

Elements of Kinetic Theory

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A fundamental analysis of macroscopic system dynamics, starting from the consideration of the individual movement of each particle, in order to obtain the properties of the fluid as a whole, is reviewed. Such an approach is known as Kinetic Theory (KT). In this monograph, we consider a dilute gas and analyze the behavior of the system, firstly, in a less rigorous way, in order to gain some insight on how to deduce the equations that describe the dynamics. Later on, we make use of the tools of KT, properly, in order to describe the dynamics without much inconsistencies, thereby showing that transport equations are closely related to conservation laws. The main goal here is to deduce the Navier-Stokes equation from elementary principles.

I. INTRODUCTION

In introductory topics on the study of the thermodynamics associated to a fluid, one generally analyzes the behavior of the system in the equilibrium condition. The same is true for early studies on statistical mechanics. Thermodynamically, the balance characteristics of macroscopic systems are presented from concepts associated with internal energy, entropy, number of particles, pressure, volume, surface tension, polarization, and magnetization. All results obtained from macroscopic analysis can be described as consequences of the microscopic evolution of the system, since one knows that those systems are composed of particles whose interactions and dynamics are fundamentally explained from the mechanical theories. The statistical mechanics becomes responsible for relating both approaches, micro and macroscopic, starting from the Lagrangian and Hamiltonian formulations, to obtain the general characteristics in equilibrium.

A configuration is dictated in thermodynamic equilibrium if it is in mechanical, chemical, and thermal equilibrium. Under those conditions, it is evident that there will be no tendency for any change of state, either of the system or of the neighborhood, over time. That state is interesting because, in particular, any system tends to balance if allowed to evolve in a sufficiently large time. The investigation of problems involving temporal dependence on changes of state is carried out by other branches of science, such as hydrodynamics and kinetic theory.

Immediately, it becomes interesting to describe the system if it is out of balance. Of course, the number of non-equilibrium states is huge in the state space of a fluid, most of which are uninteresting due to complexity, thereby hardly yielding any relevant behavior, in addition to being fleeting, changing rapidly in general terms. The situations for which they yield behaviors of interest are those for which the characteristics in the configuration dynamics remain constant for a long period of time.

Such behaviors are characteristic for systems that are close to equilibrium, i.e., "states of non-equilibrium" will, from now on, be "near equilibrium".

This monograph is organized as follows: In Section II, we present a brief description of transport properties in a simple system with a general analysis of some concepts that are involved. In Section III, we derive the transport properties using the kinetic theory (KT) approach to suppress the inconsistencies that appear in the previous section. Finally, in Section IV, we show how the Navier-Stokes (NS) equation is derived from the fluid momentum conservation properties. The text is based upon Refs. [1] to [6], as shown at the end of the monograph.

II. COLLISIONS

For collisions, we consider a gas of volume V occupied by N molecules, and ignore the possible interactions between the particles. We assume that previous results of statistical mechanics are unknown, except for the Maxwell-Boltzmann (MB) probability distribution for the velocity of the gas particles.

The probability that a molecule has velocity \vec{v} within a small volume d^3v in the neighbourhood of \vec{v} is

$$f(\vec{v}) d^3v = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\vec{v}^2}{2k_B T}} d^3v. \quad (1)$$

Considering the particle diameter as d , i.e., its radius being $d/2$, we have the particle with an area $\pi(d/2)^2$. Yet, we have that the effective cross-sectional area is πd^2 . If this particle travels a distance l , we can define the *mean free path* as the distance traveled by the molecule between successive collision. We have from $V/N = \pi d^2 l$,

$$l = \frac{V}{\pi d^2 N} = \frac{1}{n \pi d^2} \quad (2)$$

where n is the particle density.

Let us now assume that $d \ll l$, i. e., the gas is dilute.

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A. Relaxation Time

Relaxation time, or scattering time, is the average time between successive collisions. Let \bar{v}_{rel} be the average relative velocity of the gas molecules. The relaxation time is

$$\tau = \frac{l}{\bar{v}_{rel}}. \quad (3)$$

The average relative speed for two particles with velocities \vec{v} and \vec{v}' is

$$\begin{aligned} \bar{v}_{rel}^2 &= \langle (\vec{v} - \vec{v}')^2 \rangle = \int d^3\vec{v} \int d^3\vec{v}' (\vec{v} - \vec{v}')^2 f(\vec{v}) f(\vec{v}') \\ &= \langle v^2 \rangle + \langle v'^2 \rangle - 2 \langle \vec{v} \cdot \vec{v}' \rangle \end{aligned} \quad (4)$$

where $f(\vec{v})$ is the MB distribution (1), and we have the distributions $f(\vec{v})$ and $f(\vec{v}')$ because we are assuming that the velocities are uncorrelated.

In (4), the term $\langle \vec{v} \cdot \vec{v}' \rangle$ vanishes because the velocity of each particle is independent and the average velocity in i -direction vanishes ($\langle v_i \rangle = 0$), with $i = x, y, z$. However, as $\langle v^2 \rangle = \langle v'^2 \rangle$, we get $\bar{v}_{rel}^2 = 2 \langle v^2 \rangle$.

From the MB distribution, we get $\langle v^2 \rangle = 3k_B T/m$, and this result is the same as that obtained by using the equipartition theorem. Therefore, we have, for the average relative speed and relaxation time, respectively,

$$\bar{v}_{rel}^2 = \frac{6k_B T}{m} \quad ; \quad \tau = \frac{1}{n\pi d^2} \sqrt{\frac{m}{6k_B T}}. \quad (5)$$

Another interpretation for the relaxation time comes from assuming that the probability of collision for a molecule between times t and $t + dt$ is ωdt , with ω constant meaning that no memory of the previous collisions is kept. Let $P(t)$ be the probability that a particle will reach time t without collision. Then the probability of reaching time $t + dt$ without collision is

$$P(t + dt) = P(t) (1 - \omega dt), \quad (6)$$

and, in a differential equation form,

$$\frac{dP}{dt} = -\omega P \Rightarrow P(t) = \omega e^{-\omega t} \quad (7)$$

with $\int_0^\infty P(t) dt = 1$. Therefore, the average time between successive collisions is

$$\int_0^\infty t P(t) dt = \frac{1}{\omega} \quad (8)$$

that we call the relaxation time τ , and the collision rate is $1/\tau$.

B. Basics of Transport

We now turn to the question of how macroscopic properties evolve in time if the system is out of equilibrium. Processes for which the particle number, momentum, or energy change over time are referred to as a *transport*. Those quantities normally flow to the equilibrium state.

1. Diffusion

To describe a simple model that captures the dynamics of any particle, somewhat jittery, we will analyze the random walk and the diffusion equation for which the system is associated.

