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Correction au 5 novembre 2025

Master QLMN - Université Paris-Saclay

TD 5 - Non-equilibrium Statistical Physics
Boltzmann Equation - CORRECTION

1 Viscosity

The perturbed distribution is given by :

$$f(\mathbf{r},\mathbf{v}) = n_0 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-m\frac{(\mathbf{v}-\mathbf{V})^2}{2k_B T}\right)$$

to be compared to the equilibrium, unperturbed Maxwell-Boltzmann distribution :

$$f^{(0)}(\mathbf{r},\mathbf{v}) = n_0 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-m\frac{\mathbf{v}^2}{2k_B T}\right)$$

In our perturbed system, the density of the fluid remains homogeneous. However the velocity distribution does depend on z. Indeed, in a given layer at a position z, the velocity distribution is a gaussian centered, not on the null velocity, but on $\mathbf{V}(z)$, which represents the average, macroscopic velocity that defines the viscosity of the liquid.

We first write the budget of x-oriented momentum exchange across an element of surface Σ, oriented perpendicular to z, over a time dt :

$$\Delta p_x = \int d^3\mathbf{v} p_x f(\mathbf{r},\mathbf{v})\mathbf{v}\cdot\mathbf{n} dt\Sigma$$

where $\mathbf{n}$ is the unit vector oriented along the z-axis, so that we eventually write :

$$\Delta p_x = m\left(\int d^3\mathbf{v} v_x v_z f(\mathbf{r},\mathbf{v})\right) dt\Sigma$$

This expression can be interpreted as follows :

- For each class of « thermal velocity »$\mathbf{v}$ in our fluid, we count the number of particles who are able to cross the surface Σ during the time interval dt.
- Only particles that are both close enough, and are traveling fast enough (and in the correct direction !) can reach and cross the border Σ in such a short amount of time dt.
- We can write this condition explicitly : for particles of velocity class $\mathbf{v}$, only particles that are positioned within the **real space volume** $(\mathbf{v}\cdot\mathbf{n}\Sigma dt)$ can (and will) cross the border during time dt.

— We see that this real space volume depends on the thermal velocity class $\mathbf{v}$: particles that travel faster can come from a much larger distance from the border and still reach it within the same time interval dt.

The flux density is simply the exchanged quantity per unit time and per unit area :

$$\Phi_{p_x,z} = \frac{\Delta p_x}{dt\Sigma} = m \int d^3\mathbf{v} v_x v_z f(\mathbf{r}, \mathbf{v})$$

If we give an explicit formulation to the macroscopic velocity field $\mathbf{V}(z)$, the integral can be performed (numerically if needed), and the flux density can be retrieved. Our goal here is different : it is to derive formally a physical law, a differential equation connecting $\mathbf{V}(z)$ and the flux density in a perturbative approach.

First, we assume that the perturbed probability density can be expanded as : $f(\mathbf{r}, \mathbf{v}) = f^{(0)}(\mathbf{r}, \mathbf{v}) + \epsilon f^{(1)}(\mathbf{r}, \mathbf{v})$

where $f^{(0)}(\mathbf{r}, \mathbf{v})$ is the equilibrium Maxwell-Boltzmann distribution, and $\epsilon f^{(1)}(\mathbf{r}, \mathbf{v})$ is a first order perturbation, much smaller than $f^{(0)}(\mathbf{r}, \mathbf{v})$: ϵ is a dimensionless parameter much smaller than 1.

We first write Boltzmann's equation in the relaxation time approximation :

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \vec{\nabla}_{\mathbf{r}} f(\mathbf{r}, \mathbf{v}) + \frac{d\mathbf{v}}{dt} \cdot \vec{\nabla}_{\mathbf{v}} f(\mathbf{r}, \mathbf{v}) = -\frac{f - f^{(0)}}{\tau}$$

The right hand side reflects that, in presence of a collisional mechanism, the system described by the distribution f is constantly pulled towards the restoration of its thermodynamic equilibrium state, described by the distribution $f^{(0)}$.

In stationary regime, we have $\frac{\partial f}{\partial t} = 0$. In addition, there is no external force applied, and then no modification of the thermal velocity distribution. We have :

$$v_z \frac{\partial f(\mathbf{r}, \mathbf{v})}{\partial z} = -\frac{f - f^{(0)}}{\tau} = -\frac{\epsilon f^{(1)}(\mathbf{r}, \mathbf{v})}{\tau}$$

We now have to compute the gradient of the probability density.

$$\frac{\partial f(\mathbf{r}, \mathbf{v})}{\partial z} = n_0 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{\partial}{\partial z}\left(\exp\left(-m\frac{(\mathbf{v} - \mathbf{V}(z))^2}{2k_B T}\right)\right)$$

with

$$\begin{aligned}(\mathbf{v} - \mathbf{V})^2 &= (v_x - V_x(z))^2 + v_y^2 + v_z^2 \\ &= v_x^2 + v_y^2 + v_z^2 - 2v_x V_x(z) + (V_x(z))^2\end{aligned}$$

