain the momentum flux tensor (2.18) and the heat flux vector (2.26) as unknown parameters of the non-equilibrium processes. These quantities are defined as the statistical momenta of higher order, which could be evaluated only if the probability density function was known. Apparently it would be impossible to construct the separate equations for such statistical momenta as far as the collision integral would not vanish in that case. That turns us back to the main problem of solution of the Boltzmann equation at least in certain approximations, which we will do in the next part of our course.

C. Equation of motion for an ideal incompressible fluid

The equation of motion can be considered as closed for a specific example of ideal incompressible fluid. Let us assume that the mass density $\rho = \text{const}$ and ignore any manifestation of viscosity such that the momentum flux tensor has diagonal form

$$P_{ij}(\mathbf{r}, t) = \delta_{ij} P(\mathbf{r}, t) \quad (2.30)$$



FIG. 7: **Leonhard Euler**, 1707-1783 - University of Basel, Switzerland and Kingdom of Prussia; Imperial Russian Academy of Sciences, St-Petersburg, Russian Empire.

where $P = P(\mathbf{r}, t)$ should be associated with the local pressure of the fluid substance. Indeed the equation of motion (2.22) and continuity equation (2.15) are transformed to

$$\frac{D\mathbf{u}}{Dt} \equiv \frac{\partial\mathbf{u}}{\partial t} + [\mathbf{u} \cdot \nabla]\mathbf{u} = -\frac{1}{\rho} \text{grad}P + \frac{1}{\rho} \mathcal{F}$$

$$\text{div } \mathbf{u} = 0 \tag{2.31}$$

With constructing integral over an arbitrary volume of the sample and converting it to the surface integral over the bounding surface S

$$-\int d^3r \text{grad}P = -\oint d\mathbf{S} P \tag{2.32}$$

we arrive to the conventional definition of the pressure as an internal surface force pressing a unit area inside the medium. Furthermore the pressure and the active force \mathcal{F} can be considered as given external parameters driving the flow motion and equations (2.31) become closed. In hydrodynamics they are known as Euler equations (Not to be confused with Euler's equation of rigid body dynamics!). **Leonhard Euler** was the famous Russian academician who proposed a lot of brilliant ideas in mechanics, hydrodynamics and had contributed to the fundamental areas in mathematics such as theory of complex numbers, differential equations etc..

Of course, such a simplified description of the fluid dynamics can be considered only as initial and quite rough approximation. But for the flow with rather small viscosity but at the same time described by a large Reynolds number ($Re = \rho u_\infty L/\eta \gg 1$, where L is the scale of a macroscopic object, η is the matter viscosity, and u_∞ is the asymptotic speed of the fluid stream sweeping the object) it gives a good starting point for constructing a suitable solution of the entire hydrodynamic equations. As example, for the steady state regime the flow of ideal fluid obeys the so named Bernoulli's principle

$$\frac{\rho \mathbf{u}^2}{2} + P + \rho g z = \text{const} \quad (2.33)$$

which is conserved along any streamline of incompressible ideal fluid. From an engineering point of view that gives simple estimate for the balance between the pressure and local flow velocity in a fluid stream transporting through pipes or inside spatially bounded volumes.

Control exercises

Ex.1) Verify that for a two-particle collision the angular momentum conservation law $\mathbf{r} \times \mathbf{p} + \mathbf{r}_1 \times \mathbf{p}_1 = \mathbf{r}' \times \mathbf{p}' + \mathbf{r}'_1 \times \mathbf{p}'_1$ (where $\mathbf{r}, \mathbf{r}_1, \mathbf{r}', \mathbf{r}'_1$ are the spatial coordinates of the particles before and after collision defined in respect to any reference frame) is a direct consequence of the conservation laws for linear momentum and energy and therefore is already included into the macroscopic balance equations (2.7)-(2.9).

Ex.2) Evaluate integral (2.27) and show that it vanishes for any type of external force.

Ex.3) Consider the continuity equation (2.15) in the stationary case $\partial\rho/\partial t = 0$ when $\text{div}\rho\mathbf{u} = 0$. There are two types of the fluid flow associated with this conditions. The streamlines can be performed by either open lines (tubes) or by closed circuits. What kind of differential criteria for $\mathbf{u} = \mathbf{u}(\mathbf{r})$ describe the fluid motion for either of these cases.

Ex.4) Approve the identity (2.32) as a consequence of divergence theorem, also known as Gauss's theorem or Ostrogradsky's theorem.

Ex.5) For ideal two-dimensional fluid stream introduce the scalar potential and scalar stream functions. What is the mathematical and physical difference between these quantities? Find the differential equations for these functions. Combine both the functions into one complex-

number potential with expressing x, y coordinates as one complex variable $z = x + i y$ in the complex plane.