For the **Random Walk**, we can consider a model for which the particle sits on a one dimensional lattice, the spacing between the lattice sites being the mean free path l , and, after the relaxation time τ , the particle jumps to the left or right with equal probability, 50%. Consider a particle on the origin, in time $t = 0$. Our goal is to calculate the probability that the particle, at time $t = N\tau$, sits on $x = ml$, m an integer. Being $P(x, t)$ that probability and, by considering $m \ll N$, the probability to get the particle on the site $x = ml$ is given by the different ways the particle made $\frac{1}{2}(N \pm m)$ forward and backwards jumps, divided by the total number of possible combinations, 2^N . Using Stirling's approximation to the factorials, we can write

$$P(x, t) = \frac{2^{-N} N!}{[\frac{1}{2}(N+m)]! [\frac{1}{2}(N-m)]!} \approx \sqrt{\frac{2}{\pi N}} e^{-m^2/2N} \quad (9)$$

and the probability distribution of the particle is a Gaussian ensemble.

So, if we calculate the mean, variance and the growths of the root-mean-square distance for the configuration, we get

$$\langle x \rangle = 0 \quad ; \quad \langle x^2 \rangle = \frac{l^2}{\tau} t \quad ; \quad \sqrt{\langle x^2 \rangle} \sim \sqrt{t} \quad (10)$$

which characterizes a random walk behavior. For a generalization in three dimensions, we can describe this behavior by considering a cubic lattice for which the motion can proceed along each direction in an independent and equally probable way. On average, the motion of a particle along the i -direction will occur only every 3τ . Thus, $\langle i^2 \rangle = l^2 t / 3\tau$, and the variance,

$$\langle \vec{x}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = \frac{l^2}{\tau} t \quad (11)$$

remains unchanged.

Let us turn now to the diffusion equation approach. In a system out of equilibrium, the particle density, $n =$

N/V , is not a constant and we have that the gradient of n leads to a flow between the regions of high and low density. In a one dimensional configuration, consider that the density at some fixed time is $n = n(x, t)$. Then, to derive an expression for n at the same point, at a later time $t + \Delta t$, we can make use of the fact that any particle at x , at time $t + \Delta t$, was situated at some other position $x - \Delta x$, at time t . Here, Δx is a random variable because some particles move one way, some the other, and the density can be written as an average over all different Δx 's,

$$\begin{aligned} n(t + \Delta t, x) &= \langle n(t, x - \Delta x) \rangle \\ &= n(t, x) - \frac{\partial n}{\partial x} \langle \Delta x \rangle + \frac{1}{2} \frac{\partial^2 n}{\partial x^2} \langle \Delta x^2 \rangle + \dots \end{aligned} \quad (12)$$

The fact that $\langle \Delta x \rangle = 0$ implies the *diffusion equation*

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad (13)$$

where $D = \langle \Delta x^2 \rangle / 2\Delta t$ is the diffusion coefficient.

The derivation above can be extended to three dimensions by following the same logic. We find

$$\frac{\partial n}{\partial t} = D \nabla^2 n \quad (14)$$

known as *Fick's second law*. We expect the diffusion coefficient D to be related to the mean free path l and relaxation time τ as $D \sim l^2/\tau$ in both cases.

2. Viscosity

Viscosity is a measure of the resistance to fluid movement. We can describe it as a form of internal friction, by measuring the drag forces between two plates, holding the lower plate stationary and taking the upper plate with a constant speed u . To keep the top plate with velocity u , we need to apply a force F on it, because the fluid pushes it back. Close to the top plate, the fluid travels with the same speed, and, by momentum transport, the fluid close to the bottom plate remains stationary, and that characterizes a velocity gradient in the z -direction. Experimentally,

$$\frac{F}{A} = \eta \frac{du_x}{dz} \quad (15)$$

and the force per unit area exerted in the top plate is proportional to the velocity gradient. The coefficient of proportionality η is the *viscosity*.

To derive the expression (15) from first principles, we can suppose a slab of gas at some fixed value of z . How

many particles in the fluid, with density $n = N/V$, pass through the slab depends on how fast they travel in the z -direction and that is given by the MB distribution (1), and the number of particles per unit area, per unit time, whose speed is in the vicinity of \vec{v} , passing through a horizontal slab, $\#$, is

$$\# = nv_z f(\vec{v}) d^3v. \quad (16)$$

To calculate the momentum that each of those molecules imparts to the slab, let us consider the particles that hit other particles, coming from above the slab. If they arrive from a position $z + \Delta z$,

$$\Delta p = m [u_x(z + \Delta z) - u_x(z)] \approx m \frac{du_x}{dz} \Delta z \quad (17)$$

where $\Delta z = l \cos \theta$, l is the mean free path, and θ is the angle at which the particles arrive. Here, $\theta \in [0, \frac{\pi}{2}]$.

By identifying $\Delta p/\Delta t$ as the force of the fluid pushing back and F as the force applied to keep the flow moving, we can write

$$\frac{F}{A} = -\frac{1}{A} \frac{\Delta p}{\Delta t} \quad (18)$$

and by considering (16), we get

$$\begin{aligned} \frac{F}{A} &= -n \int d^3v \Delta p v_z f(\vec{v}) \\ &= -mn \frac{du_x}{dz} \int d^3v v_z \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} l \cos \theta \end{aligned} \quad (19)$$

where we have assumed, at the same time, that the fluid has an average speed $\langle v_x \rangle = u_x$, in the x -direction, and that $\langle v_x \rangle = 0$ for the particles speed due to the MB distribution. If the velocity of the flow $u \ll \langle v \rangle$, the average velocity of particles in the fluid, then this is not a bad approximation. For a heuristic derivation, that is valid. In polar coordinates, we have

$$\begin{aligned} \frac{F}{A} &= mn \frac{du_x}{dz} \int dv v^2 \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi (-v \cos \theta) l \cos \theta \\ &\quad \times \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}. \end{aligned} \quad (20)$$

Solving for the angular coordinates, we get

$$\frac{F}{A} = \frac{mnl}{3} \frac{du_x}{dz} \int dv 4\pi v^3 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta mv^2/2} \quad (21)$$

where $\beta = 1/k_B T$. We can identify the integral $\int dv$ as the expression for $\langle v \rangle$, the average speed. Therefore,

$$\frac{F}{A} = \frac{1}{3} m n l \langle v \rangle \frac{du_x}{dz}. \quad (22)$$

Comparison with (15), yields the viscosity

$$\eta = \frac{1}{3} m n l \langle v \rangle. \quad (23)$$

3. Thermal Conductivity

Suppose a fluid between two plates, each at a different temperature. We have a flow of energy in the fluid that can be represented by a heat flow vector \vec{q} defined by the energy per unit time passing through an area, perpendicular to \vec{q} . Experimentally, the heat flow

$$\vec{q} = -\kappa \nabla T \quad (24)$$

is proportional to the temperature gradient, where the constant of proportionality κ is the *thermal conductivity*.

