Non-equilibrium Statistical Physics

M. Panfil,

Faculty of Physics, University of Warsaw, ul. Pasteura 5, 02-093 Warsaw, Poland
milosz.panfil@fuw.edu.pl

March 23, 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.

Contents

Chapter 1

Classical dynamics

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`

1.1 Motivation

Navier-Stokes equations

$$\begin{aligned} \partial_t \rho &= -\nabla \cdot (\rho \mathbf{u}), && (1.1)\\ \partial_t(\rho \mathbf{u}) &= -\nabla \cdot (\rho \mathbf{u}\mathbf{u} + P + \pi)\,, && (1.2)\\ \partial_t(\rho e) &= -\nabla \cdot (\rho e \mathbf{u} + \mathbf{q}) - P \nabla \cdot \mathbf{u} - \pi : \nabla \mathbf{u}. && (1.3) \end{aligned}$$

State of the system described by $\rho, \mathbf{u}, e$. 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

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

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

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

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

and tensor multiplication ...

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

$$t \to -t, \qquad \mathbf{u} \to -\mathbf{u}. \tag{1.6}$$

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

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

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

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

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

1.2 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: $(\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$ 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

$$\frac{dq_j(t)}{dt} = \frac{\partial H(q,p)}{\partial p_j}, \qquad \frac{dp_j(t)}{dt} = -\frac{\partial H(q,p)}{\partial q_j} \tag{1.10}$$

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

$$\partial_t b(q,p;t) = \sum_{j=1}^{F} \left(\frac{\partial b}{\partial q_j}\frac{dq_j}{dt} + \frac{\partial b}{\partial p_j}\frac{dp_j}{dt} \right) = \sum_{j=1}^{F} \left(\frac{\partial b}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial b}{\partial p_j}\frac{\partial H}{\partial q_j} \right) = \{b, H\}, \tag{1.11}$$

where the Poisson bracket is

$$\{f,g\} = \sum_{j=1}^{F} \left(\frac{\partial f}{\partial q_j}\frac{\partial g}{\partial p_j} - \frac{\partial f}{\partial p_j}\frac{\partial g}{\partial q_j} \right) \tag{1.12}$$

Clearly

$$\{q_j, p_k\} = \delta_{j,k}, \qquad \{q_j, q_k\} = \{p_j, p_k\} = 0. \tag{1.13}$$

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

$$\{f,g\} = -\{g,f\}, \quad \{\alpha, f\} = 0, \tag{1.14}$$

$$\{fg, h\} = f\{g,h\} + \{f,h\}g, \tag{1.15}$$

$$\{f,\{g,h\}\} + \{g,\{h,f\}\}\{h,\{f,g\}\} = 0. \tag{1.16}$$

We can also write the evolution equation

$$\partial_t b(q,p;t) = [H]b(q,p,t), \tag{1.17}$$

where the linear operator $[H]$ is

$$[H] = \sum_{j=1}^{F} \left(\frac{\partial H}{\partial p_j}\frac{\partial}{\partial q_j} - \frac{\partial H}{\partial q_j}\frac{\partial}{\partial p_j} \right). \tag{1.18}$$

This equation can be solved formally as

$$b(q,p;t) = e^{[H]t} b(q,p) = \sum_{n}^{\infty} \frac{1}{n!} t^n [H]^n b(q,p). \tag{1.19}$$

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

$$b(q,p;t) = e^{[H]t} b(q,p;0) = b(e^{[H]t}q, e^{[H]t}p; 0) = b(q(t), p(t); 0) \tag{1.20}$$

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 consists of testing whether any of the particles in the system is actually at position $\mathbf{x}$. This is achieved by

$$\rho(q, p; \mathbf{x}, 0) = \sum_{j=1}^{N} m\delta(\mathbf{q}_j - \mathbf{x}). \tag{1.21}$$

Using the propagator we get

$$\rho(q, p; x, t) = e^{H}t \sum_{j=1}^{N} m\delta(\mathbf{q}_j - \mathbf{x}) = \sum_{j=1}^{N} m\delta(\mathbf{q}_j(t) - \mathbf{x}). \tag{1.22}$$

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.

1.2.1 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

$$H = H^0 + H', \tag{1.23}$$

where the kinetic part is

$$H^0 = \sum_{j=1}^{N} H_j^0, \qquad H_j^0 = \frac{\mathbf{p}_j^2}{2m}, \tag{1.24}$$

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

$$H' = \sum_{j<k}^{N} V_{jk}. \tag{1.25}$$

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

$$V_{jk} = V(|\mathbf{q}_j - \mathbf{q}_k|). \tag{1.26}$$

The standard cases are

- Lennard-Jones potential for neutral particles

$$V^{LJ}(r) = V_0 \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6} \right], \tag{1.27}$$

- Its hard spheres limit when the attractive part is weak

$$V^{HS}(r) = \begin{cases} \infty, & r < r_0, \\ 0, & r > r_0 \end{cases} \tag{1.28}$$