Ex.6) The streamlines are defined as the geometrical lines along which the differential increments dl_x, dl_y and dl_z obey the rule

$$\frac{dl_x}{u_x} = \frac{dl_y}{u_y} = \frac{dl_z}{u_z}$$

Approve the Bernoulli's principle (2.33) for ideal incompressible fluid. What are the physical conditions justifying the incompressibility as an accessible assumption for a real fluid? Verify that in such a case the flow velocity, contributing into the Reynolds number associated with the macroscopic object swept by the fluid stream, should be much less than the speed of sound in the medium.

III. BASIC EQUATION OF HYDRODYNAMICS IN CLOSED FORM

A. Local thermodynamic equilibrium

As we know the equilibrium conditions the solution of Boltzmann equation is given by Eq. (1.40) with a given temperature $T = \text{const}$, flow velocity $\mathbf{u} = \text{const}$, and density $n = \text{const}$. It seems quite natural to think about a general non-equilibrium systems as structured by a number of small subsystems, which are in internal equilibrium themselves but not in equilibrium each other. Then we can expect that the probability density function has the same form (1.40), but the above parameters should be considered as function of spatial position and time and be associated with an instant macroscopic state of a particular subsystem, so that $T = T(\mathbf{r}, t)$, $\mathbf{u} = \mathbf{u}(\mathbf{r}, t)$ and $n = n(\mathbf{r}, t)$. Once these parameters are slow varied functions of their arguments the entire hydrodynamic process is called as local thermodynamic equilibrium.^[2]

Considering the the system parameters as slow-varying, smooth and continuous functions of position and time, one can assume the probability density function in the following form

$$f^{(0)} = f^{(0)}(\mathbf{r}, \mathbf{p}, t) = \frac{n(\mathbf{r}, t)}{(2\pi m T(\mathbf{r}, t))^{3/2}} \exp \left[-\frac{(\mathbf{p} - m \mathbf{u}(\mathbf{r}, t))^2}{2mT} \right] \quad (3.1)$$

In accordance with our basic assumption the functions $T = T(\mathbf{r}, t)$, $n = n(\mathbf{r}, t)$, and each vector component of $\mathbf{u} = \mathbf{u}(\mathbf{r}, t)$ should obey the inequalities

$$\begin{aligned} |\nabla \ln T| \Lambda \ll 1, \quad |\nabla \ln n| \Lambda \ll 1, \quad \left| \frac{\partial u_i}{\partial x_j} \right| \Lambda \ll |\mathbf{u}| \\ \left| \frac{\partial}{\partial t} \ln T \right| \tau \ll 1, \quad \left| \frac{\partial}{\partial t} \ln n \right| \tau \ll 1, \quad \left| \frac{\partial u_i}{\partial t} \right| \tau \ll |\mathbf{u}| \end{aligned} \quad (3.2)$$

where Λ and τ are respectively the mean free path and flight time for a molecule in the medium.

Substitute approximation (3.1) in the definitions of the momentum flux tensor (2.18) and

[2] It is noteworthy to point out that the considered macroscopic state is not a general non-equilibrium matter state. Inside any elementary volume of a piece of matter its different chemical components or even different internal degrees of freedom (such as spin, vibrational, etc.) of the same component can have different temperatures and density distributions.

thermal flux (2.26)

$$\begin{aligned}
P_{ij}^{(0)}(\mathbf{r}, t) &= m \int d^3p [v_i - u_i(\mathbf{r}, t)] [v_j - u_j(\mathbf{r}, t)] f^{(0)}(\mathbf{r}, \mathbf{p}, t) = n(\mathbf{r}, t) T(\mathbf{r}, t) \delta_{ij} \\
\mathbf{J}^{(0)}(\mathbf{r}, t) &= \int d^3p \frac{m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2}{2} [\mathbf{v} - \mathbf{u}(\mathbf{r}, t)] f(\mathbf{r}, \mathbf{p}, t)
\end{aligned} \tag{3.3}$$

With accepting that the non ideal gas approximately satisfies the macroscopic equation of state of ideal gas we get $nT = P$, where $P = P(\mathbf{r}, t)$ is instant value of the local pressure. Then the basic hydrodynamic equations, introduced in the previous section, can be simplified to the following form

$$\begin{aligned}
\frac{\partial \rho}{\partial t} + \text{div} [\rho \mathbf{u}] &= 0 \\
\frac{\partial \mathbf{u}}{\partial t} + [\mathbf{u} \cdot \nabla] \mathbf{u} &= -\frac{1}{\rho} \text{grad} P + \frac{1}{\rho} \mathcal{F} \\
\frac{\partial U}{\partial t} + [\mathbf{u} \cdot \nabla] U &= -\frac{P}{\rho} \text{div} \mathbf{u}
\end{aligned} \tag{3.4}$$