Similarly to the construction made for the viscosity, we will derive that empirical law and find an expression for κ . By assuming a temperature gradient in the z -direction, the number of particles that pass through a slab per unit area per unit time, with velocity \vec{v} , is given by the equation (16), and, by making use of the equipartition theorem, the average energy is

$$E(z) = \frac{3}{2} k_B T(z) \quad (25)$$

and, by adopting that the energy grows with z , we have

$$\Delta E = E(z + \Delta z) - E(z) = \frac{3}{2} k_B \frac{dT}{dz} \Delta z \quad (26)$$

where $\Delta z = l \cos \theta$.

Here, as in the case for the viscosity, we have an inconsistency. The energy deposited or gained by a particle should depend on the speed of the particle, which is characterized by the MB distribution, and that did not occur here.

Now, by computing the heat flow, we have

$$|\vec{q}| = n \int d^3v \Delta E v_z f(v) \quad (27)$$

and, by solving the integrals, as in case for the viscosity,

$$|\vec{q}| = -\frac{1}{2} k_B n l \langle v \rangle \frac{dT}{dz} \quad (28)$$

that is the law of heat flow, and we can express the thermal conductivity, as usually given in terms of the specific heat at constant volume c_V , as

$$\kappa = \frac{1}{3} c_V l \langle v \rangle \quad ; \quad c_V = \frac{3}{2} n k_B. \quad (29)$$

4. Diffusion and Conservation

Viscosity is about the transport of momentum and thermal conductivity is about the transport of energy. Moreover, both, momentum and energy, are conserved. As the total energy of a system is conserved, we have that the variation of energy in a region is transported to its neighborhood, and that is the meaning of heat flow \vec{q} . We can express

$$\frac{dE}{dt} + \nabla \cdot \vec{q} = 0 \quad (30)$$

and, as in 3 dimensions the energy is $E(\vec{x}) = \frac{3}{2} k_B T(\vec{x})$, the continuity equation yields

$$\frac{dT}{dt} = -\frac{1}{c_V} \nabla \cdot \vec{q} = -\frac{\kappa}{c_V} \nabla^2 T \quad (31)$$

which is known as the *heat equation* and tells us that any inhomogeneity in temperature is smoothed out through diffusion with the coefficient $D = \kappa/c_V = \frac{1}{3} l \langle v \rangle \sim l^2/\tau$.

For the momentum p^i , where $i = 1, 2, 3$ labels the three directions in space, we can write the continuity equation with help of the *pressure tensor* P^{ij} , which describes the flux of i -momentum in the j -direction,

$$\frac{dp^i}{dt} + \frac{\partial P^{ij}}{\partial x^j} = 0. \quad (32)$$

From the derivation of viscosity, we see that the pressure tensor is precisely the force F/A , and from the flux of x and z momenta, we find

$$\frac{dp^x}{dt} = m n \frac{du_x}{dz} = \eta \frac{d^2 u_x}{dz^2} \quad (33)$$

where we have restricted ourselves to situations without velocity gradients in the x and y directions. The result is the diffusion equation and the diffusion constant is given by $D = \eta/mn = \frac{1}{3} l \langle v \rangle \sim l^2/\tau$, once again.

III. KINETIC THEORY

Here, our goal is to derive the transport properties outlined in the previous section without the inconsistencies that crept during our previous attempts. For that, we will use the Boltzmann equation as our main tool and will allow us to show how irreversibility arises from time-reversible classical mechanics.

Therefore, the purpose of this section is to lay down the foundations of kinetic theory (KT), starting from the Hamiltonian description of 10^{23} and ending with the Navier-Stokes (NS) equation of fluid dynamics.

A. Liouville Equation and BBGKY Hierarchy

Let us start from the Hamiltonian dynamics for N identical point particles that, as usual in statistical mechanics, is a very huge number, $N \sim \mathcal{O}(10^{23})$. We will consider the Hamiltonian in the form

$$H = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 + \sum_{i=1}^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i - \vec{r}_j) \quad (34)$$

that contains an external force $\vec{F} = -\nabla V$ which acts equally on all particles and we also consider two-body interactions between particles, represented by the potential energy $U(\vec{r}_i - \vec{r}_j)$.

The distribution $f(\vec{r}_i, \vec{p}_i; t)$ gives the probability for the system to be found in the vicinity of the point (\vec{r}_i, \vec{p}_i) and we will be interested on evaluation of the evolution of that distribution over the $2N$ -dimensional phase space.

The function is normalized to

$$\int dV f(\vec{r}_i, \vec{p}_i; t) = 1 \quad \text{with} \quad dV = \prod_{i=1}^N d^3r_i d^3p_i, \quad (35)$$

and since the probability is locally conserved, the distribution obeys a continuity equation. Here, we are working in the phase space, so

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \vec{r}_i} \cdot (\dot{\vec{r}}_i f) + \frac{\partial}{\partial \vec{p}_i} \cdot (\dot{\vec{p}}_i f) = 0 \quad (36)$$

where $\nabla = \frac{\partial}{\partial \vec{r}_i}, \frac{\partial}{\partial \vec{p}_i}$, the velocity vector is $(\dot{\vec{r}}_i, \dot{\vec{p}}_i)$, and we are assuming a sum over repeated indexes.

Once Hamilton's equations are $\dot{\vec{p}}_i = -\partial H / \partial \vec{r}_i$ and $\dot{\vec{r}}_i = \partial H / \partial \vec{p}_i$, we can write

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \vec{r}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial f}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{r}_i} = 0 \quad (37)$$

known as the *Liouville's equation*¹. We can write the Liouville equation using the *Poisson bracket*

$$\{A, B\} = \frac{\partial A}{\partial \vec{r}_i} \cdot \frac{\partial B}{\partial \vec{p}_i} - \frac{\partial A}{\partial \vec{p}_i} \cdot \frac{\partial B}{\partial \vec{r}_i} \quad (38)$$

and so,

$$\frac{\partial f}{\partial t} = \{H, f\}. \quad (39)$$

Note that, for an *equilibrium distribution*

$$\frac{\partial f}{\partial t} = 0 \quad (40)$$

that is true once $\{H, f\} = 0$, and one way to satisfy that relation is to consider f as a function of H . For the Boltzmann distribution, $f \sim e^{-\beta H}$ and the relation is satisfied, but this is not the only way, since any function that Poisson commutes with H also works.

If we have a function $A(\vec{r}_i, \vec{p}_i)$ on phase space, its expectation value is

$$\langle A \rangle = \int dV A(\vec{r}_i, \vec{p}_i) f(\vec{r}_i, \vec{p}_i; t), \quad (41)$$

whose change with time is given by

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \int dV A \frac{\partial f}{\partial t} \\ &= \int dV A \left(\frac{\partial f}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{r}_i} - \frac{\partial f}{\partial \vec{r}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} \right). \end{aligned} \quad (42)$$

Integrating by parts and neglecting boundary terms, here justified because f is normalized, which ensures that $f \rightarrow 0$ asymptotically, we obtain, from (42),

$$\int dV \left(-\frac{\partial A}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{r}_i} + \frac{\partial A}{\partial \vec{r}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} \right) f. \quad (43)$$

Thus,

$$\frac{d\langle A \rangle}{dt} = \int dV \{A, H\} f = \langle \{A, H\} \rangle \quad (44)$$

and we have an expression for the classical expectation value, very similar to that for the quantum expectation value, by using the Poisson bracket.

