

Non-equilibrium Statistical Physics

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May 28, 2025

These are very rough and incomplete notes for the course. I primarily prepare them for my personal use during the lectures. There are typos, mistakes and missing explanations. Their quality will gradually improve but use with caution.

I will be grateful for letting me know about any spotted typos and errors.

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The presentation follows mainly:

- *Statistical Dynamics: Matter out of Equilibrium* by R. Balescu

I take also inspirations from

- *Kinetic Theory: Classical, Quantum, and Relativistic Descriptions* by R.L. Liboff
- *Classical Kinetic Theory of Fluids* by P. Resibois, M. de Leener

Another suggested book is

- *Contemporary kinetic theory of matter* by J. R. Dorfman, H. Van Beijeren, T. R. Kirkpatrick.

A good online source (for our purposes mainly Lectures 1, 2 and 4)

- *Lectures on Kinetic Theory* by D. Tong, <https://www.damtp.cam.ac.uk/user/tong/kinetic.html>

1 Motivation

Navier-Stokes equations

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}), \quad (1.1)$$

$$\partial_t (\rho \mathbf{u}) = -\nabla \cdot (\rho \mathbf{u} \mathbf{u} + P + \pi), \quad (1.2)$$

$$\partial_t (\rho e) = -\nabla \cdot (\rho e \mathbf{u} + \mathbf{q}) - P \nabla \cdot \mathbf{u} - \pi : \nabla \mathbf{u}. \quad (1.3)$$

State of the system described by ρ, \mathbf{u}, e . Here P is the (scalar) pressure, $\pi(\mathbf{x}, t)$ is the dissipative pressure tensor and $\mathbf{q}(\mathbf{x}, t)$ is the heat flux. Locally in space and time the usual thermodynamics works. Pressure $P(\mathbf{x}, t)$ and internal energy $e(\mathbf{x}, t)$ follow from local temperature $T(\mathbf{x}, t)$ and density $\rho(\mathbf{x}, t)$ through from the equation of state.

The dissipative pressure tensor and heat flux are given by transport equations

$$\pi = -\eta \{\nabla \mathbf{u}\}^o - \zeta (\nabla \cdot \mathbf{u}), \quad \mathbf{q} = -\kappa \nabla T, \quad (1.4)$$

with transport coefficients: shear viscosity η , bulk viscosity ζ and thermal conductivity κ .

In writing the equations we used the following notation $(\nabla \mathbf{u})_{ij} = \nabla_i \mathbf{u}_j$,

$$\{\nabla \mathbf{u}\}^o = \nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3} (\nabla \cdot \mathbf{u}), \quad (\nabla \cdot \mathbf{u}\mathbf{u})_i = \nabla_j u_i u_j. \quad (1.5)$$

and tensor multiplication.

Observe that the Navier-Stokes equations are not invariant under the time inversion

$$t \rightarrow -t, \quad \mathbf{u} \rightarrow -\mathbf{u}. \quad (1.6)$$

They describe irreversible dynamics. The terms breaking the reversability are proportional to the transport coefficients, they describe dissipative processes. For transport coefficients equal to zero, we get reversible Euler equations

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}), \quad (1.7)$$

$$\partial_t (\rho \mathbf{u}) = -\nabla \cdot (\rho \mathbf{u}\mathbf{u} + P), \quad (1.8)$$

$$\partial_t (\rho e) = -\nabla \cdot (\rho e \mathbf{u}) - P \nabla \cdot \mathbf{u}. \quad (1.9)$$

What is the microscopic origin of the Navier-Stokes equations and how the macroscopic time irreversibility relates to the microscopic reversibility?

2 Microscopic and macroscopic dynamical systems

Consider Hamiltonian system of classical mechanics of N particles. Each particle is described by its position \mathbf{q}_j and momentum \mathbf{p}_j which are 3-dimensional vectors. A *state* of the system is then described by specifying positions and momenta of all the particles: $(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$ and we can think about it as a point in the $6N$ -dimensional space called *phase space*. We can also think about $6N = 2F$ where F is the number of degrees of freedom. We will often denote the point of a phase space as (q, p) where q is the set of F coordinates and p is the set of F momenta.

We also introduce *dynamical functions*, these are functions on the phase space $B(p, q)$. An example is the Hamiltonian $H(p, q)$. (isolated (conservative) systems)

The Hamiltonian determines the law of evolution. These are Hamilton's equations of motion

$$\frac{dq_j(t)}{dt} = \frac{\partial H(q, p)}{\partial p_j}, \quad \frac{dp_j(t)}{dt} = -\frac{\partial H(q, p)}{\partial q_j} \quad (2.1)$$

The dynamical function will evolve accordingly. Writing $b(q, p; t) = b(q(t), p(t))$ we find

$$\partial_t b(q, p; t) = \sum_{j=1}^F \left(\frac{\partial b}{\partial q_j} \frac{dq_j}{dt} + \frac{\partial b}{\partial p_j} \frac{dp_j}{dt} \right) = \sum_{j=1}^F \left(\frac{\partial b}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial b}{\partial p_j} \frac{\partial H}{\partial q_j} \right) = \{b, H\}, \quad (2.2)$$

where the Poisson bracket is

$$\{f, g\} = \sum_{j=1}^F \left(\frac{\partial f}{\partial q_j} \frac{\partial g}{\partial p_j} - \frac{\partial f}{\partial p_j} \frac{\partial g}{\partial q_j} \right) \quad (2.3)$$

Clearly

$$\{q_j, p_k\} = \delta_{j,k}, \quad \{q_j, q_k\} = \{p_j, p_k\} = 0. \quad (2.4)$$

Properties of the Poisson bracket (with f, g, h dynamical functions and α a scalar (a quantity independent of q and p))

$$\{f, g\} = -\{g, f\}, \quad \{\alpha, f\} = 0, \quad (2.5)$$

$$\{fg, h\} = f\{g, h\} + \{f, h\}g, \quad (2.6)$$

$$\{f, \{g, h\}\} + \{g, \{h, f\}\} + \{h, \{f, g\}\} = 0. \quad (2.7)$$

We can also write the evolution equation

$$\partial_t b(q, p; t) = [H]b(q, p, t), \quad (2.8)$$

where the linear operator $[H]$ is

$$[H] = \sum_{j=1}^F \left(\frac{\partial H}{\partial p_j} \frac{\partial}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial}{\partial p_j} \right). \quad (2.9)$$

This equation can be solved formally as

$$b(q, p; t) = e^{[H]t} b(q, p) = \sum_n \frac{1}{n!} t^n [H]^n b(q, p). \quad (2.10)$$

Operator $e^{[H]t}$ is called the *propagator*. It can be shown that

$$b(q, p; t) = e^{[H]t} b(q, p; 0) = b(e^{[H]t} q, e^{[H]t} p; 0) = b(q(t), p(t); 0) \quad (2.11)$$

Microscopic function describing the mass density. Macroscopically we have a continuous function $\rho(\mathbf{x}, t)$. Microscopically, we have discrete massive particles. Therefore a microscopic representation of $\rho(\mathbf{x}, t)$ must consist of testing whether any of the particles in the system is actually at position \mathbf{x} . This is achieved by

$$\rho(q, p; \mathbf{x}, 0) = \sum_{j=1}^N m \delta(\mathbf{q}_j - \mathbf{x}). \quad (2.12)$$

Using the propagator we get

$$\rho(q, p; \mathbf{x}, t) = e^{Ht} \sum_{j=1}^N m \delta(\mathbf{q}_j - \mathbf{x}) = \sum_{j=1}^N m \delta(\mathbf{q}_j(t) - \mathbf{x}). \quad (2.13)$$

The coordinate \mathbf{x} of the physical space is a scalar, whereas the coordinate \mathbf{q}_j in the phase space is a dynamical quantity.

What is the relation between $\rho(\mathbf{x}, t)$ and $\rho(q, p; \mathbf{x}, t)$? We will find out soon.

2.1 Examples

Our main test bed for the ideas will be a set of N identical point particles, each of mass m and in absence of any external field. The Hamiltonian of such system is

$$H = H^0 + H', \quad (2.14)$$

where the kinetic part is

$$H^0 = \sum_{j=1}^N H_j^0, \quad H_j^0 = \frac{\mathbf{p}_j^2}{2m}, \quad (2.15)$$

while the interaction part is a sum of two-body interactions

$$H' = \sum_{j < k}^N V_{jk}. \quad (2.16)$$

We will also assume that the interaction energy doesn't depend on the momenta but only on the coordinates of the two particles. More specifically, on the distance between them

$$V_{jk} = V(|\mathbf{q}_j - \mathbf{q}_k|). \quad (2.17)$$

The standard cases are

- Lennard-Jones potential for neutral particles

$$V^{LJ}(r) = V_0 \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \quad (2.18)$$

- Its hard spheres limit when the attractive part is weak

$$V^{HS}(r) = \begin{cases} \infty, & r < r_0, \\ 0, & r > r_0 \end{cases} \quad (2.19)$$

- Coulomb potential

$$V^C = \frac{e^2}{r^2}. \quad (2.20)$$

- Debye (screened Coulomb) potential

$$V^D(r) = e^2 \frac{\exp(-r/r_D)}{r}, \quad r_D = \left(\frac{4\pi e^2 n}{k_B T} \right)^{-1/2}. \quad (2.21)$$

In the presence of external, possibly time-dependent field there is an extra contribution H^F to the Hamiltonian

$$H^F = \sum_{j=1}^N V^F(\mathbf{q}_j, t). \quad (2.22)$$

2.2 The phase space distribution function

Statistical physics is **not** mechanics of many particles. The questions asked are different.

Example with a rod.

Mechanics: state of the system specified by a point in the phase space. Statistical physics: state of the system specified by the phase space distribution function

The objects of macroscopic physics are presented by continuous functions in the physical space: $B(\mathbf{x}, t)$. The corresponding microscopic dynamical quantities, are functions $b(q, p; \mathbf{x}, t)$ of the phase space variables additionally parametrized (dependent) on \mathbf{x} and t . We need a map

$$b(q, p; \mathbf{x}, t) \rightarrow B(\mathbf{x}, t). \quad (2.23)$$

This is a functional, that for give \mathbf{x} and t associates a number to any given function of q and p

$$B(\mathbf{x}, t) = \langle b(q, p; \mathbf{x}, t) \rangle = \langle b \rangle. \quad (2.24)$$

We require the following two conditions from this functional

- Constants on the phase space are unaffected

$$\langle \beta \rangle = \beta, \quad (2.25)$$

- It is linear (this guarantees that microscopic additivity is translated into macroscopic, e.g. mass density for a system with particles of two types)

$$\langle \beta b + \gamma c \rangle = \beta \langle b \rangle + \gamma \langle c \rangle \quad (2.26)$$

A simple candidate is

$$B(\mathbf{x}, t) = \langle b \rangle = \int dq dp b(q, p; \mathbf{x}, t) F(q, p), \quad (2.27)$$

with the requirement that

$$\int dq dp F(q, p) = 1. \quad (2.28)$$

We will also assume that function $F(q, p)$ is positive definite

$$F(q, p) \geq 0. \quad (2.29)$$

We will call it *phase space distribution function* or *distribution function*.

The state of the system is completely specified by the specification of the distribution function $F(q, p)$.

We can give $F(q, p)$ a probabilistic meaning where $F(q, p)dqdp$ is the probability of finding the system within the infinitesimal domain $(q + dq)$, $(p + dp)$ in the phase space. Functional (...) is then called the *phase space average*.

How to find $F(q, p)$?

How does $B(\mathbf{x}, t)$ evolve? Assume that $b(q, p; \mathbf{x}, t = 0) = b(q, p; \mathbf{x})$ is a given function. Then at time t

$$B(\mathbf{x}, t) = \int dp dq \left(e^{[H]t} b(q, p; \mathbf{x}) \right) F(q, p). \quad (2.30)$$

The time evolution can be now transferred from b to F with the result

$$B(\mathbf{x}, t) = \int dp dq b(q, p; \mathbf{x}) F(q, p; t), \quad (2.31)$$

with

$$F(q, p; t) = e^{-[H]t} F(q, p). \quad (2.32)$$

Which is like going from Heisenberg picture in which observables evolve in time to the Schrodinger picture in which the state evolves in time. This transformation relies on the concept of canonical transformations.

Canonical transformation is a transformation to new coordinate $\{q'_j, p'_k\}$ such that

$$\{q'_j, p'_k\} = \delta_{j,k}, \quad \{q'_j, q'_k\} = \{p'_j, p'_k\} = 0. \quad (2.33)$$

Important results of Hamiltonian dynamics that we use are: time evolution is a canonical transformation and volume element of the phase space ($dqdp$) is invariant under any canonical transformation.

This way we arrived now at the evolution equation for the phase space distribution function

$$\partial_t F(q, p; t) = LF(q, p; t), \quad (2.34)$$

where *Liouvillian* is

$$LF = \{H, L\} = \sum_{j=1}^{3N} \left(\frac{\partial H}{\partial q_j} \frac{\partial F}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial F}{\partial q_j} \right). \quad (2.35)$$

Liouvillian is like the Hamiltonian but instead of acting on a point in the phase space it acts on the distribution function.

