Lecture 9. Disequilibrium II:

Boltzmann's transport equation and H-Theorem

1 Introduction

In a dilute gas the molecules are sufficiently removed from each other so that the potential energy of molecular interaction due to collisions is a small term compared with the total kinetic energy. As a consequence the equilibrium density is to a very good approximation proportional the exponential of the total kinetic energy and is commonly known as the Maxwell distribution. Such neglect of molecular collisions is not possible however if a non-equilibrium scenario is considered and various experimental studies show that collisions are a mechanism by which equilibration occurs. The mechanism of molecular collisions allows for exchange of kinetic energy and momentum between all the molecules of the gas. The time scale associated with this process is the average time between collisions for each molecule. This is termed the mean free path time and is a function of the gas density and molecule size.

2 Singlet densities

Consider now a molecular dynamical system in which collisions did not take place. In such a case molecules would be like non-interacting ensemble members of a dynamical system. This would be entirely analogous to the case considered in the previous lecture when $\mathbf{B} = 0$. Now in this situation the object of interest is the probability density of any molecule i.e. $\rho(\boldsymbol{p}, \boldsymbol{q})$ which is proportional to the number of molecules in the hypothetical gas with configuration variables between $\boldsymbol{p}$ and $\boldsymbol{p} + d\boldsymbol{p}$ and $\boldsymbol{q}$ and $\boldsymbol{q} + d\boldsymbol{q}$. Since all the molecules of the assembly do not interact, they are statistically independent and so the probability density for the entire system is simply the product of all such "singlet" densities with one for each molecule. If the molecules were to interact however this relation would not hold and it is this complication which makes the study of general non-equilibrium statistical behaviour difficult. The singlet density for the non-interacting system satisfies a Fokker Planck equation with $\mathbf{B} = 0$. Such an equation is commonly called a Liouville equation. Moreover because the molecules themselves are controlled by a Hamiltonian formulation it follows that the probability equation can be shown to also satisfy $\nabla \bullet \mathbf{A} = 0$ in the notation of the previous lecture. To see this note that a Hamiltonian dynamical system has the six equations

$$\begin{aligned} \dot{\boldsymbol{p}} &= - \frac{\partial H(\boldsymbol{p}, \boldsymbol{q})}{\partial \boldsymbol{q}} \\ \dot{\boldsymbol{q}} &= \frac{\partial H(\boldsymbol{p}, \boldsymbol{q})}{\partial \boldsymbol{p}} \end{aligned}$$

where H is the Hamiltonian function. Forming the divergence of the six vector on the right of these equations we get the zero divergence relation from Clairaut's theorem. From the last lecture then the singlet density entropy is conserved, a result we shall comment on further below. Consider the case now of a molecule of mass m in an external potential V. For this case classical dynamics tells us that the Hamiltonian is

$$H = \sum_{i=1}^{3} \left\{ \frac{p_i^2}{2m} + V(q_i) \right\}$$

From the last lecture then the Liouville equation for the non-interacting system singlet density is given by

$$\begin{aligned} \dot{\rho} + \boldsymbol{v} \bullet \nabla_q \rho + \boldsymbol{F} \bullet \nabla_p \rho &= 0 \\ \boldsymbol{F} &= -\frac{\partial V}{\partial \boldsymbol{q}} \\ \boldsymbol{v} &= \frac{\boldsymbol{p}}{m} \end{aligned}$$

where $\boldsymbol{F}$ is the force acting on the particle which has velocity $\boldsymbol{v}$.

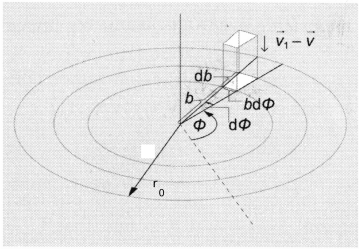
3 Molecular collisions

A real gas unlike the hypothetical non-interacting gas of the last section is subject to molecular interactions. For a dilute gas the most important of these are collisions between two (and no more) molecules. The effect of such infrequent collisions is to modify the total system probability density from the independent product form of the previous section. Another way of thinking of this is that molecules have (usually very small) correlations within an ensemble of realisations. The precise way in which this small lack of independence manifests itself is not known. Instead the gas is modelled using the singlet density Liouville equation and the effect of collisions on this density included using a hypothesis due to Boltzmann known as the Stosszahlansatz or molecular chaos hypothesis.