At this point in our analysis, we have not yet made a huge advance on the system description, once, even by considering a probability distribution, we still have a 10^{23} variables function. For simplicity, we will use the *one-particle distribution function* instead of the probability distribution for N particles. The one particle distribution function is defined by

$$f_1(\vec{r}, \vec{p}; t) = N \int \prod_{i=2}^N d^3r_i d^3p_i f(\vec{r}, \vec{r}_2, \dots, \vec{r}_N, \vec{p}, \vec{p}_2, \dots, \vec{p}_N; t). \quad (45)$$

Here, we are considering that all N particles are identical and the above expression does not refer to any specific particle. By normalizing f_1 , we get

$$\int d^3r d^3p f_1(\vec{r}, \vec{p}; t) = N \quad (46)$$

¹ Closely related to so-called Liouville's theorem

that reflects the idea mentioned above. In many situations, f_1 is the only information that we need from the system².

Our goal now is to derive an equation that governs f_1 and, for that, we can, firstly, see how it changes with time. Thus,

$$\frac{\partial f_1}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i \frac{\partial f}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i \{H, f\}, \quad (47)$$

and, by using (34), we get

$$\begin{aligned} \frac{\partial f_1}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i & \left[- \sum_{j=1}^N \frac{\vec{p}_j}{m} \cdot \frac{\partial f}{\partial \vec{r}_j} + \sum_{j=1}^N \frac{\partial V}{\partial \vec{r}_j} \cdot \frac{\partial f}{\partial \vec{p}_j} \right. \\ & \left. + \sum_{j=1}^N \sum_{k < l} \frac{\partial U(\vec{r}_k - \vec{r}_l)}{\partial \vec{r}_j} \cdot \frac{\partial f}{\partial \vec{p}_j} \right]. \end{aligned} \quad (48)$$

To simplify the expression above, we note that, whenever $j = 2, \dots, N$, we can integrate by parts, and the result is zero. That is always true because the derivatives with respect to \vec{r}_j move away from f to the other terms, and the derivatives with respect to \vec{p}_j will act on the other terms, which depend only on \vec{r}_j , and vice-versa. Only the terms involving derivatives with respect to $\vec{r}_1 \equiv \vec{r}$ and $\vec{p}_1 \equiv \vec{p}$ do not vanish, which implies

$$\begin{aligned} \frac{\partial f_1}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i & \left[- \frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\partial V}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}} \right. \\ & \left. + \sum_{k=2}^N \frac{\partial U(\vec{r} - \vec{r}_k)}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}} \right], \end{aligned} \quad (49)$$

and, by defining the one particle Hamiltonian

$$H_1 = \frac{p^2}{2m} + V(\vec{r}) \quad (50)$$

we get

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + N \int \prod_{i=2}^N d^3 r_i d^3 p_i \sum_{k=2}^N \frac{\partial U(\vec{r} - \vec{r}_k)}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}}. \quad (51)$$

² For example, the average density, average velocity, and energy flux are

$$\begin{aligned} n(\vec{r}; t) &= \int d^3 p f_1 \\ \vec{u}(\vec{r}; t) &= \int d^3 p \frac{\vec{p}}{m} f_1 \\ \vec{\varepsilon}(\vec{r}; t) &= \int d^3 p \frac{\vec{p}}{m} E(\vec{p}) f_1 \end{aligned}$$

By analyzing the equation (51), we can see that all information about the particles interaction is included in the term $U(\vec{r} - \vec{r}_k)$, and the variable H_1 quantifies the external force acting on the particle. If we compare this with the *Liouville equation*, we can see that the above equation is a Liouville-like equation with an interaction term. We can also separate the terms of the equation in the part that tells how the particles move without collision and the part that considers the interaction. By assuming that,

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \quad (52)$$

where we identify the first term on the right hand side as the *streaming term* and the second one as the *collision integral*. Once the particles are identical, each of the $(N - 1)$ terms in $\sum_{k=2}^N$ yield the same contribution, and we write

$$\begin{aligned} \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} &= N(N - 1) \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r} - \vec{r}_2)}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{p}} \\ & \left(\int \prod_{i=3}^N d^3 r_i d^3 p_i f(\vec{r}, \vec{r}_2, \dots, \vec{p}, \vec{p}_2, \dots; t) \right). \end{aligned} \quad (53)$$

It is not surprising that the collision integral is not expressed in terms of the one-particle distribution function, once it contains no information about any of the other particles relative to the first one, and the collision term exactly captures the interactions between them. However, the *two-particle distribution function* is defined as

$$f_2(\vec{r}, \vec{r}_2, \vec{p}, \vec{p}_2; t) \equiv N(N - 1) \int \prod_{i=3}^N d^3 r_i d^3 p_i f(\vec{r}, \vec{r}_2, \dots, \vec{p}, \vec{p}_2, \dots; t) \quad (54)$$

and now the collision integral is written as

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r} - \vec{r}_2)}{\partial \vec{r}} \cdot \frac{\partial f_2}{\partial \vec{p}}. \quad (55)$$

The result of the analysis is that if we want to know how f_1 changes with time, we also need to know something about f_2 . Making the same previous calculation, the two-particle distribution function evolves by a Liouville-like equation, corrected by a term dependent on the three-particle distribution function. The same is true for the evolution of f_3 , and so on. In general, the n -particle distribution function is

$$\begin{aligned} f_n(\vec{r}, \dots, \vec{r}_n, \vec{p}, \dots, \vec{p}_n; t) &= \frac{N!}{(N - n)!} \\ & \times \left[\int \prod_{i=n+1}^N d^3 r_i d^3 p_i f(\vec{r}, \dots, \vec{r}_N, \vec{p}, \dots, \vec{p}_N; t) \right] \end{aligned} \quad (56)$$

and considering that the effective n -body Hamiltonian includes any interaction between the n particles but neglects interaction with any particle outside this set, in addition to the external force

$$H_n = \sum_{i=1}^n \left(\frac{\vec{p}_i^2}{2m} + V(\vec{r}_i) \right) + \sum_{i < j \leq n} U(\vec{r}_i - \vec{r}_j) \quad (57)$$

the n -particle distribution function obeys

$$\frac{\partial f_n}{\partial t} = \{H_n, f_n\} + \sum_{i=1}^n \int d^3 r_{n+1} d^3 p_{n+1} \frac{\partial U(\vec{r}_i - \vec{r}_{n+1})}{\partial \vec{r}_i} \cdot \frac{\partial f_{n+1}}{\partial \vec{p}_i} \quad (58)$$

The equations (58) are known as the *BBGKY hierarchy*³. The meaning of those equations is that any group of n particles evolves by obeying the Liouville equation, that is, in a Hamiltonian way, corrected by interactions with one of the particle outside that group. The advantage in making use of those set of equations is apparent when adopting approximations, by truncating the hierarchy as the problem allows.