If we perform explicitly the derivation of the gaussian term, we get

$$\begin{aligned}\frac{\partial}{\partial z}\left(\exp\left(-m\frac{(\mathbf{v} - \mathbf{V}(z))^2}{2k_B T}\right)\right) &= \left(\frac{-m}{2k_B T}\right)\left[-2v_x \frac{\partial V_x(z)}{\partial z} + 2V_x(z)\frac{\partial V_x(z)}{\partial z}\right]\left(\exp\left(-m\frac{(\mathbf{v} - \mathbf{V}(z))^2}{2k_B T}\right)\right) \\ &= \left(\frac{-m}{2k_B T}\right)\left[-2v_x + 2V_x(z)\right]\left(\exp\left(-m\frac{(\mathbf{v} - \mathbf{V}(z))^2}{2k_B T}\right)\right)\frac{\partial V_x(z)}{\partial z}\end{aligned}$$

We can note that :

$$\left(\frac{-m}{2k_BT}\right)[-2v_x + 2V_x(z)]\left(\exp\left(-m\frac{(\mathbf{v}-\mathbf{V}(z))^2}{2k_BT}\right)\right) = \frac{\partial f(\mathbf{r},\mathbf{v})}{\partial v_x}$$

so that we finally get :

$$v_z\frac{\partial f(\mathbf{r},\mathbf{v})}{\partial z} = v_z\frac{\partial f(\mathbf{r},\mathbf{v})}{\partial v_x}\frac{\partial V_x(z)}{\partial z} = -\frac{\epsilon f^{(1)}(\mathbf{r},\mathbf{v})}{\tau}$$

The right-hand side is, by definition, a first order term.

In the relaxation time approximation, we consider that collisions happen very frequently : the collisions are defined by a "short" mean free path – the question is now, compared to what ? The perturbative approach suggests that the inhomogeneities of the system are "smooth" : their typical length scale of the inhomogeneities is much larger than the mean free path. This translates into the perturbative expansion : the gradients of external perturbations are responsible for the emergence of transport phenomena, but having long range inhomogeneities mean that the spatial gradients are small : they are proportional to the same dimensionless parameter $\epsilon \ll 1$ defining the weight of the expansion $\epsilon f^{(1)}$.

In short, in this perturbative approach, we do consider $\frac{\partial V_x(z)}{\partial z} = O(\epsilon)$

We now have to collect same order terms on both sides of the equation.

We limit the expansion of

$$\frac{\partial f(\mathbf{r},\mathbf{v})}{\partial v_x} = \frac{\partial f^{(0)}(\mathbf{r},\mathbf{v})}{\partial v_x} + \epsilon\frac{\partial f^{(1)}(\mathbf{r},\mathbf{v})}{\partial v_x} + \ldots$$

to the initial term $\frac{\partial f^{(0)}(\mathbf{r},\mathbf{v})}{\partial v_x}$ only. This way,

$$\frac{\partial f^{(0)}(\mathbf{r},\mathbf{v})}{\partial v_x}\frac{\partial V_x(z)}{\partial z}$$

is a first order term. Finally, the equation reads :

$$v_z\frac{\partial f^{(0)}(\mathbf{r},\mathbf{v})}{\partial v_x}\frac{\partial V_x(z)}{\partial z} = -\frac{\epsilon f^{(1)}(\mathbf{r},\mathbf{v})}{\tau}$$

$\epsilon f^{(1)}$ is the correction to the velocity distribution and is responsible for the flux existing out of equilibrium. The current density is :

$$\begin{aligned}\Phi_{p_x,z} &= \int d^3\mathbf{v} p_x f(\mathbf{r},\mathbf{v}) v_z \\ &= -\mu\frac{\partial V}{\partial z} \\ &= \iiint d^3\mathbf{v} p_x v_z[\tau v_z]\frac{\partial f^{(0)}}{\partial v_x}\frac{\partial V}{\partial z}\end{aligned}$$

We write :

$$f^{(0)}(\mathbf{r},\mathbf{v}) = n_0 P(v_x)P(v_y)P(v_z)$$

and recall that, by definition,

$$\int_{-\infty}^{+\infty} P(v_x)\mathrm{d}v_x = 1$$

and

$$\int_{-\infty}^{+\infty} g(v_x)P(v_x)\mathrm{d}v_x =< g(v_x) >$$

where the brackets $<>$ denote the statistical average. We write :

$$\begin{aligned}
\Phi_{p_x,z} &= \iiint d^3\mathbf{v} p_x v_z [\tau v_z] \frac{\partial f^{(0)}}{\partial v_x}\frac{\partial V}{\partial z} \\
&= mn_0\tau \underbrace{\left[\int dv_x v_x \frac{dP(v_x)}{dv_x}\right]}_{=[v_xP(v_x)]_{-\infty}^{+\infty}-\int P(v_x)dv_x=-1} \underbrace{\left[\int dv_y P(v_y)\right]}_{=1} \underbrace{\left[\int dv_z v_z^2 P(v_z)\right]}_{=<v_z^2>=\frac{k_BT}{m}} \frac{\partial V}{\partial z} \\
&= -n_0\tau k_B T\frac{\partial V}{\partial z}
\end{aligned}$$

1.1 Recalling results from the previous tutorial

Viscosity is a measure of internal friction between adjacent laers of a fluid. This friction can be seen as a transport of momentum between layers by particles in the fluid. In this exercise, we consider a laminar flow $V_x(z)\mathbf{e_x}$. (the liquid flows in the x-direction, but layers at different$z$ can have a different velocity). We use elements of the kinetic theory to solve the problem.