Now a collision between two molecules occurs in a very small spatial region and involves an exchange of momentum (and hence energy) between the colliding objects. We assume that the collisions are elastic and so that total momentum and energy is conserved.

The way in which the momentum of each particle changes as a result of the elastic collision is described by two parameters: Consider a frame of reference on one of the molecules. The other molecule approaches the first in a straight line. In the absence of a collision the center of the approaching molecule would reach a minimum distance from the center of the other stationary molecule. This distance b determines the degree with which the collision is "grazing" or "head on" and this of course affects the resulting momentum post-collision. In addition this distance of closest approach can occur at an arbitrary "azimuthal" angle ϕ around the facing circumference of the stationary molecule and again

this influences the resulting momentum post the collision. This situation is illustrated in the Figure. The cylinder depicted is called a collision cylinder and has radius r_0 (approximately the molecule diameter) and in a given small time interval δt has height $|\boldsymbol{v} - \boldsymbol{v}_1|\,\delta t$ because the first factor is the relative speed of molecules. We shall have cause to consider the differential elements of this cylinder illustrated below



Let the velocities[1] of the molecules pre-collision be $\boldsymbol{v}$ and $\boldsymbol{v}_1$ and those post-collision be $\boldsymbol{v}'$ and $\boldsymbol{v}_1'$. Using conservation of momentum and energy and simple trigonometry we have that

$$\begin{aligned} \boldsymbol{v}' &= f(\boldsymbol{v}, \boldsymbol{v}_1, b, \phi) \\ \boldsymbol{v}_1' &= g(\boldsymbol{v}, \boldsymbol{v}_1, b, \phi) \end{aligned} \tag{1}$$

where the functions g and f are known (but complicated). Now the effect of collisions involving a molecule with velocity $\boldsymbol{v}$ at the location $\boldsymbol{x}$ is to reduce the singlet density $\rho(\boldsymbol{v}, \boldsymbol{x})$. At the same time molecules with velocities $\boldsymbol{v}'$ and $\boldsymbol{v}_1'$ will collide and produce a scattered molecule with velocity $\boldsymbol{v}$ (and another with velcoity $\boldsymbol{v}_1$), the relation of which can be obtained from (1) by exhanging primed and unprimed quantities. Thus these other collisions will increase the singlet density $\rho(\boldsymbol{v}, \boldsymbol{x})$. The time rate at which such increases and reductions occur will depend on the relative speeds of the two colliding molecules i.e. on

$$|\boldsymbol{v} - \boldsymbol{v}_1| = |\boldsymbol{v}' - \boldsymbol{v}_1'| \tag{2}$$

where the post and pre relative velocities are the same due to the conservation of momentum and energy.

Now in order to compute the above rates we need to know the density of two molecules with appropriate velocities at a given location i.e. the number of molecule pairs at a given location. This can be obtained formally by the joint density

$$\rho(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{x}_1, \boldsymbol{x}_2)$$

The relationship between such a joint density and the singlet densities is a priori unclear but clearly needs specification in order to close the problem.

[1] We consider all molecules being of equal mass so that velocity serves as a proxy for momentum

Boltzmann postulated that for a dilute gas there is near statistical independence between molecule pairs so that to a good approximation

$$\rho(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{x}_1, \boldsymbol{x}_2) = \rho(\boldsymbol{u}_1, \boldsymbol{x}_1)\rho(\boldsymbol{u}_2, \boldsymbol{x}_2)$$

Such an assumption is called the Stosszahlansatz and is an example of a closure hypothesis. Such devices are often used to reduce joint densities to more useful lower order densities. They always have some aspect of ad hocness to them and must be justified on a case by case basis[2]. In this case the diluteness of the gas provides the justification since such a gas approaches the hypothetical non-interacting one discussed earlier.