B. The Boltzmann Equation

We can note that there are two time scales in the problem, the time between collision, known to us as the relaxation time or scattering time, τ , and the effective collision time between particles, τ_{coll} . When

$$\tau \gg \tau_{coll} \quad (59)$$

it is expected that f_1 follows its Hamiltonian evolution with occasional perturbations, and this is the situation we will consider in what follows. By assuming that regime, the goal is to write down an equation for f_1 alone and this will be the Boltzmann equation.

There are two different ways to proceed. First, we will guess what form the equation for f_1 has to take and, in a second moment, the derivation will start from the BBGKY hierarchy.

1. Motivation for the Boltzmann Equation

The most important information that we have about f_1 is its evolution, described by

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t} \right)_{coll} \quad (60)$$

but we do not have an expression for the collision integral in terms of f_1 . From the definition (55), this term carries the change in the particle momentum due to scattering. Suppose that one particle sits at (\vec{r}, \vec{p}) , and collides with another particle at (\vec{r}, \vec{p}_2) , and, after the collision, these particles come to possess momenta \vec{p}_1' and \vec{p}_2' , respectively. The collision integral should reflect the rate at which those collisions occur and we will define it as

$$\text{Rate} = \omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2; t) d^3 p_2 d^3 p_1' d^3 p_2', \quad (61)$$

where we have introduced the scattering function ω , that contains the information about the dynamics of the process. Here, it is important to note that ω and f_2 are proportional, since the two-particle distribution function tells us the chance that they sit in (\vec{r}, \vec{p}) and (\vec{r}, \vec{p}_2) .

By considering that the potential V varies considerably only in a macroscopic scale of length, we have that the force acting on the particle does not cause changes in the total energy and momentum before and after the collision. So, both are conserved in the process and

$$\vec{p} + \vec{p}_2 = \vec{p}_1' + \vec{p}_2' \quad (62)$$

$$p^2 + p_2^2 = p_1'^2 + p_2'^2. \quad (63)$$

The above assumptions are true for most external potentials, such as gravity or electric fields.

It is interesting to focus on the distribution of particles with some specified momentum \vec{p} . Here, two processes should be considered: collisions that deflect particles in a state with momentum \vec{p} into a different momentum and collisions that deflect particles into a the same momentum \vec{p} . This means that the collision integral contain two terms,

$$\left(\frac{\partial f_1}{\partial t} \right)_{coll} = \int d^3 p_2 d^3 p_1' d^3 p_2' [\omega(\vec{p}_1', \vec{p}_2' | \vec{p}, \vec{p}_2) f_2(\vec{r}, \vec{r}, \vec{p}_1', \vec{p}_2') - \omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2)] \quad (64)$$

the first term is responsible for the scattering into the state with momentum \vec{p} and the second, for the scattering into a state with a momentum different of \vec{p} .

To complete the deduction, we have to do an analysis of the scattering function. Firstly, ω does not vanish for a scattering with energy and momentum conservation. If we look at the discrete symmetries of spacetime, we can arrive at some conclusions on that function.

For any scattering, which is invariant under time reversal, $\vec{p} \rightarrow -\vec{p}$, and we have for the scattering function

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') = \omega(-\vec{p}_1', -\vec{p}_2' | -\vec{p}, -\vec{p}_2). \quad (65)$$

³ The initials stand for Bogoliubov, Born, Green, Kirkwood, and Yvon

Under parity, we have $(\vec{r}, \vec{p}) \rightarrow (-\vec{r}, -\vec{p})$, and, for invariant systems under parity transformations,

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') = \omega(-\vec{p}, -\vec{p}_2 | -\vec{p}_1', -\vec{p}_2'). \quad (66)$$

Putting those two information together,

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') = \omega(\vec{p}_1', \vec{p}_2' | \vec{p}, \vec{p}_2), \quad (67)$$

and this means that the scattering rate is invariant under exchange of ingoing and outgoing momentum. Here, we also assume transnational invariance, i.e., the scattering rate is equivalent at positions $+\vec{r}$ and $-\vec{r}$.

Thus, by making use of the symmetry property, the collision integral takes the form

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll} = \int d^3 p_2 d^3 p_1' d^3 p_2' \omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') \times [f_2(\vec{r}, \vec{r}, \vec{p}_1', \vec{p}_2') - f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2)] \quad (68)$$

and, to finish the derivation, we need to express the collision integral in terms of f_1 rather than f_2 . For that, we make the assumption⁴ that the velocities of the two particles are uncorrelated, so that

$$f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) = f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2). \quad (69)$$

We can imagine that, during the collision process, the velocities of the two particles become correlated. There is, however, a time τ before which one of those particles experienced a collision. Once two collisions in sequence typically occurs with a completely different particle, it is plausible that the velocity of the first particle has nothing to do with the velocity of the second one. The fact that velocities are uncorrelated before the collision, but not after it, introduces an "arrow of the time" in the process.

Therefore, we can write an equation for the evolution of f_1 , (60), with

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll} = \int d^3 p_2 d^3 p_1' d^3 p_2' \omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') \times [f_1(\vec{r}, \vec{p}_1') f_1(\vec{r}, \vec{p}_2') - f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2)] \quad (70)$$

and this is the *Boltzmann equation*.

2. Equilibrium and Detailed Balance

Let us consider the system in equilibrium, i.e., the equilibrium distribution f^{eq} . We have that $\partial f^{eq}/\partial t = 0$. For

that condition to be met, we must have $\{f, H_1\} = 0$, and this is true for any function that Poisson commutes with H_1 . If we restrict ourselves to the case of absence of an external force, $V(r) = 0$, any function of momentum is an equilibrium distribution. For the vanishing of the collision integral, it is sufficient that

$$f_1^{eq}(\vec{r}, \vec{p}_1') f_1^{eq}(\vec{r}, \vec{p}_2') = f_1^{eq}(\vec{r}, \vec{p}) f_1^{eq}(\vec{r}, \vec{p}_2) \quad (71)$$

known as the *detailed balance* condition.

By writing that condition as

$$\log(f_1^{eq}(\vec{r}, \vec{p}_1')) + \log(f_1^{eq}(\vec{r}, \vec{p}_2')) = \log(f_1^{eq}(\vec{r}, \vec{p})) + \log(f_1^{eq}(\vec{r}, \vec{p}_2)), \quad (72)$$

we can see that the momenta on the left are those after the collision, and, on the right, those before the collision, and this means that the sum of $\log f_1^{eq}$ must be conserved during the collisions, in order to vanish the collision integral.