Viscosity μ is given by $F_{xz} = -\mu\frac{\partial V_x}{\partial z}$. Let us consider of small volume, defined by a cross-section Σ separating two layers and a lateral extension zd. The net momentum transfer in this layer is given by contributions from upper and lower layers closer than the free mean path, and from particles with appropriate velocities. We consider that particles have a random thermal velocity v, same in all directions, that adds up to the collective laminar flow velocity V_x.

$$\begin{aligned}
\frac{dp_{syst,x}}{dt} &= \Sigma\frac{1}{6}\left(nv_z[mV_x(z-l)] - nv_z[mV_x(z+l)]\right) \\
&= -\Sigma\frac{n}{6}vml2\frac{\partial V_x}{\partial z}
\end{aligned}$$

The shear force is a force per unit surface. We divide the previous momentum transfer by Σ and use the other expressions of the mean free path $l = v\tau$ and root mean square velocity $v^2 = \frac{3kT}{m}$ to get :

$$F_{xz} = -nkT\tau\frac{\partial V_x}{\partial z}$$

and we identify directly the viscosity : $\mu = nkT\tau$.

2 Diffusion current in a p-n junction

The procedure is the same as the previous exercise, with only small changes. By using the definition of the probability density ;

$$\mathbf{j_n} = \int (-e) \underbrace{f(\mathbf{r}, \mathbf{v})}_{=f^{(0)}+\epsilon f^{(1)}} \mathbf{v} d^3\mathbf{v}$$

But we also know Fick's law of diffusion :

$$\mathbf{j_n} = -D\vec{\nabla}_{\mathbf{r}} n(\mathbf{r})$$

This is all in vector form. TO retrieve one of the component of the current density (in x, y, or z direction), one just needs to perform a dot product with the adequate unit vector $\mathbf{u_x}$, $\mathbf{u_y}$, $\mathbf{u_z}$.

Our goal is to derive the expression of Fick's law from a Boltzmann approach.

First, let us write that the total density of particles is an integral of the probability density over velocity space ;

$$n(\mathbf{r}) = \int f(\mathbf{r}, \mathbf{v}) d^3\mathbf{v}$$

with now a factorizable form for the perturbed probability density

$$f(\mathbf{r}, \mathbf{v}) = n(\mathbf{r}) P(v_x) P(v_y) P(v_z)$$

The spatial inhomogeneity appears here in the particle density $n(\mathbf{r})$.

In the Boltzmann equation, we consider once again being n stationary regime and having zero force applied. Hence :

$$\mathbf{v} \cdot \vec{\nabla}_{\mathbf{r}} f(\mathbf{r}, \mathbf{v}) = -\frac{\epsilon f^{(1)}}{\tau}$$

And we reinject the expression of $\epsilon f^{(1)}$ as the source term of our current density :

$$\begin{aligned} \mathbf{j_n} &= \iiint e\tau \left(\mathbf{v} \cdot \vec{\nabla}_{\mathbf{r}} f(\mathbf{r}, \mathbf{v}) \right) \mathbf{v} d^3\mathbf{v} \\ &= \iiint e\tau \left(\mathbf{v} \cdot \vec{\nabla}_{\mathbf{r}} n(\mathbf{r}) \right) P(\mathbf{v}) \mathbf{v} d^3\mathbf{v} \end{aligned}$$

For the x component, we explicitly perform the dot product :

$$\begin{aligned} j_{n,x} &= \left(\iiint e\tau \left(\mathbf{v} \cdot \vec{\nabla}_{\mathbf{r}} n(\mathbf{r}) \right) P(\mathbf{v}) \mathbf{v} d^3\mathbf{v} \right) \cdot \mathbf{u_x} \\ &= e\tau \iiint dv_x dv_y dv_z \left[v_x^2 \frac{\partial n}{\partial x} + v_x v_y \frac{\partial n}{\partial y} + v_x v_z \frac{\partial n}{\partial z} \right] P(v_x) P(v_y) P(v_z) \\ &= e\tau \left(\underbrace{< v_x^2 >}_{\frac{k_B T}{m}} \frac{\partial n}{\partial x} + \underbrace{< v_x >< v_y > \frac{\partial n}{\partial y}}_{=0} + \underbrace{< v_x >< v_z > \frac{\partial n}{\partial z}}_{=0} \right) \end{aligned}$$

so that :

$$\mathbf{j_n} = -D\vec{\nabla}_{\mathbf{r}} n(\mathbf{r}) = \frac{e\tau k_B T}{m}\vec{\nabla}_{\mathbf{r}} n(\mathbf{r})$$

this is valid if Maxwell Boltzmann distribution can be used, i.e. if we are in the classical approximation.