Now to compute the number of molecules with velocity $\boldsymbol{v}$ and position $\boldsymbol{x}$ which are being eliminated and created by collisions in a small time interval δt we need to multiply the joint density above by an appropriate volume element in configuration space. Consider the reduction case first: This volume element is simply[3] the collision cylinder volume integrated over all values of $\boldsymbol{v}_1$ and muliplied by the differential volumes surrounding $\boldsymbol{v}$ and $\boldsymbol{x}$. Thus the number of eliminations in time δt is

$$\begin{aligned} n_E(\boldsymbol{v}, \boldsymbol{x}) &= \int d^3 v_1 \int_0^{r_0} b db \int_0^{2\pi} d\phi \, |\boldsymbol{v} - \boldsymbol{v}_1| \, \delta t \rho(\boldsymbol{v}, \boldsymbol{x}) \rho(\boldsymbol{v}_1, \boldsymbol{x}) d^3\boldsymbol{x} d^3\boldsymbol{v} \\ &\equiv \dot{\rho}_{CE}(\boldsymbol{v}, \boldsymbol{x}) \delta t d^3\boldsymbol{x} d^3\boldsymbol{v} \end{aligned}$$

where we are defining a reduction rate density on the second line. For the increase case we are dealing with a series of collision cylinders defined by various values of $\boldsymbol{v}'$ but are only interested in the appropriate differential volume elements within such cylinders (see Figure) which ensure that a velocity after collision is $\boldsymbol{v}$. Integrating these volume elements over the appropriate values of $\boldsymbol{v}'$ and $\boldsymbol{v}'_1$ and then changing variables using the fact that

$$d^3\boldsymbol{v}' d^3\boldsymbol{v}'_1 = d^3\boldsymbol{v} d^3\boldsymbol{v}_1 \tag{3}$$

we obtain

$$\begin{aligned} n_I(\boldsymbol{v}, \boldsymbol{x}) &= \int d^3 v_1 \int_0^{r_0} b db \int_0^{2\pi} d\phi \, |\boldsymbol{v} - \boldsymbol{v}_1| \, \delta t \rho(\boldsymbol{v}', \boldsymbol{x}) \rho(\boldsymbol{v}'_1, \boldsymbol{x}) d^3\boldsymbol{x} d^3\boldsymbol{v} \\ &\equiv \dot{\rho}_{CI}(\boldsymbol{v}, \boldsymbol{x}) \delta t d^3\boldsymbol{x} d^3\boldsymbol{v} \end{aligned}$$

where we have used the collision conservation of relative velocity (2) and the velocities $\boldsymbol{v}'$ and $\boldsymbol{v}'_1$ are constrained by collision equations of the form (1)[4] in order to ensure that after collision we obtain a molecule with velocity $\boldsymbol{v}$. This implies mathematically of course that in the integrand we need to express the primed velocities in terms of the unprimed velocities in order to carry out the multiple integral. For the reduction case it was possible to carry out the integrals

[2] They are frequently found in studies of turbulence

[3] For a detailed justification see the supplementary notes

[4] with primes and unprimes exchanged

over b and ϕ directly since the integrand did not depend on them but for the increase case this is not possible because of the above mentioned constraint. Combining the equations for the increase and reduction we obtain the singlet density rate due to molecular collisions:

$$\dot{\rho}_C(\boldsymbol{v},\boldsymbol{x}) = \int d^3v_1 \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left[\rho(\boldsymbol{v}',\boldsymbol{x})\rho(\boldsymbol{v}'_1,\boldsymbol{x}) - \rho(\boldsymbol{v},\boldsymbol{x})\rho(\boldsymbol{v}_1,\boldsymbol{x})\right] \tag{4}$$

A detailed version of the above derivation may be found in [2] section 7.2.4[5].