We know that, during the collision process, the conserved quantities are the momentum and energy, as it has been shown in (62) and (63), respectively. Therefore, we should take

$$\log(f_1^{eq}(\vec{r}, \vec{p})) = \beta(\mu - E(\vec{p}) + \vec{u} \cdot \vec{p}) \quad (73)$$

where μ , β and \vec{u} are constants, with μ being adjusted from the normalization of f_1 , and $E(\vec{p}) = p^2/2m$. Then, since $\vec{p} = m\vec{v}$,

$$f_1^{eq}(\vec{r}, \vec{p}) = \frac{N}{V} \left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{-\beta m(\vec{v}-\vec{u})^2/2} \quad (74)$$

which is the MB distribution, provided β be proportional to the inverse temperature. Here, \vec{u} allows for the possibility of an overall drift velocity.

Note that if we ignore the streaming term, then there are a greater number of solutions that satisfy the condition (71). In that case, μ , β , and \vec{u} are now functions of space and time, and we get

$$f_1^{\text{local}}(\vec{r}, \vec{p}; t) = n(\vec{r}, t) \left(\frac{\beta(\vec{r}, t)}{2\pi m}\right)^{3/2} \times \exp\left(-\beta(\vec{r}, t) \frac{m}{2} [(\vec{v} - \vec{u}(\vec{r}, t))]^2\right), \quad (75)$$

that do not describe an equilibrium distribution, as a whole, because the streaming term does not vanish. Distributions of that kind are said to be in *local equilibrium*, with the temperature, drift velocity, and particle density varying over space.

⁴ Sometimes named as *molecular chaos*

C. Hydrodynamics

Hydrodynamics is, in general, the science of fluid flow, the behavior of a fluid system in local equilibrium and its evolution. In this section, we are going to analyze what would be the dynamic quantities that describe a fluid, why these variables would be relevant for such a description, and finally derive an equation that describes their dynamics.

1. Conserved Quantities

We have already pointed out that the dynamical quantities of interest are density $\rho(\vec{r}, t)$, temperature $T(\vec{r}, t)$, and velocity $\vec{u}(\vec{r}, t)$, and this is due to the fact that these variables change very slowly in a system. We will see below that this characteristic is a consequence of the fact that they are all associated to conserved quantities.

For that, consider, over the single particle phase space, a general function $A(\vec{r}, \vec{p})$ and define the average of this function as

$$\langle A(\vec{r}, \vec{p}) \rangle = \frac{\int d^3p A(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}; t)}{\int d^3p f_1(\vec{r}, \vec{p}; t)} \quad (76)$$

where we identify in (76) the number density of particles

$$n(\vec{r}, t) = \int d^3p f_1(\vec{r}, \vec{p}; t). \quad (77)$$

Note that the result (76) is different from the average in (41) because, here, we are interested in how things vary with \vec{r} and t .

Let us analyze how the average of A changes with time and relate this to the Boltzmann equation. Beforehand, we can guess that we will have a streaming term and a collision term and, since we want to study quantities that vary slowly, the following condition needs to be satisfied:

$$\int d^3p A(\vec{r}, \vec{p}) \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = 0. \quad (78)$$

Thus, using the collision integral expression (70), we get

$$\begin{aligned} & \int d^3p_1 d^3p_2 d^3p_1' d^3p_2' \omega(\vec{p}_1', \vec{p}_2' | \vec{p}_1, \vec{p}_2) \\ & \times [f_1(\vec{p}_1') f_1(\vec{p}_2') - f_1(\vec{p}_1) f_1(\vec{p}_2)] \\ & \times [A(\vec{r}, \vec{p}_1) + A(\vec{r}, \vec{p}_2) - A(\vec{r}, \vec{p}_1') - A(\vec{r}, \vec{p}_2')] = 0 \end{aligned} \quad (79)$$

and this is true for any distribution that satisfies

$$A(\vec{r}, \vec{p}_1) + A(\vec{r}, \vec{p}_2) = A(\vec{r}, \vec{p}_1') + A(\vec{r}, \vec{p}_2'). \quad (80)$$

Functions that remain constant before and after collisions are called *collisional invariants*. Therefore, we get

$$\int d^3p A(\vec{r}, \vec{p}) \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{r}} + \vec{F} \cdot \frac{\partial}{\partial \vec{p}} \right) f_1(\vec{r}, \vec{p}, t) = 0 \quad (81)$$

where $\vec{F} = -\nabla V$ is the external force.

Then, we can rewrite the equation (81) in the form

$$\begin{aligned} & \frac{\partial}{\partial t} \int d^3p A f_1 + \frac{\partial}{\partial \vec{r}} \cdot \int d^3p \frac{\vec{p}}{m} A f_1 \\ & - \int d^3p \frac{\vec{p}}{m} \cdot \frac{\partial A}{\partial \vec{r}} f_1 - \int d^3p \vec{F} \cdot \frac{\partial A}{\partial \vec{p}} f_1 = 0 \end{aligned} \quad (82)$$

and, using our previous result for $\langle A(\vec{r}, t) \rangle$, we have

$$\frac{\partial}{\partial t} \langle nA \rangle + \frac{\partial}{\partial \vec{r}} \cdot \langle n\vec{v}A \rangle - n \left\langle \vec{v} \cdot \frac{\partial A}{\partial \vec{r}} \right\rangle - n \left\langle \vec{F} \cdot \frac{\partial A}{\partial \vec{p}} \right\rangle = 0 \quad (83)$$

which governs how any collisional invariant evolves.

We already know three collisional invariants, which are the trivial solution $A = 1$, the momentum, and the energy, and we now evaluate each of these cases.

a. Density From the trivial solution, by applying it to the equation (83), we have, for the particle density,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot (n\vec{u}) = 0 \quad (84)$$

where $\vec{u}(\vec{r}, t) = \langle \vec{v} \rangle$ is the average velocity of the particles. In the following approach, we will replace the particle density $n(\vec{r}, t)$ by the mass density $\rho(\vec{r}, t)$, since $\rho(\vec{r}, t) = mn(\vec{r}, t)$.

b. Momentum For the second collisional invariant, since $A = m\vec{v}$, we obtain, from (83),

$$\frac{\partial}{\partial t} (mnu_i) + \frac{\partial}{\partial r_j} \langle mnv_j v_i \rangle - \langle nF_i \rangle = 0 \quad (85)$$

where, algebraically developing the middle term, and using the continuity equation (84), we get [1]

$$\rho \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i = \frac{\rho}{m} F_i - \frac{\partial}{\partial r_j} P_{ij}, \quad (86)$$

obtaining an equation for momentum conservation.