Within the made approximations, and after evaluating integral (2.23), the thermal energy can be expressed by the temperature distribution

$$\begin{aligned}
\rho U &= \int d^3p \frac{m[\mathbf{v} - \mathbf{u}]^2}{2} f^{(0)} = \frac{3}{2} n T \\
U &= U(\mathbf{r}, t) = \frac{3 T(\mathbf{r}, t)}{2 m}
\end{aligned} \tag{3.5}$$

and the hydrodynamic equations can be performed in the following closed form

$$\begin{aligned}
\frac{\partial \rho}{\partial t} + \text{div} [\rho \mathbf{u}] &= 0 \\
\frac{\partial \mathbf{u}}{\partial t} + [\mathbf{u} \cdot \nabla] \mathbf{u} &= -\frac{1}{\rho} \text{grad} P + \frac{1}{\rho} \mathcal{F} \\
\frac{\partial T}{\partial t} + [\mathbf{u} \cdot \nabla] T &= -\frac{2}{3} T \text{div} \mathbf{u}
\end{aligned} \tag{3.6}$$

where in the second line we accept the equation of state $P = \rho T/m$.

Although we obtain here an evident generalization of the Euler equations (2.31), which are now valid for compressible gas, nevertheless its applicability is strongly restricted by quite rough approximation of the weak and even negligible non-ideality. Such important physical phenomena as fluid viscosity, thermal conductivity etc. are completely lost in the above derivation. These phenomena are strongly connected with the internal interaction processes and can be properly introduced after solution of the kinetic Boltzmann equation with better accuracy than simple zero-level approximation (3.1).

B. Chapman-Enskog method for solution of the Boltzmann kinetic equation

The method allows to find the solution of the Boltzmann equation with considering non-ideality as leading to a small correction of the basic approximation (3.1). The interaction itself can be strong but the deviation of the system state from the local thermal equilibrium is scaled by large spatial inhomogeneity and by long relaxation time. In other words, all the derivatives in the left-hand size of the Boltzmann equation give only small increments on a spatial scale Λ and for duration τ . For the system parameters that is justified by inequalities (3.2). We will also assume that the external driving force only slightly affects the random motion of the molecule on a distance Λ and on a time scale τ .

Let us reproduce the Boltzmann equation (1.33) in the following form

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \frac{1}{\epsilon} \iint d^3 p_1 d\sigma(\Omega, v_0) v_0 [f' f'_1 - f f_1] \equiv \frac{1}{\epsilon} S[f, f_1] \quad (3.7)$$

which emphasizes that the collision integral, denoted here as $S[f, f_1]$, can be entirely understood as a functional of the probability density function. The formal number parameter $\epsilon = 1$, but it lets us construct the searched solution by its expansion in the power series of $\epsilon^0, \epsilon^1, \epsilon^2, \dots$ as analytical function

$$f(\mathbf{r}, \mathbf{p}, t) = f^{(0)}(\mathbf{r}, \mathbf{p}, t) + \epsilon f^{(1)}(\mathbf{r}, \mathbf{p}, t) + \epsilon^2 f^{(2)}(\mathbf{r}, \mathbf{p}, t) + \dots \quad (3.8)$$

In the main order in this power expansion, substituted into the Boltzmann equation, i.e. for power ϵ^{-1} , $f^{(0)}$ is given by the local equilibrium distribution (3.1) and fulfils the equation

$$0 = S[f^{(0)}, f_1^{(0)}] \quad (3.9)$$

in the order of ϵ^0 we get

$$\frac{\partial f^{(0)}}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial f^{(0)}}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f^{(0)}}{\partial \mathbf{p}} = S[f^{(0)}, f_1^{(1)}] + S[f^{(1)}, f_1^{(0)}] \quad (3.10)$$

and in the next order of ϵ^1 we obtain

$$\frac{\partial f^{(1)}}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial f^{(1)}}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f^{(1)}}{\partial \mathbf{p}} = S[f^{(0)}, f_1^{(2)}] + S[f^{(2)}, f_1^{(0)}] + S[f^{(1)}, f_1^{(1)}] \quad (3.11)$$

and so on. In accordance with the above arguments we will consider this expansion as rapidly converging, such that $f^{(0)} \gg f^{(1)} \gg f^{(2)} \gg \dots$

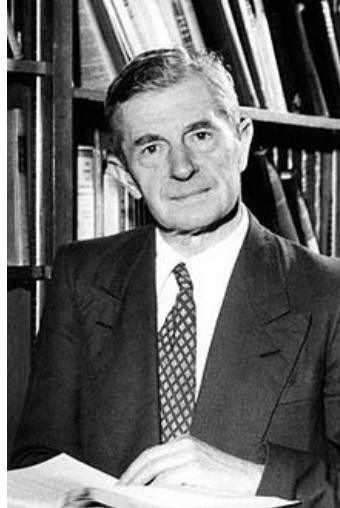


FIG. 8: **Sydney Chapman**, 1888-1970 - University of Manchester, University of Cambridge, Imperial College London, University of Oxford, The Queen's College, Oxford Royal Observatory, Greenwich, Great Britain.



FIG. 9: **David Enskog**, 1884-1947 - Université d'Uppsala, Sweden.