This source term for the singlet density may now be inserted on the righthand side of the singlet Liouville equation to obtain a closed form PDE for density:

$$\dot{\rho} + \boldsymbol{v} \bullet \nabla_q \rho + \boldsymbol{F} \bullet \nabla_p \rho = \dot{\rho}_C \tag{5}$$

This equation is of major historical significance in statistical physics and is known as Boltzmann's transport equation. Notice the importance to the derivation of the Stosszahlansatz closure hypothesis.

Consider now the following integral for a general function $\chi(\boldsymbol{v})$:

$$M_\chi(\boldsymbol{x}) \equiv \int d^3\boldsymbol{v}\chi(\boldsymbol{v}) \int d^3v_1 \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left(\rho'\rho'_1 - \rho\rho_1\right)$$

where $\rho'_1 \equiv \rho(\boldsymbol{v}'_1,\boldsymbol{x})$ etc. Switching $\boldsymbol{v} \to \boldsymbol{v}_1$ it is easily seen that

$$M_\chi(\boldsymbol{x}) = \int d^3\boldsymbol{v} \int d^3v_1 \chi(\boldsymbol{v_1}) \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left(\rho'\rho'_1 - \rho_1\rho\right)$$

Similarly switching $\boldsymbol{v} \to \boldsymbol{v}'$ and $\boldsymbol{v_1} \to \boldsymbol{v'}_1$ and using equations (2) and (3) we obtain

$$M_\chi(\boldsymbol{x}) = \int d^3\boldsymbol{v} \int d^3v_1 \chi(\boldsymbol{v'}) \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left(\rho\rho_1 - \rho'_1\rho'\right)$$

and finally switching $\boldsymbol{v} \to \boldsymbol{v}'_1$ and $\boldsymbol{v_1} \to \boldsymbol{v'}$ we get

$$M_\chi(\boldsymbol{x}) = \int d^3\boldsymbol{v} \int d^3v_1 \chi(\boldsymbol{v'_1}) \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left(\rho\rho_1 - \rho'\rho'_1\right)$$

Adding all four equations we get

$$M_\chi(\boldsymbol{x}) = \frac{1}{4}\int d^3\boldsymbol{v} \int d^3v_1 \left(\chi(\boldsymbol{v}) + \chi(\boldsymbol{v_1}) - \chi(\boldsymbol{v'}) - \chi(\boldsymbol{v'_1})\right) \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v}-\boldsymbol{v}_1| \left(\rho'\rho'_1 - \rho\rho_1\right) \tag{6}$$

[5] A copy of this supplementary material may be found on the course webpage

4 H-Theorem

The transport equation just derived holds for a dilute gas out of equilibrium but an interesting question concerns the equilibration process which we discussed in the context of stochastic models in the previous lecture. An analogous procedure works for the transport equation. We restrict our attention here to the case that the gas is uniform[6] and investigate the behaviour of (minus) the entropy functional defined on the singlet density:

$$H(t) \equiv \int d^3v \rho \log \rho$$

As in the previous lecture we differentiate obtaining easily

$$\frac{dH}{dt} = \int d^3v \frac{d\rho}{dt} (1 + \ln \rho)$$

Now $\frac{d\rho}{dt}$ is given by the final three terms in equation (5). The first two terms are just the Liouville terms for the case that $\nabla \bullet A = 0$ and so result in zero when inserted in the last equation using the logic of the previous lecture. Note that physically this means that any change in singlet density entropy is due to molecular collisions only. We are left then with

$$\frac{dH}{dt} = \int d^3x d^3v \dot{\rho}_C (1 + \ln \rho)$$

Using equation (6) this may be rewritten as

$$\begin{aligned} \frac{dH}{dt} &= \int d^3\boldsymbol{v} \int d^3v_1 \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v} - \boldsymbol{v}_1| \, (\rho' \rho'_1 - \rho\rho_1) \\ &\quad \times \frac{1}{4} (\log \rho + \log \rho_1 - \log \rho' - \log \rho'_1) \\ &= \frac{1}{4} \int d^3\boldsymbol{v} \int d^3v_1 \int_0^{r_0} bdb \int_0^{2\pi} d\phi \, |\boldsymbol{v} - \boldsymbol{v}_1| \\ &\quad \times (\rho' \rho'_1 - \rho\rho_1) \log \frac{\rho\rho_1}{\rho' \rho'_1} \end{aligned} \tag{7}$$