We write now the Liouvillian for the Hamiltonian of interacting particles. We introduce the velocity

$$\mathbf{v}_j = \frac{\mathbf{p}_j}{m}, \quad (2.36)$$

and the following abbreviations

$$\nabla_j = \frac{\partial}{\partial \mathbf{q}_j}, \quad \partial_j = \frac{\partial}{\partial \mathbf{p}_j}, \quad \partial_{jk} = \partial_j - \partial_k \quad (2.37)$$

Then the Liouvillian is

$$L = L^0 + L' = \sum_{j=1}^N L_j^0 + \sum_{j < k}^N L'_{jk}, \quad (2.38)$$

where

$$L_j^0 = -\mathbf{v}_j \cdot \nabla_j, \quad L'_{jk} = (\nabla_j V_{jk}) \cdot \partial_{jk}. \quad (2.39)$$

2.3 Equilibrium states

Stationary solutions to the Liouville equation

$$\{H(q, p), F^0(q, p)\} = 0. \quad (2.40)$$

Solution is any function of the Hamiltonian,

$$F^0(q, p) = \Phi[H(q, p)], \quad (2.41)$$

that is positive and normalizable. There are still many options. The central assumption of equilibrium statistical physics is the principle of equal a priori probabilities. Assuming then a closed system that can exchange energy with its environment we get

$$F^0(q, p) = \frac{1}{h^{3N} N! Z(T, V, N)} \exp\left(-\frac{H(q, p)}{k_B T}\right), \quad (2.42)$$

with the partition function that ensures the normalization, namely

$$Z(T, V, N) = \frac{1}{h^{3N} N!} \int dq dp \exp\left(-\frac{H(q, p)}{k_B T}\right). \quad (2.43)$$

The fundamental relation of equilibrium statistical physics expresses the Helmholtz free energy $A(T, V, N)$ in terms of the partition function

$$A(T, V, N) = -k_B T \ln Z(T, V, N). \quad (2.44)$$

2.4 Exercises

1. Find the stationary state of the Navier-Stokes equations in the presence of an external potential
2. Solve the Harmonic oscillator by a canonical transformation of the coordinates.
3. Show the relation between the Heisenberg picture (2.30) and Schroedinger picture (2.31).
4. Prove that the Liouville operator is anti-Hermitian.
5. Solve Liouville equation for a system of non-interacting particles. Compute the propagator for such system.

3 Reduced distributions, correlations and the BBGKY hierarchy

Shorthand notation $x_j = (\mathbf{q}_j, \mathbf{p}_j)$ for $j = 1, \dots, N$. Hamiltonian is a function of all variables (x_1, \dots, x_N) and for the Hamiltonians of our interest

$$H(x_1, \dots, x_N) = \sum_{j=1}^N H^0(x_j) + \sum_{j < k}^N V(x_j, x_k). \quad (3.1)$$

Consider an arbitrary dynamical function $b(x_1, \dots, x_N)$ of a system of N identical particles. Since particles are identical, this function has to be symmetric under permutation of any two variables. Therefore it can be decomposed in the following way

$$b(x_1, \dots, x_N) = b_0 + \sum_{j=1}^N b_1(x_j) + \sum_{j < k}^N b_2(x_j, x_k) + \sum_{j < k < n}^N b_3(x_j, x_k, x_n) + \dots + b_N(x_1, \dots, x_N). \quad (3.2)$$

Note that functions $b_s(x_1, \dots, x_s)$ has to be non-additive functions of the s variables x_1, \dots, x_s . Therefore, they cannot be of the form

$$b_2(x_1, x_2) = f(x_1, x_2) + g(x_1) + g(x_2), \quad (3.3)$$

because contribution of the form $g(x_1) + g(x_2)$ is already included in b_1 . Similarly for higher s . The functions b_s are called *irreducible s -particle dynamical functions*.

Alternative representation is

$$b(x_1, \dots, x_N) = b_0 + \sum_{j=1}^n b_1(x_j) + \frac{1}{2!} \sum_{j \neq k}^N b_2(x_j, x_k) + \dots + b_N(x_1, \dots, x_N). \quad (3.4)$$

Most dynamical functions of physical interest contain only small number of irreducible dynamical functions, b_0, b_1, \dots, b_S with $S \ll N$ and with $b_s = 0$ for $s > S$. Most often $S = 2$ or 3.

The distribution function for identical particles is also a symmetric function under permutation of any pair of variables. Consider now the average value of a dynamical function decomposed into irreducible contributions. The constant term b_0 yields b_0 . The one-particle contribution is

$$\int dx_1 \dots dx_N \left[\sum_{j=1}^N b_1(x_j) \right] F(x_1, \dots, x_N) = N \int dx_1 \dots dx_N b_1(x_1) F(x_1, \dots, x_N). \quad (3.5)$$

Only the integration over x_1 depends on the dynamical function. Therefore, the information contained in the integration over the other variables is irrelevant for the evaluation of the one-particle contribution. This motivates defining the reduced one-particle distribution function

$$f_1(x_1) = N \int dx_2, \dots, dx_N F(x_1, x_2, \dots, x_N). \quad (3.6)$$

We then obtain

$$\int dx_1 dx_N \left[\sum_{j=1}^N b_1(x_j) \right] F(x_1, \dots, x_N) = \int dx_1 b_1(x_1) f_1(x_1). \quad (3.7)$$

In a similar fashion, for the s -particle contribution

$$\begin{aligned} \int dx_1 \dots dx_N \left[\frac{1}{s!} \sum_{j_1 \neq j_2 \neq \dots \neq j_s} b_s(x_{j_1}, \dots, x_{j_s}) \right] F(x_1, \dots, x_N) \\ = \frac{N!}{(N-s)!s!} \int dx_1 \dots dx_N b_s(x_1, \dots, x_s) F(x_1, \dots, x_N) \\ = \frac{1}{s!} \int dx_1 \dots dx_s b_s(x_1, \dots, x_s) f_s(x_1, \dots, x_s), \end{aligned} \quad (3.8)$$

where we defined the s -particle reduced distribution function

$$f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!} \int dx_{s+1} \dots dx_N F(x_1, \dots, x_N). \quad (3.9)$$

The reduced distribution functions are symmetric and $f_0 = 1$ while for the others the following normalization holds (show it)

$$\int dx_1 \dots dx_s f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!}. \quad (3.10)$$

There is also the following relation between the reduced distribution functions for $r < s$,

$$f_r(x_1, \dots, x_r) = \frac{(N-s)!}{(N-r)!} \int dx_{r+1} \dots dx_s f_s(x_1, \dots, x_s) \quad (3.11)$$

Function f_r with $r < s$ contains less information than f_s and therefore this relation is not invertible.

An average value of any dynamical quantity we can now write

$$\langle b \rangle = b_0 + \sum_{s=1}^N \frac{1}{s!} \int dx_1 \dots dx_s b_s(x_1, \dots, x_s) f_s(x_1, \dots, x_s). \quad (3.12)$$

Thermodynamic limit: meaningless for F . Makes sense for f_s with s fixed and $s \ll N$.

3.1 Evolution equations for the reduced distributions

Equations for F

$$\partial_t F = \sum_{j=1}^N L_j^0 F + \sum_{j < k}^N L'_{jk} F. \quad (3.13)$$

Integrate this over all x 's. The right hand vanishes from the normalization condition of F . Thus we obtain

$$\int dx_1 \dots dx_N \left(\sum_{j=1}^N L_j^0 + \sum_{j < k}^N L'_{jk} \right) F = 0, \quad (3.14)$$

which has to hold for each term separately

$$\int dx_1 \dots dx_N L_j^0 F = 0, \quad \int dx_1 \dots dx_N L'_{jk} F = 0. \quad (3.15)$$

This will be useful in deriving evolution equations for the reduced distribution functions. Integrate equation for F over particles $s+1, \dots, N$. We obtain

$$\partial_t f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!} \int dx_{s+1} \dots dx_N \left(\sum_{j=1}^N L_j^0 F + \sum_{j < k}^N L'_{jk} F \right). \quad (3.16)$$

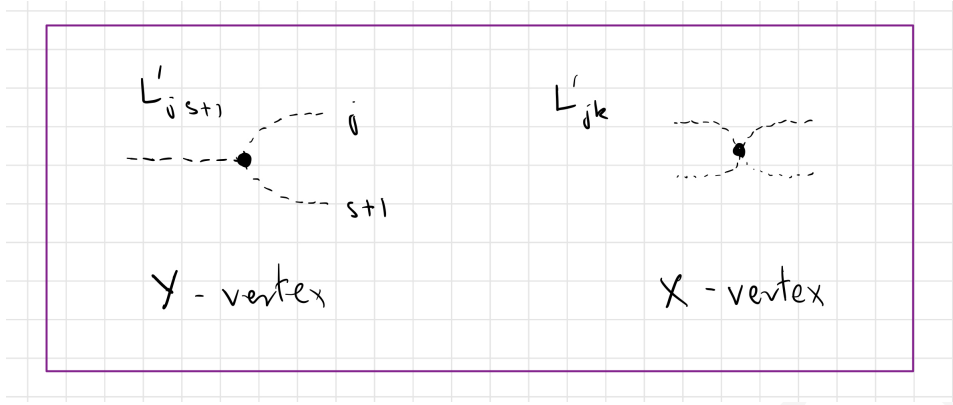


Figure 1: The right hand side of the equations for reduced distribution functions can be represented diagrammatically using two types of diagrams. In the Y-vertex the position $(s+1)$ is integrated over.

For the first term we have

$$\sum_{j=1}^N L_j^0 F = \sum_{j=1}^s L_j^0 F + \sum_{j=s+1}^N L_j^0 F, \quad (3.17)$$

For the first contribution, the integration and the operator L_j^0 can be exchanged. The second contribution vanishes due to the above result. Similar analysis of the second contribution gives

$$\begin{aligned} \partial_t f_s(x_1, \dots, x_s) - \sum_{j=1}^s L_j^0 f_s(x_1, \dots, x_s) &= \sum_{j < k} L'_{jk} f_s(x_1, \dots, x_s) \\ &+ \sum_{j=1}^s \int dx_{s+1} L'_{j,s+1} f_{s+1}(x_1, \dots, x_{s+1}). \end{aligned} \quad (3.18)$$

Few comments are in place.

1. We have moved the term with L_j^0 to the left hand side. The right hand side contains now only terms which are due to the interactions between the particles. If the system is free, the right hand side is equal to zero.
2. The equation for f_s is coupled to f_{s+1} . This creates a hierarchy of the coupled equations. This hierarchy is known as BBGKY (Bogoliubov, Born, Green, Kirkwood and Yvon).
3. The hierarchy is linear in f_s .
4. The hierarchy is completely equivalent to the Liouville equation.

Note that, as discussed above, for most of practical purpose we need only f_1 , f_2 and maybe f_3 . However, due to the hierarchical structure of the equations they all depend on the higher reduced distribution functions.

Let us write explicitly the equations for the one-body and two-body reduced functions

$$\begin{aligned} \partial_t f_1(x_1) - L_1^0 f_1(x_1) &= \int dx_2 L'_{12} f_2(x_1, x_2), \\ \partial_t f_2(x_1, x_2) - (L_1^0 + L_2^0) f_2(x_1, x_2) &= L_{12} f_2(x_1, x_2) + \int dx_3 (L'_{13} + L'_{23}) f_3(x_1, x_2, x_3). \end{aligned} \quad (3.19)$$

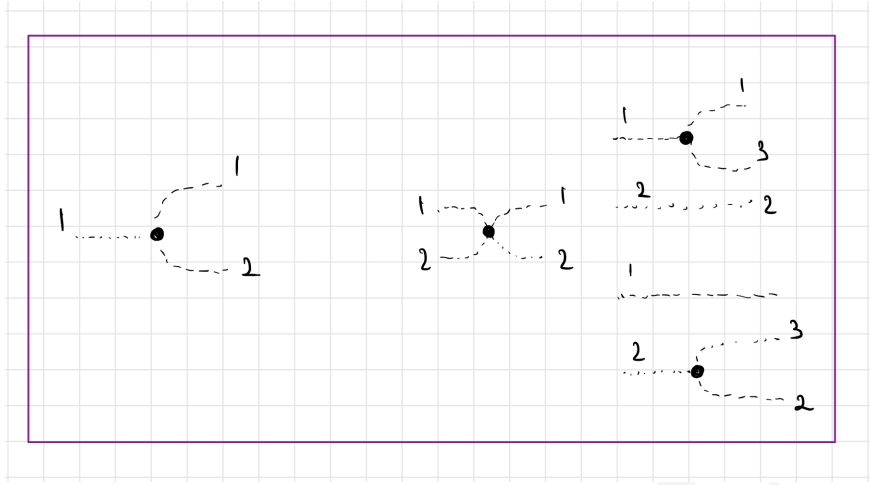


Figure 2: Diagrams for the one-body and two-body reduced distribution functions

3.2 Correlation functions and their evolution

If the system is uncorrelated at some given time t then

$$f_s(x_1, \dots, x_s) = \prod_{j=1}^s f_1(x_j). \quad (3.20)$$

In general the time evolution will produce correlations and the reduced distribution functions will vary from the uncorrelated form. To capture true s -particle correlations we consider partition of the set of particles into disjoint sets containing at least one particle. We write

$$f_2(x_1, x_2) = f_1(x_1)f_1(x_2) + g_2(x_1, x_2), \quad (3.21)$$

while for $s = 3$,

$$f_3(x_1, x_2, x_3) = f_1(x_1)f_1(x_2)f_1(x_3) + f_1(x_1)g_2(x_2, x_3) + f_1(x_2)g_2(x_1, x_3) + f_1(x_3)g_2(x_1, x_2) + g_3(x_1, x_2, x_3), \quad (3.22)$$

with the last term describing the truly correlated effect of 3 particles.