Here, we define the pressure tensor⁶ $P_{ij} = P_{ji} = \rho \langle (v_j - u_j)(v_i - u_i) \rangle$, that is the flux of the i (j) - momentum in the j (i) - direction. We can, sometimes, write the equation (86) by using the *material derivative*,

$$D_t \equiv \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j}. \quad (87)$$

⁶ This definition for pressure tensor, evaluated for the MB distribution, gives us $P_{ij} = nk_B T \delta_{ij}$.

c. Kinetic Energy From the third collision invariant, we will work here with $A = m(\vec{v} - \vec{u})^2/2$, and substitute it into the equation (83), to get

$$\begin{aligned} \frac{1}{2} \frac{\partial}{\partial t} \langle \rho (\vec{v} - \vec{u})^2 \rangle + \frac{1}{2} \frac{\partial}{\partial r_i} \langle \rho v_i (\vec{v} - \vec{u})^2 \rangle \\ - \rho \left\langle v_i \frac{\partial u_j}{\partial r_i} (\vec{v} - \vec{u})^2 \right\rangle = 0. \end{aligned} \quad (88)$$

Using the idea of equipartition, we have

$$\frac{1}{2} \langle (\vec{v} - \vec{u}(\vec{r}, t))^2 \rangle = \frac{3}{2} m k_B T(\vec{r}, t), \quad (89)$$

which defines the quantity *heat flux*

$$q_i = \frac{1}{2} m \rho \langle (v_i - u_i) (\vec{v} - \vec{u})^2 \rangle \quad (90)$$

and, with the P_{ij} definition, we can rewrite the equation (88) as

$$\frac{3}{2} \frac{\partial}{\partial t} (\rho k_B T) + \frac{\partial}{\partial r_i} \left(q_i + \frac{3}{2} \rho u_i k_B T \right) + m P_{ij} \frac{\partial u_j}{\partial r_i} = 0. \quad (91)$$

Note that, since $P_{ij} = P_{ji}$, we can define the *rate of strain* $U_{ij} = (\partial u_i / \partial r_j + \partial u_j / \partial r_i) / 2$ to substitute for the term $\partial u_j / \partial r_i$. Therefore, we obtain

$$\rho \left(\frac{\partial}{\partial t} + u_i \frac{\partial}{\partial r_i} \right) k_B T + \frac{2}{3} \frac{\partial q_i}{\partial r_i} + \frac{2m}{3} U_{ij} P_{ij} = 0. \quad (92)$$

Then, we have equations to describe how each of the variables, density (84), velocity (86), and temperature (92) evolves. Those equations, however, are not closed and we need to solve the Boltzmann equation, and compute f_1 to determine these quantities.

2. Ideal Fluids

To solve Boltzmann equation, we will use some information to guess a form for the distribution function, calculate the variables, and finally describe their change in time.

We are interested in distributions that satisfy $(\partial f_1 / \partial t)_{\text{coll}} = 0$, and this

$$\begin{aligned} f_1^{(0)}(\vec{r}, \vec{p}; t) = n(\vec{r}, t) \left(\frac{1}{2\pi m k_B T(\vec{r}, t)} \right)^{3/2} \\ \exp \left(-\frac{m}{2k_B T(\vec{r}, t)} [(\vec{v} - \vec{u}(\vec{r}, t))]^2 \right) \end{aligned} \quad (93)$$

does that.

Then, since $f_1^{(0)}$ is normalized, we have, from (77) and (89), that the density and temperature coincide with the quantities in our previous analysis. By using (93) to compute the pressure tensor and the heat flux, we get

$$P_{ij} = k_B n(\vec{r}, t) T(\vec{r}, t) \delta_{ij} \quad (94)$$

$$\vec{q} = 0 \quad (95)$$

We are now able to express the previous conservation laws from our guess of the form of the distribution. For the continuity equation, we have

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) \rho + \rho \frac{\partial u_i}{\partial r_i} = 0 \quad (96)$$

where $\rho = mn$. From the equation for momentum conservation, we obtain the Euler equation

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i + \frac{1}{\rho} \frac{\partial P}{\partial r_i} = \frac{F_i}{m} \quad (97)$$

The equation for the conservation of energy is now

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) T + \frac{2T}{3} \frac{\partial u_i}{\partial r_i} = 0. \quad (98)$$

The equations (96), (97), and (98) describe the motion of an ideal fluid, because they are missing dissipation.

D. Transport with Collision

So far, we have deduced equations that describe the behavior of the variables of interest, but we suffer from the loss of information about how the system returns to the equilibrium state. To quantify that loss of information, let us check how $f_1^{(0)}$ behaves in relation to the streaming terms. Using the one particle Hamiltonian, and the definition of the Poisson bracket, we get

$$\frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} = \frac{\partial f_1^{(0)}}{\partial t} + \vec{F} \cdot \frac{\partial f_1^{(0)}}{\partial \vec{p}} + \vec{v} \cdot \frac{\partial f_1^{(0)}}{\partial \vec{r}}. \quad (99)$$

Calculating the terms on the right-hand side of the equation above, and by making use of the fact that both r and t dependences lie in the functions n , T , and \vec{u} , we have

$$\begin{aligned} \frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} = \left[\frac{1}{n} \tilde{D}_t n + \left(\frac{m(\vec{v} - \vec{u})^2}{2k_B T^2} - \frac{3}{2T} \right) \tilde{D}_t T \right. \\ \left. + \frac{m}{k_B T} (\vec{v} - \vec{u}) \cdot \tilde{D}_t \vec{u} - \frac{1}{k_B T} \vec{F} \cdot (\vec{v} - \vec{u}) \right] f_1^{(0)} \end{aligned} \quad (100)$$

where \tilde{D}_t differs from the material derivative D_t , and is defined by

$$\tilde{D}_t \equiv \frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{r}}. \quad (101)$$

Then, as we know the equations that describe how n (96), \vec{u} (97), and T (98) change, we can algebraically manipulate the equation (100), by making use of the definition for U_{ij} and the result $P = nk_B T$, to write

$$\begin{aligned} \frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} &= \left[\frac{1}{T} \left(\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right) \right. \\ &\quad \left. \times (\vec{v} - \vec{u}) \cdot \nabla T \right. \\ &\quad \left. + \frac{m}{k_B T} \left((v_i - u_i)(v_j - u_j) - \frac{1}{3} (\vec{v} - \vec{u}) \delta_{ij} \right) U_{ij} \right] f_1^{(0)} \end{aligned} \quad (102)$$

and the right-hand side is not zero. Note that, if we have T and \vec{u} varying slowly with the position, we will have almost a solution. Thus, let us consider a small correction in the distribution function, so that

$$f_1 = f_1^{(0)} + \delta f_1 \quad (103)$$

and let us see what does change in our analysis.