Now it is a simple exercise in calculus to demonstrate that

$$(x - y) \log \frac{y}{x} \leq 0$$

with equality only when $x = y$. It follows immediately then from the positivity of the integrand in the second last line of (7) that H strictly decreases with time until

$$\rho\rho_1 = \rho' \rho'_1 \tag{8}$$

which may therefore be identified with a condition of equilibrium. It is also referred to in other contexts as a condition of detailed balance. This result

[6] Thus the singlet density depends only on momentum and time.

constitutes the celebrated Boltzmann H-Theorem which shows strict equilibration with time and H is minus the Shannon entropy for the (spatially uniform) singlet density. The condition of equilibrium equation (8) can be used to deduce

$$\log \rho + \log \rho_1 = \log \rho' + \log \rho'_1$$

Now $\log \rho$ is a function of velocity (and time) and this equation is of the form of the conservation of functions of velocity during an arbitrary collision. For the simple molecules we have considered here this implies that it must be a linear combination of the momentum and energy since these are the only conserved quantities during a collision[7]. Thus we must have

$$\log \rho = a + \boldsymbol{b} \bullet \boldsymbol{v} + c\boldsymbol{v} \bullet \boldsymbol{v}$$

i.e. the equilibrium ρ must be a Gaussian function of velocity components. Now if we assume that the gas container is at rest then the mean velocity with respect to the singlet equilibrium density must be zero. From the properties of Gaussian densities it follows that $\boldsymbol{b} = \boldsymbol{0}$ and hence

$$\rho = C \exp\left(-c\boldsymbol{v} \bullet \boldsymbol{v}\right)$$

The Stosszahlansatz assumption then shows that the equilibrium uniform probability for all molecules is a Maxwell distribution as is indeed observed to a high degree of accuracy for dilute gases.

5 Concluding remarks

The Stosszahlansatz closure assumption was clearly of crucial importance in deriving the Boltzmann transport equation. Generalizations of such closures are possible to deal with more dense materials. A formal way of constructing these is offered by a closure heirarchy theory known as the BBGKY (Bogoliubov–Born–Green–Kirkwood–Yvon) heirarchy. More details on this topic may be found in the book by Dorfman [1]. The discussion of the work in this book by Kac in this area is also of particular fundamental interest. Transport equations in general are a large subject with many fine reference books.

Close to equilibrium the Boltzmann equation may be linearized about this density and the resulting (linear) equations for the singlet density are called Master equations. These are of the form of a Chapman Kolmogorov equation which we discussed briefly at the conclusion of the previous lecture. Such an equation ensures that both relative entropy and differential entropy satisfy monotonic declines and increases respectively. Interested students can find more discussion in the book by Van Kampen [3] who did significant work on such equations in the present context in the 1960s.

[7] These are called the collision invariants for the molecules of interest and for monatomic molecules the only such invariants are momentum, energy and mass. The latter is always fixed so is not important. This result may be proven rigorously as was done originally by Boltzmann. It also generalizes naturally to the relativistic case implying an equilibrium density of the form $C \exp\left(-A^a p_a\right)$ where p_a is the energy-momentum four vector and A^a an "inverse temperature" four vector.

References

[1] J. R. Dorfman. *An introduction to chaos in nonequilibrium statistical mechanics*. Cambridge University Press, 1999.

[2] G. F. Mazenko. *Nonequilibrium Statistical Mechanics*. Wiley-Vch, 2006.

[3] N. G. Van Kampen. *Stochastic processes in physics and chemistry*. Access Online via Elsevier, 1992.