Consider now normalization of the correlation functions. For the two point function we have

$$\frac{1}{N^2} \int dx_1 dx_2 f_2(x_1, x_2) = \left(\frac{1}{N} \int dx_1 f_1(x_1) \right)^2 + \frac{1}{N^2} \int dx_1 dx_2 g_2(x_1, x_2). \quad (3.23)$$

Using the normalization of the reduced distribution functions we find

$$-\frac{1}{N} = \frac{1}{N^2} \int dx_1 dx_2 g_2(x_1, x_2), \quad (3.24)$$

which implies that, in the thermodynamic limit,

$$\frac{1}{N^s} \int dx_1 \dots dx_s g_s(x_1, \dots, x_s) \rightarrow 0, \quad (3.25)$$

and the whole normalization of f_s is in the uncorrelated term.

The evolution equations are now

$$\partial_t f(x_1) - L_1^0 f(x_1) = \int dx_2 (L'_{12} f(x_1) f(x_2) + L'_{12} g_2(x_1, x_2)), \quad (3.26)$$

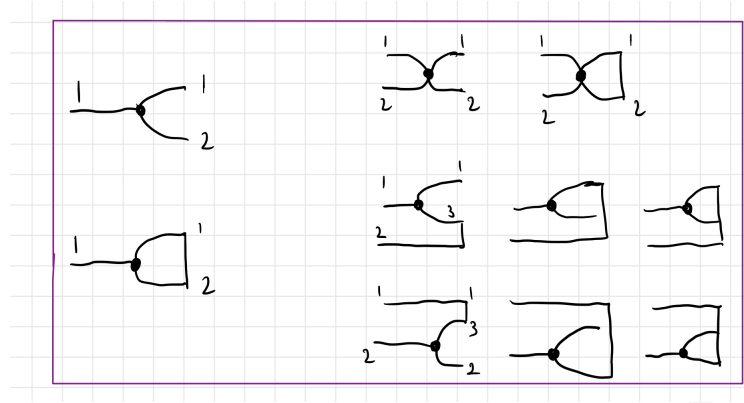


Figure 3: Diagrams for the evolution of the connected correlation functions. The horizontal bar implies that the variables enter the same correlator.

and

$$\begin{aligned} \partial_t g_2(x_1, x_2) - (L_1^0 + L_2^0)g_2(x_1, x_2) = & L_{12}' f(x_1)f(x_2) + L_{12}' g_2(x_1, x_2) \\ & + \int dx_3 [L_{13}' f(x_1)g_2(x_2, x_3) + L_{23}' f(x_2)g_2(x_1, x_3) \\ & + (L_{13}' + L_{23}') (f(x_3)g_2(x_1, x_2) + g_3(x_1, x_2, x_3))] . \end{aligned} \quad (3.27)$$

The resulting equations are *nonlinear* contrary to the equations for the reduced distribution functions.

3.3 Exercises

1. Exercise from R.L.Liboff "Kinetic Theory":

1.24. A collection of four identical particles moving in one dimension are known to be in the following state at a given time $t > 0$. One particle is moving with velocity v_1^0 and another with v_2^0 . Both these particles were at the origin $x = 0$ at $t = 0$. The remaining two particles are stationary at x_3^0 and x_4^0 , respectively.

- (a) Write down a determinantal joint-probability distribution that describes this state.
- (b) Obtain an expression for $f_1(x, v)$ from your answer to (a).

2. Show (3.15) by invoking the form (2.39) of the Liouville operators

3. Derive the equation (3.27) for g_2 .

4. Exercise from R.L.Liboff "Kinetic Theory" (solution is in the book):

1.42. If $f_N(1, 2, \dots, N)$ is translationally invariant,

$$f_N(\mathbf{x}_1 + \mathbf{a}, \mathbf{p}_1; \mathbf{x}_2 + \mathbf{a}, \mathbf{p}_2; \dots; \mathbf{x}_N + \mathbf{a}, \mathbf{p}_N) = f_N(\mathbf{x}_1, \mathbf{p}_1; \mathbf{x}_2, \mathbf{p}_2; \dots; \mathbf{x}_N, \mathbf{p}_N)$$

and rotationally invariant,

$$f_N(\mathbf{x}_1, \mathbf{p}_1; \mathbf{x}_2, \mathbf{p}_2; \dots) = f_N(\mathbf{x}_1 + \boldsymbol{\varepsilon} \times \mathbf{x}_1, \mathbf{p}_1; \mathbf{x}_2 + \boldsymbol{\varepsilon} \times \mathbf{x}_2, \mathbf{p}_2, \dots)$$

where $\boldsymbol{\varepsilon}$ is infinitesimal, then show that

- (a) $f_1(\mathbf{x}_1, \mathbf{p}_1) = g(\mathbf{p}_1)$
and



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- (b) $f_2(\mathbf{x}_1, \mathbf{p}_1; \mathbf{x}_2, \mathbf{p}_2) = h(|\mathbf{x}_1 - \mathbf{x}_2|, \mathbf{p}_1, \mathbf{p}_2)$
The functions g and h are arbitrary.

5. Show that g_2 in free system is 0. [Use the solution for F in a free system to compute f_1 and f_2]

4 Vlasov and Landau equations

Hierarchy couples dynamics of f_1 to all the g 's. We will now make an approximation that truncates the hierarchy. This approximation essentially assumes that we can neglect correlations of order higher than some number S and in the same time, express the lower order correlations through f_1 . As the result we obtain a closed equation for f_1 . Depending on the details of the truncation we will find different equations. They are all called *kinetic equations*.

We change notation from momenta p to velocities v where $p = mv$, such that

$$f(\mathbf{q}, \mathbf{p}; t) = f(\mathbf{q}, m\mathbf{v}; t) = m^3 \hat{f}(\mathbf{q}, \mathbf{v}; t). \quad (4.1)$$

This implies correct normalization

$$N = \int d\mathbf{p} d\mathbf{q} f(\mathbf{q}, \mathbf{p}; t) = \int d\mathbf{v} d\mathbf{q} \hat{f}(\mathbf{q}, \mathbf{v}; t). \quad (4.2)$$

From now on we will also suppress the hat symbol and redefine $x_j = (\mathbf{q}_j, \mathbf{v}_j)$ and $\partial_j = \partial/\partial v_j$.

4.1 Weakly coupled systems

We want to do a perturbation theory in the strength of the interactions. To this end we assume that

$$V(r) = \lambda v(r) \quad (4.3)$$

with $\lambda \ll 1$ and $|v(r)/v(r_0)| = \mathcal{O}(1)$ for every r and for some r_0 . In other words

$$|V(r)| = \mathcal{O}(\lambda), \quad |H^0| = \mathcal{O}(1). \quad (4.4)$$

Let us see how the scalling with λ propagates through different quantities of our formalism. For the components of the Liouville operator we have

$$L_j^0 = \mathcal{O}(\lambda^0), \quad L'_{jk} = \mathcal{O}(\lambda). \quad (4.5)$$

The distribution function f_1 is normalized to N hence it must be of order λ^0 . The correlation functions need interactions and therefore they scale with λ , $g_s \sim \lambda^{s-1}$. Note that these scaling is consistent with the time evolution. The time evolution does not produce terms of lower order than given here. Thus, this assignment of orders is self-consistent.

Finally, let us discuss also the range of interactions. We assume that $V(r) \approx 0$ for $r \gg l_0$. We call l_0 the range of the interactions. In a similar fashion also the correlation functions have finite ranges which should be of the same order as l_0 , since they are a product of the interaction potential. We take L_C as the maximal range present in the system and therefore

$$g_2(\mathbf{q}_1, \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; t) \approx 0, \quad \text{for} \quad |\mathbf{q}_1 - \mathbf{q}_2| \gg l_C. \quad (4.6)$$

4.2 Derivation of the Vlasov equation and its properties

Note that the simple expansion of the propagator will not work

$$e^{-\lambda t} = 1 - t\lambda + \frac{1}{2}t^2\lambda^2 + \dots, \quad (4.7)$$

so no matter how many terms we take and how small λ is, there will be some time after which the expansion blows up. This is despite the original function is bounded. This is a secular expansion.

Let us write equation for f_1

$$\partial_t f_1(x_1; t) - L_1^0 f_1(x_1; t) = \int dx_2 L'_{12} (f(x_1; t) f(x_2; t) + g_2(x_1, x_2; t)). \quad (4.8)$$

The first term on the rhs is of order λ while the second is of order λ^2 . Therefore, the kinetic equation to order λ is

$$\partial_t f_1(x_1; t) - L_1^0 f_1(x_1; t) = \int dx_2 L'_{12} f(x_1; t) f(x_2; t). \quad (4.9)$$

The right hand side can still be simplified using the expression for L'_{12} . We have

$$\begin{aligned} \int dx_2 L'_{12} f(x_1; t) f(x_2; t) &= \int d\mathbf{q}_2 d\mathbf{v}_2 V'(\mathbf{q}_1 - \mathbf{q}_2) (\partial_1 - \partial_2) f(x_1; t) f(x_2; t) \\ &= \int d\mathbf{q}_2 d\mathbf{v}_2 V'(\mathbf{q}_1 - \mathbf{q}_2) \partial_1 f(x_1; t) f(x_2; t), \end{aligned} \quad (4.10)$$

cause derivative $\partial_2 = \partial/\partial\mathbf{v}_2$ gives a contribution vanishing upon integration over \mathbf{v}_2 . The remaining integral can be interpreted with the help of average interaction potential at \mathbf{q}_1 caused by all the other particles

$$\bar{V}(\mathbf{q}_1; t) = \int d\mathbf{q}_2 d\mathbf{v}_2 V(\mathbf{q}_1 - \mathbf{q}_2) f(\mathbf{q}_2, \mathbf{v}_2; t), \quad (4.11)$$

and

$$\partial_t f_1(x_1; t) - L_1^0 f_1(x_1; t) = \nabla_1 \bar{V}(x_1; t) \partial_1 f_1(x_1; t). \quad (4.12)$$

This is *Vlasov equation* and is a closed equation for $f(x; t)$.

Let us see what are stationary states of Vlasov. We note that for a homogeneous state $f(\mathbf{q}, \mathbf{v}; t) = n\phi(\mathbf{v}; t)$ the average potential \bar{V} is uniform and hence its gradient vanishes. Thus, any homogeneous state is a stationary state of the Vlasov equation.

4.3 Landau equation

We expand the hierarchy to order λ^2 . We have two equations

$$\partial_t f(x_1) - L_1^0 f(x_1) = \int dx_2 L'_{12} (f(x_1) f(x_2) + g_2(x_1, x_2)), \quad (4.13)$$

$$\partial_t g_2(x_1, x_2) - (L_1^0 + L_2^0) g_2(x_1, x_2) = L'_{12} f(x_1) f(x_2). \quad (4.14)$$

The correlation function is now fully determined from the knowledge of the one-body function. The second equation can be solved with the help of the propagator

$$g_2(x_1, x_2; t) = U_{12}^0(t) g_2(x_1, x_2; 0) + \int_0^t d\tau U_{12}^0(\tau) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau). \quad (4.15)$$

Let us verify this solution by direct computations. Recall that

$$U_{12}^0(t) = \exp\left(\left(L_1^0 + L_2^0\right)t\right). \quad (4.16)$$

Differentiating the solution, we get

$$\begin{aligned} \partial_t g_2(x_1, x_2; t) &= \left(L_1^0 + L_2^0\right) U_{12}^0(t) g_2(x_1, x_2; 0) + U_{12}^0(t) L'_{12} f_1(x_1; t) f_1(x_2; t) \\ &\quad + \int_0^t d\tau U_{12}^0(\tau) L'_{12} \partial_t (f(x_1; t - \tau) f(x_2; t - \tau)). \end{aligned}$$

The integral can be transformed in the following way. The derivative with respect to t can be transformed into a (minus) derivative with respect to τ and then the expression can be integrated by parts. The result is

$$\begin{aligned} \int_0^t d\tau U_{12}^0(\tau) L'_{12} \partial_t (f(x_1; t - \tau) f(x_2; t - \tau)) &= - \int_0^t d\tau U_{12}^0(\tau) L'_{12} \partial_\tau (f(x_1; t - \tau) f(x_2; t - \tau)) \\ &= \int_0^t d\tau \left(\partial_\tau U_{12}^0(\tau) \right) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau) - (\text{boundary terms}) \\ &= (L_1^0 + L_2^0) \int_0^t d\tau U_{12}^0(\tau) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau) - (\text{boundary terms}). \end{aligned}$$

The boundary terms are

$$\text{boundary terms} = U_{12}^0(t) L'_{12} f(x_1; 0) f(x_2; 0) - U_{12}^0(0) L'_{12} f(x_1; t) f(x_2; t), \quad (4.17)$$

thus first of them cancels the same time appearing in the derivative of g_2 . The second term enters then the final expression and

$$\begin{aligned} \partial_t g_2(x_1, x_2; t) &= (L_1^0 + L_2^0) \left(U_{12}^0(t) g_2(x_1, x_2; 0) + \int_0^t d\tau U_{12}^0(\tau) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau) \right) \\ &\quad + U_{12}^0(t) L'_{12} f_1(x_1; t) f_1(x_2; t). \end{aligned}$$

Recognising $g_2(x_1, x_2, t)$ in the bracket verifies the solution.