1. Relaxation Time Approximation

The introduction of the correction term in the distribution clearly changes the form of the collision integral. Now we have

$$\begin{aligned} \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} &= \int d^3 p_2 d^3 p_1' d^3 p_2' \omega (\vec{p}_1', \vec{p}_2' | \vec{p}_1, \vec{p}_2) \\ &\quad \left[f_1^{(0)}(\vec{p}_1') \delta f_1(\vec{p}_2') + \delta f_1(\vec{p}_1') f_1^{(0)}(\vec{p}_2') \right. \\ &\quad \left. - f_1^{(0)}(\vec{p}_1) \delta f_1(\vec{p}_2) - \delta f_1(\vec{p}_1) f_1^{(0)}(\vec{p}_2) \right] \end{aligned} \quad (104)$$

where we have neglected quadratic terms. However, it is not easy solve ⁷, the collision integral in that form, and we will make use of the *relaxation time approximation*⁸ to simplify our description, by defining the operator

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = -\frac{\delta f_1}{\tau} \quad (105)$$

Although the relaxation time τ could be a function of the moment, we will here consider it as a constant. Therefore, we have

$$\frac{\partial (f_1^{(0)} + \delta f_1)}{\partial t} - \{H_1, (f_1^{(0)} + \delta f_1)\} = -\frac{\delta f_1}{\tau} \quad (106)$$

and, since $\delta f_1 \ll f_1^{(0)}$, we can consider that the δf_1 , on the left-hand side, vanishes. By making use of the expression (102), we get the correction

$$\begin{aligned} \delta f_1 &= -\tau \left[\frac{1}{T} \left(\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right) (\vec{v} - \vec{u}) \cdot \nabla T \right. \\ &\quad \left. + \frac{m}{k_B T} \left((v_i - u_i)(v_j - u_j) - \frac{1}{3} (\vec{v} - \vec{u}) \delta_{ij} \right) U_{ij} \right] f_1^{(0)}. \end{aligned} \quad (107)$$

Now, let us see how that influences the transport properties.

2. Thermal Conductivity

Our goal now is to write an expression for the thermal conductivity κ by making use of the corrected distribution function (103), and then obtain an equation for the heat flow, as our (31). From our previous considerations, we know that the distribution $f_1^{(0)}$ implies $\vec{q} = 0$. Then, only δf_1 contributes to compute the heat flux (90). Furthermore, the second term in (107) vanishes when we do the integral, and then we have

$$\vec{q} = -\kappa \nabla T \quad (108)$$

with κ given by

$$\begin{aligned} \kappa &= \frac{m\tau\rho}{2T} \int d^3 p (\vec{v} - \vec{u})^4 \left[\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right] f_1^{(0)} \\ &= \frac{m\tau\rho}{6T} \left[\frac{m}{2k_B T} \langle v^6 \rangle_0 - \frac{5}{2} \langle v^4 \rangle_0 \right] \end{aligned} \quad (109)$$

where the subscript 0 means that the average is to be taken with $u = 0$.

Now, by computing⁹ κ , we get

$$\kappa = \frac{5}{2} \tau n k_B^2 T. \quad (110)$$

⁷ The method involve the Chapman-Enskog expansion.

⁸ This approximation is also known as the Bathnagar-Gross-Krook (BGK) approximation.

⁹ By solving the integrals, we obtain $\langle v^6 \rangle_0 = 105k_B^3 T^3/m^3$ and $\langle v^4 \rangle_0 = 15k_B^2 T^2/m^2$.

From (92), by assuming a static fluid, $\vec{u} = 0$, without change in the thermal conductivity, $\partial\kappa/\partial\vec{r} = 0$, we obtain an equation for the heat flow

$$\rho k_B \frac{\partial T}{\partial t} = -\frac{2}{3} \kappa \nabla^2 T. \quad (111)$$

3. Viscosity

We now analyze the shear viscosity. We need to compute the flux of the i -momentum in the j -direction, but this is the definition for the pressure tensor P_{ij} . From our previous discussion, we have that the distribution $f_1^{(0)}$ implies a pressure tensor in the form (94), which means that the viscosity vanishes, and then only the correction (107) contributes to the viscosity.

From that correction, we can conclude that only the second term is important to compute the viscosity. We write

$$P_{ij} = P\delta_{ij} + \Pi_{ij} \quad (112)$$

where $P \equiv k_B n T$ and Π_{ij} is the stress tensor

$$\begin{aligned} \Pi_{ij} &= \frac{m\tau\rho}{k_B T} U_{kl} \int d^3p (v_j - u_j) (v_i - u_i) \\ &\times \left[(v_k - u_k) (v_l - u_l) - \frac{1}{3} (\vec{v} - \vec{u})^2 \delta_{kl} \right] f_1^{(0)} \quad (113) \\ &= \frac{m\tau\rho}{k_B T} U_{kl} \left[\langle v_i v_j v_k v_l \rangle_0 - \frac{1}{3} \delta_{kl} \langle v_i v_j v^2 \rangle \right]. \end{aligned}$$

Due to a mathematical property¹⁰, from the above expression, we get the form of Π_{ij} ,

$$\Pi_{ij} = -2\eta \left(U_{ij} - \frac{1}{3} \delta_{ij} \nabla \cdot \vec{u} \right) \quad (114)$$

and if we substitute for the condition $\partial u_x / \partial z$, as discussed in the section (II B 2), we have

$$\Pi_{xz} = -\eta \frac{\partial u_x}{\partial z}. \quad (115)$$

Algebraically manipulating the equation (113), and comparing it to the equation (114), we obtain the form of η ,

$$\eta = nk_B \tau T. \quad (116)$$

¹⁰ Π_{ij} is a traceless tensor and depends linearly on the tensor U_{ij}

IV. THE NAVIER-STOKES EQUATION

Finally, by considering the corrected distribution function, we can write the set of equations that govern the conservation of density, momentum, and energy. For fluctuations in density, we have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 \quad (117)$$

since this does not change. From the equation (86), by making use of the pressure tensor in the form (112), and by considering that there is no change in the viscosity, $\nabla \eta \approx 0$, we can write, for the momentum conservation,

$$\left(\frac{\partial}{\partial t} + \vec{u} \cdot \nabla \right) \vec{u} = \frac{\vec{F}}{m} - \frac{1}{\rho} \nabla P + \frac{\eta}{\rho} \nabla^2 \vec{u} + \frac{\eta}{3\rho} \nabla (\nabla \cdot \vec{u}) \quad (118)$$

known as the *Navier-Stokes (NS) equation*. To finish, we will analyze the change in the equation for the conservation of energy (92). By assuming that variations in the thermal conductivity κ and the quantity $U_{ij} \Pi_{ij}$ can be neglected, we get

$$\rho \left(\frac{\partial}{\partial t} + \vec{u} \cdot \nabla \right) T - \frac{2}{3} \kappa \nabla^2 T + \frac{2m}{3} P \nabla \cdot \vec{u} = 0 \quad (119)$$

and we arrive at the end of our analysis in the dilute gas approximation.

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