Having now a solution to g_2 we can substitute into an equation for f_1 . The result is

$$\begin{aligned} \partial_t f(x_1) - L_1^0 f(x_1) &= \int dx_2 L'_{12} \left(f(x_1) f(x_2) + U_{12}^0(t) g_2(x_1, x_2; 0) \right) \\ &\quad + \int dx_2 L'_{12} \int_0^t d\tau U_{12}^0(\tau) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau). \end{aligned} \quad (4.18)$$

This is now a closed equation for f_1 given the initial form of the correlator $g_2(x_1, x_2; 0)$. The first term is the Vlasov term. Let us discuss the other two terms. The second term describe the effect of the *initial* correlations on the state of the system at later time t . The third term describes the effect of the correlation that build-up during the evolution of the system due to the interactions and then their influence on the particles distribution. However, this term does not depend only on the instantaneous value of the correlator but also on their whole history. Thus, the equation is *non-Markovian*.

In the Vlasov limit the particles are smeared out and any given particle feels an averaged force field. Here, the presence of other particles is controlled by the correlations. This gives a sense of scattering between two particles. As we have seen above, it is natural to expect that given a finite range of the interaction potential, implies an existence of *correlation length* l_C . Particles further than this length are uncorrelated. Existence of a correlation length implies an existence of a *correlation time* t_C , under an observation, that we might introduce a characteristic velocity of particles in the system.

We can then view interaction to happen as an effect of succeeding collisions. If there are many particles, it is very unlikely that a given particle will collide in a row with the same particle. Therefore, the correlations that build up as an effect of collisions should be short-lived. In the same time, between the collisions particles move in a straight lines. The distance that they travel is called the *mean free path* l_{mfp} and the corresponding time, the *relaxation time* t_R . This tells us how often particles collide and from equation (4.13) we see that it should be proportional to λ^2 .

There exists also a third length-scale associated with the spatial variation of one-particle distribution function. We call it hydrodynamic length and denote l_H . The corresponding timescale we call *hydrodynamic time* and denote t_H .

We will assume the following ordering of the lengthscales (or corresponding timescales)

$$l_C \ll l_{\text{mfp}} \ll l_H \quad \text{or} \quad t_C \ll t_R \ll t_H \quad (4.19)$$

Note that the first assumption relies on

$$\frac{l_C}{l_{\text{mfp}}} = \mathcal{O}(\lambda^2) \quad \frac{t_C}{t_R} = \mathcal{O}(\lambda^2), \quad (4.20)$$

whereas the second tells us the variations of macroscopic variables are of a different length-scale than the microscopic description. This does not have to be the case, as sometimes mean path can be very large or, for example in the presence of shocks, the variations of temperature can be large.

We shall also assume that the lengthscale l_C and timescales t_C are experimentally inaccessible. However, we might be interested in dynamics at time scale t_R as those are relevant timescales for homogeneous systems (where $t_H \rightarrow \infty$). Since we are interested in timescale $t \gg t_C$ then the second term in the eq. (4.18),

$$U_{12}^0(t)g_2(x_1, x_2; 0) = g_2(\mathbf{q}_1 - \mathbf{v}_1 t, \mathbf{q}_2 - \mathbf{v}_2 t, \mathbf{v}_1, \mathbf{v}_2; t) \approx 0, \quad (4.21)$$

since correlations are expected to vanish after time $t \sim t_C$.

Let us now analyze the last term of (4.18)

$$\int d\mathbf{x}_2 L'_{12} \int_0^t d\tau U_{12}^0(\tau) L'_{12} f(x_1; t - \tau) f(x_2; t - \tau). \quad (4.22)$$

Let us first observe that we are interested in terms of order λ^2 and this expression already contains two factors L'_{12} . Therefore, the time-evolved one-particle functions can be expressed with the help of a free propagator

$$f(x_1; t - \tau) \approx U_{12}^0(-\tau) f(x_1, t). \quad (4.23)$$

This gives then a factor (m appears because L'_{12} has now derivatives with respect to v not p)

$$\begin{aligned} L'_{12} U_{12}^0(\tau) L'_{12} U_{12}^0(-\tau) &= m^{-2} (\nabla_1 V(\mathbf{q}_{12})) \cdot \partial_{12} U_{12}^0(\tau) (\nabla_1 V(\mathbf{q}_{12})) \cdot \partial_{12} U_{12}^0(-\tau) \\ &= m^{-2} (\nabla_1 V(\mathbf{q}_{12})) \cdot \partial_{12} (\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)) \cdot U_{12}^0(\tau) \partial_{12} U_{12}^0(-\tau) \\ &= m^{-2} \partial_{12} \cdot (\nabla_1 V(\mathbf{q}_{12})) (\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)) \cdot U_{12}^0(\tau) \partial_{12} U_{12}^0(-\tau). \end{aligned} \quad (4.24)$$

Let us look at the last factor

$$U_{12}^0(\tau) \partial_{12} U_{12}^0(-\tau) = \partial_{12} + \tau \nabla_{12}. \quad (4.25)$$

Therefore

$$L'_{12} U_{12}^0(\tau) L'_{12} U_{12}^0(-\tau) = m^{-2} \partial_{12} \cdot (\nabla_1 V(\mathbf{q}_{12})) (\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)) \cdot (\partial_{12} + \tau \nabla_{12}). \quad (4.26)$$

The memory term of the Master equation is then

$$m^{-2} \int d\mathbf{x}_2 \int_0^t d\tau \partial_{12} \cdot (\nabla_1 V(\mathbf{q}_{12})) (\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)) \cdot (\partial_{12} + \tau \nabla_{12}) f(x_1; t) f(x_2; t). \quad (4.27)$$

So far we haven't done any approximations, merely rewritten it. Let us now change the integration variables from $x_2 = (\mathbf{q}_2, \mathbf{v}_2)$ to $\mathbf{r} = \mathbf{q}_{12}$ and \mathbf{v}_2 . The effect is

$$m^{-2} \int d\mathbf{r} d\mathbf{v}_2 \int_0^t d\tau \partial_{12} \cdot (\nabla_1 V(\mathbf{r})) (\nabla_1 V(\mathbf{r} - \mathbf{v}_{12}\tau)) \cdot (\partial_{12} + \tau \nabla_{12}) f(\mathbf{q}_1, \mathbf{v}_1; t) f(\mathbf{q}_1 - \mathbf{r}, \mathbf{v}_2; t). \quad (4.28)$$

Here comes a number of approximations

1. Since interactions are non-zero only up to distances l_C and we are interested in times $t \gg t_C$, the upper range of the temporal integral can be extended to infinity.
2. The term $\tau \nabla_{12}$ is small compared with ∂_{12} which is of order of inverse of typical velocity, say t_R/l_{mfp} . The other term is instead of order t_C/l_H . Taking their ratio we find $t_C/t_R l_{mfp}/l_H \sim \lambda^2 \lambda$ and is small.
3. We also have $f(\mathbf{q}_1 - \mathbf{r}, \mathbf{v}_2; t) \approx (1 - \mathbf{r} \nabla_1) f(\mathbf{q}_1, \mathbf{v}_2; t)$. The correction is of order l_C/l_h and thus small.

With these approximations we get

$$m^{-2} \int d\mathbf{r} d\mathbf{v}_2 \int_0^\infty d\tau \partial_{12} \cdot (\nabla_1 V(\mathbf{r})) (\nabla_1 V(\mathbf{r} - \mathbf{v}_{12}\tau)) \cdot \partial_{12} f(\mathbf{q}_1, \mathbf{v}_1; t) f(\mathbf{q}_1, \mathbf{v}_2; t), \quad (4.29)$$

or introducing the Landau tensor

$$m^{-2} \int d\mathbf{v}_2 \partial_{12} \cdot \mathbf{G}(\mathbf{v}_1 - \mathbf{v}_2) \cdot \partial_{12} f(\mathbf{q}_1, \mathbf{v}_1; t) f(\mathbf{q}_1, \mathbf{v}_2; t), \quad (4.30)$$

where

$$\mathbf{G}(\mathbf{g}) = \int d\mathbf{r} \int_0^\infty d\tau (\nabla_1 V(\mathbf{r})) (\nabla_1 V(\mathbf{r} - \mathbf{g}\tau)). \quad (4.31)$$

Explicit computations give

$$G(\mathbf{g}) = 8\pi^4 \int d\mathbf{k} \delta(\mathbf{k} \cdot \mathbf{g}) \tilde{V}^2(k) \mathbf{k} \mathbf{k}, \quad (4.32)$$

or

$$\mathbf{G}_{rs}(\mathbf{g}) = \left(\delta_{rs} - \frac{g_r g_s}{g^2} \right) \frac{B}{g}, \quad B = 8\pi^5 \int_0^\infty dk \tilde{V}^2(k) k^3. \quad (4.33)$$

The Landau equation is then

$$\partial_t f(x_1) - L_1^0 f(x_1) = \mathcal{V}(f, f) + \mathcal{K}^L(f, f), \quad (4.34)$$

where

$$\mathcal{K}^L(f, f) = m^{-2} \int d\mathbf{v}_2 \partial_{12} \cdot \mathbf{G}(\mathbf{v}_1 - \mathbf{v}_2) \cdot \partial_{12} f(\mathbf{q}_1, \mathbf{v}_1; t) f(\mathbf{q}_1, \mathbf{v}_2; t), \quad (4.35)$$

4.4 Exercises

1. write down an equation for particle density and average velocity from the first equation of the BBGKY hierarchy
2. scaling argument that variation of the density gradient should be small compared to the range of interactions to have some dynamics for Vlasov equation
3. show that Vlasov equation is time reversible while Landau equation is not

4. self-consistent solution
5. linearized Vlasov equation
6. explicit form of the Landau collision term (Balescu Sec. 6.3)
7. write down homogeneous Landau equation and show that Maxwell distribution is stationary.

5 Boltzmann equation

The weak interaction assumption is problematic in many systems because of hard-core short-range repulsion between the particles. At short distances the repulsion is very strong, an example being the Lennard-Jones potential. However, this potential has another feature, a finite range l_0 and as a consequence a finite correlation length l_C . There exists another characteristic length, which is a distance between the particles, d . It depends on the number density $n = N/V$ such that $d = n^{-1/3}$. This allows us to introduce a new dimensionless parameter

$$\gamma = nl_C^3 \ll 1. \quad (5.1)$$

What are now orders of different terms in the BBGKY hierarchy in terms of γ ? The Hamiltonian, and thus the Liouvillian, do not depend on the density and

$$L_j^0 = \mathcal{O}(\gamma^0), \quad L_{jn} = \gamma'. \quad (5.2)$$

The one-body function is clearly proportional to the density while correlation functions involve increasing powers of the density

$$f(x_1) = \mathcal{O}(\gamma), \quad g_n(x_1, \dots, x_n) = \mathcal{O}(\gamma^n). \quad (5.3)$$

The X-vertices connect terms with the same number of particles hence they don't contribute any additional density factors. However, the Y-vertices connect n -particle state to the $(n+1)$ particle state and therefore they do introduce an additional n factor.

Let us consider a homogeneous system. The evolution equation for f_1 is then

$$\partial_t f(x_1; t) = \int dx_2 L'_{12} g_2(x_1, x_2; t), \quad (5.4)$$

and it introduces a factor n because it is of the Y-type. Indeed f is of order n while g_2 is of order n^2 . Therefore, we only need g_2 to the leading order. In equation for g_2 we can thus keep only the two terms involving the X-vertex. We find

$$(\partial_t - L_1^0 - L_2^0 - L'_{12}) g_2(x_1, x_2; t) = L'_{12} f(x_1; t) f(x_2; t). \quad (5.5)$$

Let us introduce now the complete two-body propagator $Y_{12}(t)$ as a solution to the following equation

$$(\partial_t - L_1^0 - L_2^0 - L'_{12}) Y_{12}(t), \quad (5.6)$$

with $Y_{12}(0) = I$ (the identity operator). We then find

$$\partial_t \phi(\mathbf{v}_1; t) = n \int_0^t d\tau \int d\mathbf{q}_2 \mathbf{v}_2 L'_{12} Y_{12}(\tau) L'_{12} \phi(\mathbf{v}_1; t - \tau) \phi(\mathbf{v}_2; t - \tau) \quad (5.7)$$

$$+ \frac{1}{n} \int d\mathbf{q}_2 d\mathbf{v}_2 L'_{12} Y_{12}(t) g_2(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; 0). \quad (5.8)$$

It has the same structure as a non-Markovian Landau equation. Using the same arguments we obtain

$$\partial_t \phi(\mathbf{v}_1; t) = n \int d\mathbf{v}_2 J(\mathbf{v}_1, \mathbf{v}_2), \quad (5.9)$$

where

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int d\mathbf{r} \int_0^\infty d\tau L'_{12} Y_{12} L'_{12} \phi(\mathbf{v}_1; t) \phi(\mathbf{v}_2; t). \quad (5.10)$$

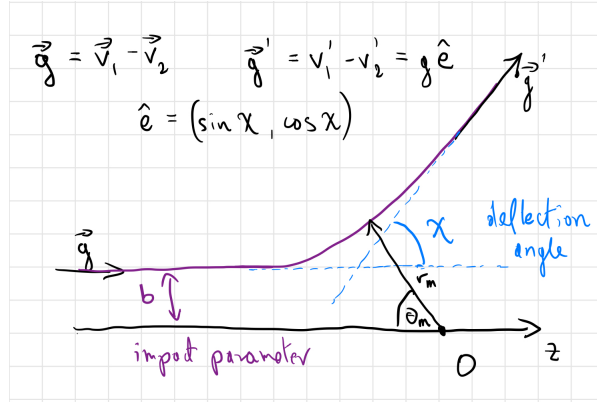


Figure 4: ...

It can be shown that

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int_0^{2\pi} d\phi \int_0^\infty db bg (\phi(\mathbf{v}'_1; t) \phi(\mathbf{v}'_2; t) - \phi(\mathbf{v}_1; t) \phi(\mathbf{v}_2; t)), \quad (5.11)$$

where $g = |\mathbf{v}_1 - \mathbf{v}_2|$, $\mathbf{v}'_1 = \mathbf{v}'_1(\mathbf{v}_1, \mathbf{v}_2)$ and $\mathbf{v}'_2 = \mathbf{v}'_2(\mathbf{v}_1, \mathbf{v}_2)$ with

$$\mathbf{v}'_1 + \mathbf{v}'_2 = \mathbf{v}_1 + \mathbf{v}_2, \quad |\mathbf{v}'_1|^2 + |\mathbf{v}'_2|^2 = |\mathbf{v}_1|^2 + |\mathbf{v}_2|^2. \quad (5.12)$$

The geometry of the scattering process is shown in fig. 4.

The Boltzmann equation (generalizing back to the inhomogeneous case) reads

$$(\partial_t - \mathbf{v} \cdot \nabla) \phi(\mathbf{v}; t) = \mathcal{V}(f, f) + \mathcal{K}^B(f, f) \quad (5.13)$$

where

$$\mathcal{K}^B(f, f) = \int d\mathbf{v}_2 \int_0^{2\pi} d\phi \int_0^\infty db bg (f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)). \quad (5.14)$$

5.1 Entropy and stationary states

Consider a homogeneous system and define the following function

$$s(t) = -k_B \int d\mathbf{v} \phi(\mathbf{v}; t) \ln(n\phi(\mathbf{v}; t)) + b. \quad (5.15)$$

Consider now time derivative of $s(t)$,

$$\begin{aligned} k_B^{-1} \dot{s}(t) &= - \int d\mathbf{v}_1 [\ln(n\phi(\mathbf{v}_1; t)) + 1] \partial_t \phi(\mathbf{v}_1; t) \\ &= -2\pi n \int d\mathbf{v}_1 d\mathbf{v}_2 db bg [\ln(n\phi(\mathbf{v}_1; t)) + 1] \times (\phi - \phi) \\ &= -\pi n \int d\mathbf{v}_1 d\mathbf{v}_2 db bg [\ln(n\phi(\mathbf{v}_1; t)) + \ln(n\phi(\mathbf{v}_2; t)) + 2] \times (\phi - \phi) \\ &= \pi n \int d\mathbf{v}_1 d\mathbf{v}_2 db bg \ln \frac{\phi(\mathbf{v}'_1; t) \phi(\mathbf{v}'_2; t)}{\phi(\mathbf{v}_1; t) \phi(\mathbf{v}_2; t)} \times (\phi(\mathbf{v}'_1; t) \phi(\mathbf{v}'_2; t) - \phi(\mathbf{v}_1; t) \phi(\mathbf{v}_2; t)). \end{aligned}$$

We first use the symmetry upon exchanging \mathbf{v}_1 with \mathbf{v}_2 and later symmetry with exchanging initial with final velocities. Thus $\dot{s}(t) \geq 0$ and function $s(t)$ increases monotonically during the time evolution.

The stationary state is thus given by a configuration that maximises the entropy. This requires

$$\ln \frac{\phi^0(\mathbf{v}'_1)\phi^0(\mathbf{v}'_2)}{\phi^0(\mathbf{v}_1)\phi^0(\mathbf{v}_2)} = 1, \quad (5.16)$$

which is satisfied by the Maxwell distribution

$$\phi^0(\mathbf{v}) = c \exp \left[-a|\mathbf{v} - \mathbf{u}|^2 \right], \quad (5.17)$$

with $a, c > 0$ and \mathbf{u} arbitrary constants.

5.2 Collision invariants

Let us denote

$$\langle \psi \rangle = \int d\mathbf{q} d\mathbf{v} \psi(\mathbf{q}, \mathbf{v}) f(\mathbf{q}, \mathbf{v}; t). \quad (5.18)$$

The collision invariant is then a function for which

$$\int d\mathbf{q} d\mathbf{v} \psi_n(\mathbf{q}, \mathbf{v}) \mathcal{K}(f, f) = 0, \quad (5.19)$$

for any one-body function f . Substituting the Boltzmann collision integral we have

$$\begin{aligned} \int d\mathbf{q} d\mathbf{v} \psi_n(\mathbf{q}, \mathbf{v}) \mathcal{K}(f, f) &= \\ &= 2\pi \int d\mathbf{q} \int db b \int d\mathbf{v}_1 d\mathbf{v}_2 g \psi(\mathbf{q}, \mathbf{v}_1) (f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)). \end{aligned} \quad (5.20)$$

Consider now the double integral over the velocities

$$\begin{aligned} \int d\mathbf{v}_1 d\mathbf{v}_2 g \psi(\mathbf{q}, \mathbf{v}_1) [f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)] &= \\ &= \frac{1}{4} \int d\mathbf{v}_1 d\mathbf{v}_2 g [\psi(\mathbf{q}, \mathbf{v}_1) + \psi(\mathbf{q}, \mathbf{v}_2) - \psi(\mathbf{q}, \mathbf{v}'_1) - \psi(\mathbf{q}, \mathbf{v}'_2)] \times \\ &\times [f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)] \end{aligned} \quad (5.21)$$

The first bracket vanishes for

- for a function independent of \mathbf{v} , $\psi_0(\mathbf{q}, \mathbf{v}) = \psi(\mathbf{q})$,
- for a function proportional to one of the components of the velocity, $\psi_n(\mathbf{q}, \mathbf{v}) = v_n \psi(\mathbf{q})$ with $n = 1, 2, 3$.
- for a function proportional to the velocity squared, $\psi_4(\mathbf{q}, \mathbf{v}) = |\mathbf{v}|^2 \psi(\mathbf{q})$.

This follows from the fact that number of particles, their momentum and energy are conserved in the collision process.

5.3 Hydrodynamic quantities

Recall the expression for the one-body local observable as an average with respect to the dynamic function

$$B(\mathbf{x}, t) = \int d\mathbf{v} \int d\mathbf{q} \beta(\mathbf{v}) \delta(\mathbf{x} - \mathbf{q}) f(\mathbf{q}, \mathbf{v}; t). \quad (5.22)$$

This can be interpreted as

$$B(\mathbf{x}, t) \int d\mathbf{v} \beta(\mathbf{v}) f(\mathbf{v}; \mathbf{x}, t) \quad (5.23)$$

where we introduce a *local* one-body function

$$f(\mathbf{v}; \mathbf{x}, t) = \int d\mathbf{q} \delta(\mathbf{x} - \mathbf{q}) f(\mathbf{q}, \mathbf{v}; t). \quad (5.24)$$

Note that now the observables computed with the help of $f(\mathbf{v}; \mathbf{x}, t)$ involve averaging over only the velocities. The \mathbf{x} is position in the real space not in the phase space. We can reformulate the kinetic equation as an equation for $f(\mathbf{v}; \mathbf{x}, t)$

$$(\partial_t + \mathbf{v} \cdot \nabla) f(\mathbf{v}; \mathbf{x}, t) = \mathcal{K} \{f, f\}. \quad (5.25)$$

We define the following hydrodynamic fields

- Mass density

$$\rho(\mathbf{x}, t) = m \int d\mathbf{v} f(\mathbf{v}; \mathbf{x}, t) \quad (5.26)$$

- Momentum density

$$\rho(\mathbf{x}, t) \mathbf{u}(\mathbf{x}, t) = m \int d\mathbf{v} \mathbf{v} f(\mathbf{v}; \mathbf{x}, t), \quad (5.27)$$

- (Internal) energy density

$$\rho(\mathbf{x}, t) e(\mathbf{x}, t) = \frac{1}{2} m \int d\mathbf{v} |\mathbf{v} - \mathbf{u}|^2 f(\mathbf{v}; \mathbf{x}, t). \quad (5.28)$$

5.4 Hydrodynamic balance equations

We will now write equations for the 3 hydrodynamic fields. We use the collision invariants. For the mass density we find

$$\partial_t \rho(\mathbf{x}, t) = -\nabla \cdot (\rho \mathbf{u}), \quad (5.29)$$

which is the first hydrodynamic equation and it describes the conservation of mass. Consider now the collision invariant mv_r . According to the definition of the momentum density

$$\begin{aligned} \partial_t (\rho u_n) &= -m \int d\mathbf{v} v_n v_s \nabla_s f(\mathbf{v}; \mathbf{x}, t) = -m \nabla_s \int d\mathbf{v} v_n v_s f(\mathbf{v}; \mathbf{x}, t) \\ &= -\nabla_s \int d\mathbf{v} (m u_n u_s + m(v_n - u_n)(v_s - u_s)) f(\mathbf{v}; \mathbf{x}, t) \\ &= -\nabla_s (\rho u_n u_s + P \delta_{ns} + \pi_{ns}), \end{aligned} \quad (5.30)$$

where we introduced the hydrostatic pressure

$$P(\mathbf{x}, t) = \frac{1}{3} m \int d\mathbf{v} |\mathbf{v} - \mathbf{u}|^2 f(\mathbf{v}; \mathbf{x}, t), \quad (5.31)$$

and the dissipative pressure tensor is

$$\pi_{rs}(\mathbf{x}, t) = m \int d\mathbf{v} (v_r - u_r)(v_s - u_s) f(\mathbf{v}; \mathbf{x}, t) - \delta_{rs} P(\mathbf{x}, t). \quad (5.32)$$

Note the ideal gas relations

$$P(\mathbf{x}, t) = n(\mathbf{x}, t) T(\mathbf{x}, t), \quad \rho(\mathbf{x}, t) e(\mathbf{x}, t) = \frac{3}{2} n(\mathbf{x}, t) T(\mathbf{x}, t). \quad (5.33)$$

with $3/2$ being the heat capacity of the ideal gas.

Considering the last collision invariant, we find the balance equation for the energy

$$\partial_t (\rho e) = -\nabla \cdot (\rho e \mathbf{u} + \mathbf{q}) - P \nabla \cdot \mathbf{u} - \pi : \nabla \mathbf{u}. \quad (5.34)$$

with the heat flux

$$q_r(\mathbf{x}, t) = \frac{1}{2} m \int d\mathbf{v} (v_r - u_r) |\mathbf{v} - \mathbf{u}|^2 f(\mathbf{v}; \mathbf{x}, t). \quad (5.35)$$

5.5 Exercises

1. Show that from the conservation of momentum and energy we can write

$$\mathbf{v}'_1 = \frac{1}{2} (\mathbf{v}_1 + \mathbf{v}_2 + g\mathbf{e}), \quad \mathbf{v}'_2 = \frac{1}{2} (\mathbf{v}_1 + \mathbf{v}_2 - g\mathbf{e}), \quad (5.36)$$

where \mathbf{e} is an unit vector in an arbitrary direction.

2. Derive the balance equation for the energy.
3. Write down the linearized Boltzmann equation

6 More on the Boltzmann equation

We will complete the derivation of the Boltzmann equation and rewrite the Boltzmann equation using the scattering cross-section. We will also recall the original arguments of Boltzmann that led him to write down his equation. We start with discussion of the scattering process.

We need to study a 2-body problem with particles interacting with $V(|\mathbf{q}_1 - \mathbf{q}_2|)$ potential. The Hamiltonian is

$$H_{2\text{body}} = \frac{m\mathbf{v}_1^2}{2} + \frac{m\mathbf{v}_2^2}{2} + V(\mathbf{q}_1 - \mathbf{q}_2). \quad (6.1)$$

We introduce the center of mass and relative coordinates and velocities

$$\begin{aligned} \mathbf{Q}_G &= \frac{\mathbf{q}_1 + \mathbf{q}_2}{2}, & \mathbf{r} &= \mathbf{q}_1 - \mathbf{q}_2, \\ \mathbf{V}_G &= \frac{\mathbf{v}_1 + \mathbf{v}_2}{2}, & \mathbf{g} &= \mathbf{v}_1 - \mathbf{v}_2. \end{aligned} \quad (6.2)$$

The Hamiltonian becomes

$$H_{2\text{body}} = \frac{m|\mathbf{V}_G|^2}{2} + \frac{\mu|\mathbf{g}|^2}{2} + V(|\mathbf{r}|), \quad (6.3)$$

where we introduced reduced mass $\mu = m/2$. The center of mass velocity is a constant of motion, whereas the fictitious particle follows the relative trajectory $\mathbf{r} = \mathbf{q}_1 - \mathbf{q}_2$ and experiences potential $V(|\mathbf{r}|)$. Because the potential is central it is convenient to work in the spherical coordinates (r, θ, ϕ) . Due to symmetry around the polar axis ϕ we can choose $\phi = 0$. The (fictitious) particle energy is

$$E = \frac{\mu}{2} \left[\left(\frac{dr}{dt} \right)^2 + r^2 \left(\frac{d\theta}{dt} \right)^2 \right] + V(r) = \text{constant}, \quad (6.4)$$

whereas the angular momentum L is

$$L = \mu r^2 \left(\frac{d\theta}{dt} \right) = \text{constant}, \quad (6.5)$$

and both are constants of motion and they are fixed by the initial conditions. Take the initial velocity to be \mathbf{g}_0 . Then (to compute both quantities it is useful to momentarily go back to the Cartesian coordinates and assume that at large \mathbf{r} the potential is zero)

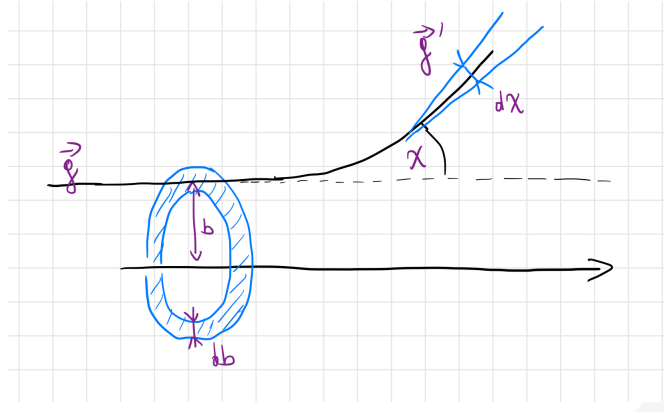
$$E = \frac{\mu g_0^2}{2}, \quad L = \mu g_0 b, \quad g_0 = |\mathbf{g}_0|. \quad (6.6)$$

From expressions for the two conservation laws we find

$$\frac{dr}{dt} = \pm \left[\frac{2}{\mu} \left(E - V(r) - \frac{L^2}{2\mu r^2} \right) \right]^{1/2}. \quad (6.7)$$

The trajectory $\theta(r)$ can be written in a differential form as

$$d\theta = \frac{L}{\mu r^2 (dr/dt)} dr, \quad (6.8)$$



which can be integrated now from the initial condition ($r = \infty, \theta = 0$) to the point of the closest approach ($r = r_{\min}, \theta = \theta_{\min}$). The latter is determined by the largest root of

$$E - V(r_{\min}) - \frac{L^2}{2\mu r_{\min}^2} = 0. \quad (6.9)$$

Integrating the differential trajectory we obtain

$$\theta = -L \int_{\infty}^{r_{\min}} \frac{dr}{\mu r^2 \left[\frac{2}{\mu} \left(E - V(r) - \frac{L^2}{2\mu r^2} \right) \right]^{1/2}}. \quad (6.10)$$

The angle describing the final trajectory is 2θ and the deflection angle is

$$\chi = |\pi - 2\theta|. \quad (6.11)$$

The final velocity of the particle is $\mathbf{g}' = g_0(\cos \chi, \sin \chi, 0)$ or $\mathbf{e} = (\cos \chi, \sin \chi, 0)$ with χ depending on the initial velocity \mathbf{g}_0 and the impact parameter b .

6.1 Cross section

We introduce a concept of *cross section*. This will allow us to characterize the collisions through a concept familiar from the scattering theory.

Instead of a single particle, we think about a beam of particles, all moving with the same velocity \mathbf{g} . We introduce also I , the flow of incident particles crossing a unit area perpendicular to \mathbf{g} . The *cross section* σ is then defined by the following relation

$$dN = I \sigma d\Omega dt \quad (6.12)$$

We now want to relate σ to the deflection angle. To this end we observe that number of particles scattered into the solid angle defined by the cones of aperture χ and $\chi + d\chi$ (by ring given by these two angles) is.

$$dN = 2\pi b(\chi) db(\chi) I dt \quad (6.13)$$

Comparing the two expressions we obtain

$$\sigma = \frac{b(\chi)}{\sin \chi} \left| \frac{db(\chi)}{d\chi} \right|. \quad (6.14)$$

where we used the element of a solid angle $d\Omega = 2\pi \sin \chi d\chi$.

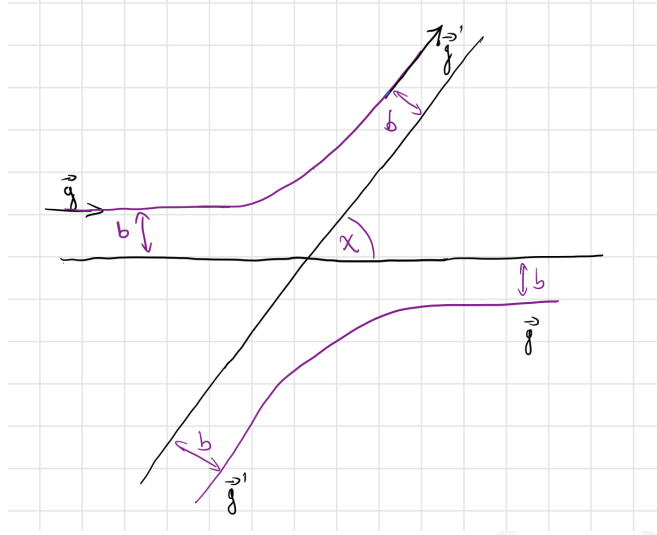


Figure 5: The inverse scattering process has the same cross-section since $|\mathbf{g}| = |\mathbf{g}'|$ and the deflection angles are the same.

We note that the cross section $\sigma = \sigma(|\mathbf{g}|, \chi)$ namely its a function of the velocity and the deflection angle. For a hard-sphere potential (tutorials)

$$\sigma = \frac{1}{4}a^2. \quad (6.15)$$

With the notion of the cross section we can rewrite the Boltzmann collision integral as

$$\begin{aligned} \mathcal{K}^B(f, f) &= 2\pi \int d\mathbf{v}_2 \int_0^\infty db b g (f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)) \\ &= \int d\mathbf{v}_2 d\Omega \sigma g (f(\mathbf{q}, \mathbf{v}'_1; t) f(\mathbf{q}, \mathbf{v}'_2; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)). \end{aligned} \quad (6.16)$$

6.2 Heuristic derivation of the Boltzmann equation

The central object is the one-body function $f(\mathbf{q}, \mathbf{v}; t)$. Quantity $f(\mathbf{q}, \mathbf{v}; t)d\mathbf{q}d\mathbf{v}$ is the number of particles that at time t are within volume $d\mathbf{q}$ around point \mathbf{q} and have velocity in the element $d\mathbf{v}$ around \mathbf{v} .

It is crucial that $d\mathbf{v}$ is microscopically large but macroscopically small, namely inside the volume there are many particles and in the same time the volume is small enough that macroscopic properties of the system do not vary over it.

If we observe $f(\mathbf{q}, \mathbf{v}; t)d\mathbf{q}d\mathbf{v}$ it will fluctuate. We observe it over time Δt , which is large compared with the average time spent by a single particle inside the volume element but again small with respect to the macroscopic properties. Therefore, we can think about it probabilistically – $f(\mathbf{q}, \mathbf{v}; t)d\mathbf{q}d\mathbf{v}$ is the most probable number of molecules in the physical element $d\mathbf{q}d\mathbf{v}$ during the time Δt .

From both deterministic and probabilistic perspective it is natural to assume that the one-body function, in the case of noninteracting particles, obeys a continuity equation

$$(\partial_t + \mathbf{v} \cdot \nabla) f = 0 \quad (6.17)$$

The idea of Boltzmann was to modify the right hand side as the effect of collisions (interactions) between the particles

$$(\partial_t + \mathbf{v} \cdot \nabla) f = (\partial_t f)_\text{coll}. \quad (6.18)$$

We will heuristically come up with an expression for $(\partial_t f_1)_{\text{coll}}$. We shall make two assumptions. First one, is the dilute gas limit. Namely we assume that we only need to consider two-body processes. This is the same assumption that we did when deriving the Boltzmann equation from the BBGKY hierarchy.

With this assumption we write

$$(\partial_t f_1)_{\text{coll}} = C'' - C', \quad (6.19)$$

where

1. C' describes a process in which a particle with initial velocity \mathbf{v} scatters with any other particle. More precisely $C' d\mathbf{q} d\mathbf{v} dt$ is the number of such collisions in time dt .
2. C'' describes a process in which one particle, in the aftermath of the scattering process, has velocity \mathbf{v} . Again more precisely, $C'' d\mathbf{q} d\mathbf{v} dt$ is the number of such collisions in time dt .

The two types of processes are respectively loss and gain processes where the occupancy of the monitored velocity either decreases or increases due to the scattering events.

To describe the two-body collision we need to know the distribution function for the distribution of the two velocities that assign to the two colliding particles. Here comes the *molecular-chaos assumption*: the number of pairs of particles with respective velocities \mathbf{v} and \mathbf{v}_1 that participate in the collision is

$$f_1(\mathbf{q}, \mathbf{v}; t) d\mathbf{q} d\mathbf{v} \times f_1(\mathbf{q}, \mathbf{v}_1; t) d\mathbf{q} d\mathbf{v}_1. \quad (6.20)$$

In other words, the velocities prior to the collision are uncorrelated. They are clearly correlated after the collision at least for a short time before the two particles collide with other particles and the correlations average out to zero.

Let us describe now the situation in the language of the scattering theory. Consider a single particle with velocity \mathbf{v} , we will think about it as a target and let us put ourselves in a coordinate system in which it is stationary. We then have an incident beam of particles

$$dI = g f_1(\mathbf{q}, \mathbf{v}_1; t) d\mathbf{v}_1 \quad (6.21)$$

which, due to the molecular-chaos assumption is not correlated with the target. The number of particles deflected by the target into the solid angle $d\Omega$ during time dt is

$$dN = \sigma dI d\Omega dt = \sigma g f_1(\mathbf{q}, \mathbf{v}_1; t) d\mathbf{v}_1 d\Omega dt. \quad (6.22)$$

Number of the target particles is $f_1(\mathbf{q}, \mathbf{v}; t) d\mathbf{q} d\mathbf{v}$ and therefore

$$\sigma g f_1(\mathbf{q}, \mathbf{v}; t) f_1(\mathbf{q}, \mathbf{v}_1; t) d\mathbf{v}_1 d\Omega dt d\mathbf{q} d\mathbf{v} \quad (6.23)$$

is the number of collisions with initial velocities \mathbf{v} and \mathbf{v}_1 in which particles are deflected into the solid angle $d\Omega$ in time dt and in volume $d\mathbf{q}$.

To describe now the loss process it is enough to integrate over all velocities \mathbf{v}_1 and over all deflection angles

$$C' d\mathbf{q} d\mathbf{v} dt = \int d\mathbf{v}_1 d\Omega \sigma g f_1(\mathbf{q}, \mathbf{v}; t) f_1(\mathbf{q}, \mathbf{v}_1; t) dt d\mathbf{q} d\mathbf{v}, \quad (6.24)$$

or

$$C' = \int d\mathbf{v}_1 d\Omega \sigma g f_1(\mathbf{q}, \mathbf{v}; t) f_1(\mathbf{q}, \mathbf{v}_1; t), \quad (6.25)$$

To describe the gain process we can look at the inverse scattering event, that is the one with the initial velocities \mathbf{v}' and \mathbf{v}'_1 and consider processes in which one of the final velocities is \mathbf{v} . We can write

$$C'' = \int d\mathbf{v}' d\mathbf{v}'_1 d\Omega \delta(\mathbf{v} - \mathbf{v}(\mathbf{v}', \mathbf{v}'_1)) \sigma g f_1(\mathbf{q}, \mathbf{v}'; t) f_1(\mathbf{q}, \mathbf{v}'_1; t). \quad (6.26)$$

In writing this expression we think about an inverse scattering process with initial velocities \mathbf{v}' and \mathbf{v}'_1 and final velocities \mathbf{v} and \mathbf{v}' . The inverse scattering process is geometrically related to the original one, see fig. 5 and where $\sigma = \sigma(|\mathbf{g}'|, \chi')$ is the cross section for the inverse scattering. By changing the integration variables from $(\mathbf{v}', \mathbf{v}'_1)$ to $(\mathbf{v}, \mathbf{v}')$, this expression becomes

$$C'' = \int d\mathbf{v}'_1 d\Omega \sigma g f_1(\mathbf{q}, \mathbf{v}'; t) f_1(\mathbf{q}, \mathbf{v}'_1; t), \quad (6.27)$$

with now \mathbf{v}' and \mathbf{v}'_1 being functions of the velocities \mathbf{v} and \mathbf{v}_1 .

Combing the partial results we find

$$(\partial_t + \mathbf{v} \cdot \nabla) f = \int d\mathbf{v}_1 d\Omega g \sigma [f_1(\mathbf{q}, \mathbf{v}'; t) f_1(\mathbf{q}, \mathbf{v}'_1; t) - f_1(\mathbf{q}, \mathbf{v}; t) f_1(\mathbf{q}, \mathbf{v}_1; t)]. \quad (6.28)$$

6.3 Exercise

1. Compute the scattering cross-section for the hard-sphere model (see Balescu eq. (7.45))
2. Complete the computation of the "gain" term by deriving (6.27) from (6.26).

7 Linearized Boltzmann equation and transport coefficients

The balance equations we found in Section 5.4 still require the knowledge of the full one-body distribution $f(\mathbf{v}; \mathbf{x}, t)$. In order to turn the balance equations into a closed set of equations for 5 hydrodynamic fields we need to "integrate out" the dynamics of non-hydrodynamic fields. One way to achieve this is by considering a linearized problem. On the side of the Boltzmann equation this will allow us to solve for the dynamics of the hydrodynamic fields. We will then match this solution to a solution obtained from the linearized Navier-Stokes equation. In the process we will determine the dissipative terms in the Navier-Stokes equations and find formulas for the transport coefficients which control how strong the dissipative processes are.

7.1 Linearized Boltzmann equation

We consider a situation in which the one-body distribution is close to the equilibrium distribution

$$f = f^{\text{eq}} + \delta f, \quad (7.1)$$

where f^{eq} is homogeneous (\mathbf{x} independent) and $K^B(f^{\text{eq}}, f^{\text{eq}}) = 0$. The Boltzmann equation for the perturbation is

$$\partial_t \delta f + \mathbf{v} \cdot \nabla \delta f = nC \delta f + \mathcal{O}(\delta f^2), \quad (7.2)$$

where

$$C \delta f = \int d\mathbf{v}_1 \int d\Omega \sigma g [\delta f' \phi_1^{\text{eq}'} + \delta f'_1 \phi_1^{\text{eq}} - \delta f \phi_1^{\text{eq}} - \delta f_1 \phi^{\text{eq}}], \quad (7.3)$$

where we used that $f^{\text{eq}} = n\phi^{\text{eq}}$ with Maxwell distribution ϕ^{eq} . Using the equilibrium condition

$$\phi_1^{\text{eq}'} \phi^{\text{eq}'} = \phi_1^{\text{eq}} \phi^{\text{eq}}, \quad (7.4)$$

we find a more symmetric form

$$C \delta f = \int d\mathbf{v}_1 \int d\Omega \sigma g \phi^{\text{eq}} \phi_1^{\text{eq}} \left[\left(\frac{\delta f}{\phi^{\text{eq}}} \right)' + \left(\frac{\delta f}{\phi^{\text{eq}}} \right)'_1 - \left(\frac{\delta f}{\phi^{\text{eq}}} \right) - \left(\frac{\delta f}{\phi^{\text{eq}}} \right)_1 \right], \quad (7.5)$$

To analyze further the linearized Boltzmann equation we go to the Fourier space in the position variable. Because the fluid is isotropic, at linear regime we can assume that the perturbation is along a single direction, say x -axis.

$$\delta f_q(\mathbf{v}; t) = \int dx e^{-iqx} \delta f(x, \mathbf{v}; t), \quad (7.6)$$

which gives

$$\partial_t f_q = (nC - iqv_x) f_q. \quad (7.7)$$

Imagine that we have now a solution to the eigenvalue problem

$$(nC - iqv_x) |\phi_j^q\rangle = \lambda_j^q |\phi_j^q\rangle, \quad (7.8)$$

and that functions $\phi_j^k(\mathbf{v})$ form a complete basis. Then the solution to the linearized Boltzmann equation is

$$f_q(\mathbf{v}; t) = \sum_j c_j^q \exp(\lambda_j^q t) \phi_j^q(\mathbf{v}), \quad (7.9)$$

with c_j^k determined from the initial value.

We need to study the eigenvalue problem (7.7). Because we are interested in the hydrodynamic limit described by small wavelengths, we can solve it perturbatively in k . The zeroth order in k reduces to the spectral problem of the linearized Boltzmann operator C . We introduce a scalar product

$$\langle g|h \rangle = \int d\mathbf{v} \phi^{\text{eq}}(v)^{-1} g^*(\mathbf{v}) h(\mathbf{v}). \quad (7.10)$$

It can be shown that operator C is hermitian

$$\langle g|C|h \rangle = \langle h|C|g \rangle^*, \quad (7.11)$$

and hence the eigenvalues of the problem $nC|\phi_j^0\rangle = \lambda_j^0|\phi_j^0\rangle$ are real. We also have that

$$\langle h|C|h \rangle \leq 0. \quad (7.12)$$

This implies that $\lambda_j^0 \leq 0$ as well. The equality sign holds only for eigenfunctions related to the collision invariants. Hence, there are exactly five zero eigenvalues and the corresponding eigenfunctions we denote ϕ_α^0 with $\alpha = 0, 1, \dots, 4$. Their explicit form is

$$\begin{aligned} \phi_0^0(\mathbf{v}) &= \phi^{\text{eq}}(v), \\ \phi_i^0(\mathbf{v}) &= \frac{v_i}{\sqrt{k_B T/m}} \phi^{\text{eq}}(v), \\ \phi_4^0(\mathbf{v}) &= \sqrt{\frac{2}{3}} \left(\frac{mv^2}{2k_B T} - \frac{3}{2} \right) \phi^{\text{eq}}(v), \end{aligned} \quad (7.13)$$

and they are orthonormalized $\langle \phi_j^0 | \phi_{j'}^0 \rangle = \delta_{j,j'}$.

Let's now go back to the full, k -dependent, problem. We wrote the solution in (7.9). If we assume that the eigenvalues λ_j^q can be expanded in q , then 5 of them will tend to zero with q , while others remain finite. Therefore, at small momenta ($q \rightarrow 0$) and at large times ($t \rightarrow \infty$)

$$f_q(\mathbf{v}; t) \approx \sum_{\alpha=0}^4 c_\alpha^q \exp(\lambda_\alpha^q t). \quad (7.14)$$

In such regime, dynamics is described by the 5 hydrodynamic degrees of freedom and all the information about the dynamics is encoded through the 5 eigenvalues λ_α^q . Using the relation between the moments of the one-body distribution and the hydrodynamic fields we have

$$\begin{aligned} \Psi_q(t) &= m \int d\mathbf{v} f_q(\mathbf{v}; t) \times \begin{pmatrix} 1 \\ \frac{\mathbf{v}}{\rho} \\ \frac{mv^2}{3k_B \rho} \end{pmatrix} = m \sum_{\alpha=0}^4 c_\alpha^q \exp(\lambda_\alpha^q t) \int d\mathbf{v} \phi_\alpha^q(\mathbf{v}) \times \begin{pmatrix} 1 \\ \frac{\mathbf{v}}{\rho} \\ \frac{mv^2}{3k_B \rho} \end{pmatrix} \\ &= m \sum_{\alpha=0}^4 c_\alpha^q \exp(\lambda_\alpha^q t) \Phi_\alpha^q, \end{aligned} \quad (7.15)$$

where

$$\Phi_\alpha^q = \int d\mathbf{v} \phi_\alpha^q(\mathbf{v}) \times \begin{pmatrix} 1 \\ \frac{\mathbf{v}}{\rho} \\ \frac{mv^2}{3k_B \rho} \end{pmatrix}. \quad (7.16)$$

In writing the equations we changed from the energy field e to the temperature field T using the equation of state of ideal gas

$$p = \frac{\rho k_B T}{m} = \frac{2\rho e}{3}. \quad (7.17)$$

To see this more directly let us turn now our attention to the linearized Navier-Stokes equations

7.2 Linearised hydrodynamics

We assume that the hydrodynamic fields are close to their equilibrium values

$$\rho(\mathbf{x}, t) = \rho + \delta\rho(\mathbf{r}, t), \quad \mathbf{u}(\mathbf{x}, t) = \delta\mathbf{u}(\mathbf{x}, t), \quad e(\mathbf{x}, t) = e + \delta e(\mathbf{x}, t). \quad (7.18)$$

The full nonlinear hydrodynamic equations are

$$\begin{aligned} \partial_t \rho &= -\nabla \cdot (\rho \mathbf{u}), \\ \partial_t (\rho u_n) &= -\nabla_s (\rho u_n u_s + \mathbf{P}_{ns}), \\ \partial_t (\rho e) &= -\nabla \cdot (\rho e \mathbf{u} + \mathbf{q}) - \mathbf{P}_{ns} : \nabla_n \mathbf{u}_s, \end{aligned} \quad (7.19)$$

with hydrodynamic pressure tensor \mathbf{P} and heat current \mathbf{q} ,

$$\begin{aligned} \mathbf{P}_{rs} &= m \int d\mathbf{v} (v_r - u_r)(v_s - u_s) f(\mathbf{v}; \mathbf{x}, t), \\ q_r(\mathbf{x}, t) &= \frac{1}{2} m \int d\mathbf{v} (v_r - u_r) |\mathbf{v} - \mathbf{u}|^2 f(\mathbf{v}; \mathbf{x}, t). \end{aligned} \quad (7.20)$$

We were also using the notation

$$\mathbf{P}_{rs} = P \delta_{rs} + \pi_{rs}, \quad \pi_{rs}(\mathbf{x}, t) = m \int d\mathbf{v} (v_r - u_r)(v_s - u_s) f(\mathbf{v}; \mathbf{x}, t) - \delta_{rs} P(\mathbf{x}, t). \quad (7.21)$$

To linearize the equations around the equilibrium values we need to understand the form of the pressure tensor and heat current in the equilibrium. Let us look at the pressure tensor

$$\mathbf{P}_{rs}^{\text{eq}} = m \int d\mathbf{v} v_r v_s f^{\text{eq}}(v) = \delta_{rs} m \int d\mathbf{v} v_r^2 f^{\text{eq}}(v) = \delta_{rs} \frac{2}{3} \int d\mathbf{v} \frac{mv^2}{2} f^{\text{eq}}(v) = \delta_{rs} \frac{2\rho e}{3}, \quad (7.22)$$

while the heat current vanishes in the equilibrium. Note that in the process we got $P = 2\rho e/3$. The dissipative part π_{rs} of the pressure tensor vanishes for constant u and hence in the first approximation it should be proportional to $\partial u_i / \partial x_j$. Moreover, since no friction should appear if fluid rotates with uniform angular velocity ($\mathbf{u} = \boldsymbol{\omega} \times \mathbf{x}$) it should depend only on combinations $\partial u_i / \partial x_j + \partial u_j / \partial x_i$. The most general tensor that satisfies the two conditions is

$$\pi_{rs} = a \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} \right) + b \left(\sum_{j=1}^3 \frac{\partial u_j}{\partial x_j} \right) \delta_{rs}, \quad (7.23)$$

where a, b are scalars. It is customary to rewrite it in the following form

$$\pi_{rs} = -\eta \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \left(\sum_{j=1}^3 \frac{\partial u_j}{\partial x_j} \right) \delta_{rs} \right) - \zeta \left(\sum_{j=1}^3 \frac{\partial u_j}{\partial x_j} \right) \delta_{rs}, \quad (7.24)$$

with the first part traceless and η being the *shear viscosity* and ζ the *bulk viscosity*.

For the heat current, we use an experimental fact, that gradient of the temperature generates the heat current, hence

$$\mathbf{q} = -\kappa \nabla T. \quad (7.25)$$

We now linearize the equations finding

$$\begin{aligned} \partial_t \delta\rho &= -\rho \nabla \cdot \delta\mathbf{u}, \\ \rho \partial_t \delta u_n &= -\partial_n P - \partial_s \pi_{ns}, \\ \rho \partial_t \delta e &= \kappa \nabla^2 T - P \nabla \cdot \delta\mathbf{u}, \end{aligned} \quad (7.26)$$

where in writing the third equation we used the first one to rewrite the time derivative of $\delta\rho$. It's convenient to eliminate the pressure P and energy e in favour of the temperature T and density ρ . We use

$$\delta P = \left(\frac{\partial P}{\partial T} \right)_\rho \delta T + \left(\frac{\partial P}{\partial \rho} \right)_T \delta \rho, \quad \delta e = \left(\frac{\partial e}{\partial T} \right)_\rho \delta T + \left(\frac{\partial e}{\partial \rho} \right)_T \delta \rho, \quad (7.27)$$

and further from the thermodynamics (see Resibois, pg. 104)

$$\left(\frac{\partial e}{\partial T} \right)_\rho = C_v, \quad \left(\frac{\partial e}{\partial \rho} \right)_T = \frac{P}{\rho^2} - \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho. \quad (7.28)$$

After further algebraic manipulations we obtain

$$\begin{aligned} \partial_t \delta \rho &= -\rho \nabla \cdot \delta \mathbf{u}, \\ \rho \partial_t \delta u_n &= -\frac{1}{\rho} \left(\frac{\partial P}{\partial T} \right)_\rho \nabla \delta T + \frac{1}{\rho} \left(\frac{\partial P}{\partial \rho} \right)_T \nabla \delta \rho - \partial_s \pi_{ns}, \\ \rho \partial_t \delta T &= -\frac{T}{\rho C_v} \left(\frac{\partial P}{\partial T} \right)_\rho \nabla \cdot \delta \mathbf{u} + \kappa \nabla^2 T. \end{aligned} \quad (7.29)$$

The derivative of the dissipative pressure is

$$\partial_s \pi_{ns} = \eta \nabla^2 \delta u_n + \left(\zeta + \frac{\eta}{3} \right) \partial_n (\nabla \cdot \delta \mathbf{u}). \quad (7.30)$$

We consider now Fourier expansion of the hydrodynamic fields in the position

$$\rho_{\mathbf{q}}(t) = \int d\mathbf{x} e^{-i\mathbf{q} \cdot \mathbf{x}} \delta \rho(\mathbf{x}, t), \quad (7.31)$$

and similarly for $\mathbf{u}_{\mathbf{q}}(t)$ and $T_{\mathbf{q}}(t)$. The spatial derivative $\partial_{\mathbf{q}}$ becomes $i\mathbf{q}$ and

$$\begin{aligned} \partial_t \rho_{\mathbf{q}}(t) &= -i\rho \mathbf{q} \cdot \mathbf{u}_{\mathbf{q}}, \\ \partial_t \mathbf{u}_{\mathbf{q}}(t) &= -i\alpha \mathbf{q} \rho_{\mathbf{q}} - i\beta \mathbf{q} T_{\mathbf{q}} - \nu q^2 \mathbf{u}_{\mathbf{q}} - \delta \mathbf{q} (\mathbf{q} \cdot \mathbf{u}_{\mathbf{q}}), \\ \partial_t T_{\mathbf{q}}(t) &= -i\mu \mathbf{q} \cdot \mathbf{u}_{\mathbf{q}} - \xi q^2 T_{\mathbf{q}}, \end{aligned} \quad (7.32)$$

where we introduced the following notation

$$\begin{aligned} \alpha &= \frac{1}{\rho} \left(\frac{\partial P}{\partial \rho} \right)_T, & \beta &= \frac{1}{\rho} \left(\frac{\partial P}{\partial T} \right)_\rho, & \nu &= \frac{\eta}{\rho}, \\ \delta &= \frac{1}{\rho} \left(\zeta + \frac{\eta}{3} \right), & \mu &= \frac{T}{\rho C_v} \left(\frac{\partial P}{\partial T} \right)_\rho, & \xi &= \frac{\kappa}{\rho C_v}. \end{aligned} \quad (7.33)$$

Because of the spatial isotropy of the fluid we can assume that the dynamics is only along the x -axis such that $\mathbf{q} = q\hat{\mathbf{x}}$.

We can write the linearized hydrodynamics equations more compactly by introducing 5-dimensional vector

$$\Psi_{\mathbf{q}}(t) = \begin{pmatrix} \rho_{\mathbf{q}}(t) \\ \mathbf{u}_{\mathbf{q}}(t) \\ T_{\mathbf{q}}(t) \end{pmatrix}, \quad (7.34)$$

such that

$$\partial_t \Psi_{\mathbf{q}}(t) = M_{\mathbf{q}} \cdot \Psi_{\mathbf{q}}(t). \quad (7.35)$$

The matrix M reads

$$M_q = \begin{pmatrix} 0 & -iq\rho & 0 & 0 & 0 \\ -i\alpha q & -(\nu + \delta)q^2 & 0 & 0 & -i\beta q \\ 0 & 0 & -\nu q^2 & 0 & 0 \\ 0 & 0 & 0 & -\nu q^2 & 0 \\ 0 & -i\mu q^2 & 0 & 0 & -\xi q^2 \end{pmatrix} \quad (7.36)$$

The matrix can be diagonalized and in the limit of small q , keeping terms up to order q^2 we find

$$\lambda_{1,2}^q = \mp i v_s q - \Gamma_s q^2, \quad \lambda_{3,4}^q = -\frac{\eta}{\rho} q^2, \quad \lambda_5^q = -\frac{\kappa}{\rho C_p} q^2, \quad (7.37)$$

where the specific heat at constant pressure is

$$C_p = C_v + \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho^2 / \left(\frac{\partial P}{\partial \rho} \right)_T, \quad (7.38)$$

and the sound velocity and sound absorption coefficient are

$$v_s = \left[\frac{C_p}{C_v} \left(\frac{\partial p}{\partial \rho} \right)_T \right]^{1/2}, \quad \Gamma_s = \frac{1}{2\rho} \left[\frac{4\eta}{3} + \zeta + \left(\frac{1}{C_v} - \frac{1}{C_p} \right) \kappa \right]. \quad (7.39)$$

The general solution to the dynamics of the hydrodynamic fields is then

$$\Psi_q(t) = \sum_{\alpha=0}^4 c_\alpha^q(0) \exp(\lambda_\alpha^q t) \Phi_\alpha^q, \quad (7.40)$$

with Φ_α^q eigenvectors associated with eigenvalues λ_α^q .

The eigenvalues λ_j^q are now computed in two ways, either from linearized hydrodynamics or from the linearized Boltzmann equation. Equating results of the two computations we find formulas for the transport coefficients.

The computations give

$$\eta = -\frac{\rho m}{k_B T} \int d\mathbf{v} v_x v_y \chi^{xy}(\mathbf{v}), \quad \zeta = 0, \quad (7.41)$$

$$\kappa = -\frac{\rho m}{k_B T^2} \int d\mathbf{v} \frac{v^2}{2} v_x \chi^x(\mathbf{v}), \quad (7.42)$$

where

$$nC\chi^{xy} = v_x v_y \phi^{\text{eq}}, \quad nC\chi^x = v_x \left(\frac{v^2}{2} - \frac{5k_B T}{2m} \right) \phi^{\text{eq}}, \quad (7.43)$$

subject to conditions

$$\langle \phi_\alpha^0 | \chi^{xy} \rangle = 0, \quad \langle \phi_\alpha^0 | \chi^x \rangle = 0, \quad \alpha = 0, 1, \dots, 4. \quad (7.44)$$

8 Self-diffusion

Imagine a fluid with some number of particles which are tagged but otherwise identical with other particles. We denote by $c(\mathbf{x}, t)$ their concentration. Their number is conserved

$$\partial_t c(\mathbf{x}, t) + \nabla \cdot \vec{j}(\mathbf{x}, t) = 0, \quad (8.1)$$

with current $\vec{j}(\mathbf{x}, t)$ of the concentration. We can find the current in two ways.

8.1 Boltzmann equation

Let's write the Boltzmann equation for two distribution functions f_c of the tagged particles and f of the remaining (untagged) particles

$$(\partial_t + \vec{v} \cdot \nabla) f_c = \mathcal{K}(f_c, f) + \mathcal{K}(f_c, f_c), \quad (8.2)$$

$$(\partial_t + \vec{v} \cdot \nabla) f = \mathcal{K}(f_c, f) + \mathcal{K}(f, f). \quad (8.3)$$

We assume that the density of the tagged particles is much less than the density of the other particles. Under this assumption, it is reasonable to expect that the distribution f will evolve at slower rate than the distribution f_c . We can go to a large imbalance limit in which we take f to be constant in time. This reduces the pair of Boltzmann equation to

$$(\partial_t + \vec{v} \cdot \nabla) f_c = \mathcal{K}(f_c, f). \quad (8.4)$$

In writing the equation we also took into account that since density of tagged particles is low a collision between the two tagged particles is less likely than collision between a tagged and untagged particle. Note that because f is constant this equation conserves only the particle number but not momentum nor energy. This gives a single balance equation

$$\partial_t c + \nabla \cdot (c \vec{u}_c) = 0, \quad (8.5)$$

where we used

$$c(\mathbf{x}, t) = m \int d\mathbf{v} f_c(\mathbf{v}, \mathbf{x}, t), \quad c(\mathbf{x}, t) \vec{u}_c(\mathbf{x}, t) = m \int d\mathbf{v} \mathbf{v} f_c(\mathbf{v}, \mathbf{x}, t). \quad (8.6)$$

Equation (8.5) is not closed. To close we can consider a linearized theory as we did for the Navier-Stokes equations. Instead we pursue here a more phenomenological approach.

8.2 Phenomenology

We assume that current \vec{j}_c can be expanded in gradients of $c(\mathbf{x}, t)$,

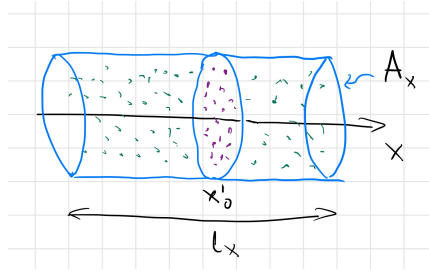
$$\vec{j}_c = D(c) \nabla c + \text{higher derivatives}, \quad (8.7)$$

Note that there is no gradient free term because if the concentration is constant we don't expect any current. The result is the diffusion equation

$$\partial_t c + \nabla \cdot (D(c) \nabla c) = 0. \quad (8.8)$$

This is a non-linear diffusion equation since, at this level, $D(c)$ is some unknown function of c . Under the assumption that D is actually constant we get the usual diffusion equation

$$\partial_t c + D \nabla^2 c = 0. \quad (8.9)$$



Let us solve it for the initial configuration

$$c(\mathbf{x}, t = 0) = N\delta(x - x_0)/A_x. \quad (8.10)$$

The solution is

$$c(x, t|x_0, 0) = \frac{N}{2A_x\sqrt{D\pi}} \exp\left[-\frac{(x - x_0)^2}{4Dt}\right]. \quad (8.11)$$

We can now compute the second moment

$$\int dx (x - x_0)^2 c(x, t|x_0, 0) = \frac{2NDt}{A_x}. \quad (8.12)$$

Inverting this relation we find a formula for the diffusion coefficient

$$D = \frac{A_x}{2Nt} \int dx (x - x_0)^2 c(x, t|x_0, 0). \quad (8.13)$$

8.3 Green-Kubo formula

We would like to express now this formula in terms of the distribution function $f(\mathbf{v}, \mathbf{q}, t)$. The observable is the total concentration of tagged particles at given point in space and given time. From the assumption of axial symmetry the dependence is only in x -direction and time. Moreover, since the tagged particles are identical, we have

$$\sum_{j=0}^N \delta(q_j, x - x)/A_x = N\delta(q_{j,x} - x)/A_x, \quad (8.14)$$

such that the concentration is

$$c(x, t|x_0, 0) = \frac{N}{A_x} \int d\mathbf{q} d\mathbf{v} \delta(q_{j,x} - x) f_0(\mathbf{q}, \mathbf{p}, t) = \frac{N}{A_x} \int d\mathbf{q} d\mathbf{v} \delta(q_{j,x}(t) - x) f_0(\mathbf{q}, \mathbf{p}). \quad (8.15)$$

In the second step we moved the dynamics from the distribution function to the observable. The time-independent distribution function $f_0(\mathbf{q}, \mathbf{v})$ is fixed by the initial condition as a subset of thermal distribution functions $f(\mathbf{q}, \mathbf{p})$ for which the x -coordinate of the j -th particle is equal to x_0 ,

$$f_0(\mathbf{q}, \mathbf{v}) = l_x \delta(q_{j,x} - x_0) f(\mathbf{q}, \mathbf{p}). \quad (8.16)$$

This gives

$$c(x, t|x_0, 0) = \frac{Nl_x}{A_x} \int d\mathbf{q} d\mathbf{v} \delta(q_{j,x}(t) - x) \delta(q_{j,x}(0) - x_0) f(\mathbf{q}, \mathbf{p}). \quad (8.17)$$

Consider now the diffusion coefficient (multiplied by $2t$) averaged over the initial position x_0 ,

$$2Dt = \frac{A_x}{Nl_x} \int dx_0 \int dx (x - x_0)^2 c(x, t|x_0, 0). \quad (8.18)$$

The expression for the concentration in terms of the distribution function gives

$$2Dt = \int d\mathbf{q} d\mathbf{v} (q_{j,x}(t) - q_{j,x}(0))^2 f(\mathbf{q}, \mathbf{v}). \quad (8.19)$$

This is the sought after expression for the diffusion coefficient expressing it in terms of the thermal equilibrium data. We can further manipulate it by taking time derivative of both sides. The result is

$$D = \int d\mathbf{q} d\mathbf{v} \dot{q}_{j,x}(t) (q_{j,x}(t) - q_{j,x}(0)) f(\mathbf{q}, \mathbf{v}) = \int dt' \int d\mathbf{q} d\mathbf{v} v_{j,x}(t) v_{j,x}(t') f(\mathbf{q}, \mathbf{v}). \quad (8.20)$$

Finally, taking $t \rightarrow \infty$ we obtain the Green-Kubo formula for the diffusion coefficient,

$$D = \int_0^\infty dt \langle v_{j,x}(t) v_{j,x}(t') \rangle. \quad (8.21)$$

where we introduced the auto-correlation function of the velocities

$$\langle v_{j,x}(t) v_{j,x}(t') \rangle = \int d\mathbf{q} d\mathbf{v} v_{j,x}(t) v_{j,x}(t') f(\mathbf{q}, \mathbf{v}) \quad (8.22)$$

9 Additional exercises

1. Write down the Liouville equation for a two component system made of N_1 particles of mass m_1 and N_2 particles of mass m_2 . The particles interact with two-body conservative forces described by the potential energy $V^{(ij)}$ with (11) and (22) describing interactions between particles of the same type and (12) between particles of different types.
2. Consider a system that contains N particles in equilibrium (hence $\partial_t F = 0$) whose Hamiltonian is given by

$$H(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + V(\mathbf{q}),$$

with kinetic and potential parts respectively. Show that if the distribution function is of the product form

$$F(\mathbf{q}, \mathbf{p}) = X(\mathbf{q})P(\mathbf{p}),$$

where $P(\mathbf{p}) = \prod_{j=1}^N g_j(p_j^2)$, then the Liouville equation implies the canonical distribution

$$F_c(\mathbf{q}, \mathbf{p}) = A \exp[-\beta H(\mathbf{q}, \mathbf{p})],$$

with A and $\beta > 0$ constant.

3. Is the Boltzmann equation time reversible? If $f(\mathbf{q}, \mathbf{v}, t)$ is a solution, is $f(\mathbf{q}, -\mathbf{v}, -t)$ also a solution?
4. Show that the stress tensor π_{rs} vanishes if $\mathbf{u} = \mathbf{\Omega} \times \mathbf{v}$, where $\mathbf{\Omega}$ is a constant angular velocity vector.
5. Consider fluid at rest and in equilibrium with homogeneous density ρ_0 and temperature T_0 . Starting with the Euler equations, write down equations for the dynamics of a small perturbation around this equilibrium state $\rho = \rho_0 + \delta\rho$, $u = 0 + \delta u$ and $T = T_0 + \delta T$. Find the equation for the sound velocity.