- Coulomb potential

$$V^{C} = \frac{e^2}{r^2}. \tag{1.29}$$

- Debye (screened Coulomb) potential

$$V^D(r) = e^2\frac{\exp(-r/r_D}{r}, \qquad r_D = \left(\frac{4\pi e^2 n}{k_B T}\right)^{-1/2}. \tag{1.30}$$

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

$$H^F = \sum_{j=1}^{N} V^F(\mathbf{q}_j, t). \tag{1.31}$$

1.2.2 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

$$b(q, p; \mathbf{x}, t) \to B(\mathbf{x}, t). \tag{1.32}$$

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

$$B(\mathbf{x}, t) = \langle b(q, p; \mathbf{x}, t)\rangle = \langle b\rangle. \tag{1.33}$$

We require the following two conditions from this functional

- Constants on the phase space are unaffected

$$\langle \beta \rangle = \beta, \tag{1.34}$$

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

$$\langle \beta b + \gamma c\rangle = \beta\langle b\rangle + \gamma\langle c\rangle \tag{1.35}$$

A simple candidate is

$$B(\mathbf{x}, t) = \langle b\rangle = \int \mathrm{d}q\mathrm{d}p\, b(q, p; \mathbf{x}, t) F(q, p), \tag{1.36}$$

with the requirement that

$$\int \mathrm{d}q\mathrm{d}p\, F(q, p) = 1. \tag{1.37}$$

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

$$F(q, p) \geqslant 0. \tag{1.38}$$

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 $F(q,p)\mathrm{d}q\mathrm{d}p$ is the probability of finding the system within the infinitesimal domain $(q+\mathrm{d}q)$, $(p+\mathrm{d}p$ 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

$$B(\mathbf{x},t) = \int \mathrm{d}p\mathrm{d}q \left(e^{[H]t} b(q,p;\mathbf{x}) \right) F(q,p). \tag{1.39}$$

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

$$B(\mathbf{x},t) = \int \mathrm{d}p\mathrm{d}q \, b(q,p;\mathbf{x}) F(q,p;t), \tag{1.40}$$

with

$$F(q,p;t) = e^{-[H]t} F(q,p). \tag{1.41}$$

Which is like going from Heisenberg picture in which observables evolve in time to the Schroedinger picture in which the state evolves in time. In any case we arrived now at the evolution equation for the phase space distribution function

$$\partial_t F(q,p;t) = LF(q,p;t), \tag{1.42}$$

where *Liouvillian* is

$$LF = \{H, L\} = \sum_{j=1}^{3N} \left(\frac{\partial H}{\partial q_j} \frac{\partial F}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial F}{\partial q_j} \right). \tag{1.43}$$

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

$$\mathbf{v}_j = \frac{\mathbf{p}_j}{m}, \tag{1.44}$$

and the following abbreviations

$$\nabla_j = \frac{\partial}{\partial \mathbf{q}_j}, \qquad \partial_j = \frac{\partial}{\partial \mathbf{p}_j}, \qquad \partial_{jk} = \partial_j - \partial_k \tag{1.45}$$

Then the Liouvillian is

$$L = L^0 + L' = \sum_{j=1}^{N} L_j^0 + \sum_{j<k}^{N} L'_{jk}, \tag{1.46}$$

where

$$L_j^0 = -\mathbf{v}_j \cdot \nabla_j, \qquad L'_{jk} = (\nabla_j V_{jk}) \cdot \partial_{jk}. \tag{1.47}$$

1.2.3 Equilibrium states

Stationary solutions to the Liouville equation

$$\{H(q,p), F^0(q,p)\} = 0. \tag{1.48}$$

Solution is any function of the Hamiltonian,

$$F^0(q,p) = \Phi[H(q,p)], \tag{1.49}$$

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

$$F^0(q,p) = \frac{1}{h^{3N} N! Z(T,V,N)} \exp\left(-\frac{H(q,p)}{k_B T}\right), \tag{1.50}$$

with the partition function that ensures the normalization, namely

$$Z(T,V,N) = \frac{1}{h^{3N} N!} \int \mathrm{d}q \mathrm{d}p \, \exp\left(-\frac{H(q,p)}{k_B T}\right). \tag{1.51}$$

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

$$A(T,V,N) = -k_B T \ln Z(T,V,N). \tag{1.52}$$

1.2.4 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 (1.39) and Schroedinger picture (1.40).
4. Prove that the Liouville operator is anit-Hermitian.
5. Solve Liouville equation for a system of non-interacting particles. Compute the propagator for such system.

1.3 Reduced distributions, correlations and the BBGKY hierarchy

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

$$H(x_1, \ldots, x_N) = \sum_{j=1}^{N} H^0(x_j) + \sum_{j<k}^{N} V(x_j, x_k). \tag{1.53}$$

Consider an arbitrary dynamical function $b(x_1, \ldots, x_N)$ 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

$$b(x_1, \ldots, x_N) = b_0 + \sum_{j=1}^{N} b_1(x_j) + \sum_{j<k}^{N} b_2(x_j, x_k) + \sum_{j<k<n}^{N} b_3(x_j, x_k, x_n) + \cdots + b_N(x_1, \ldots, x_N). \tag{1.54}$$

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

$$b_2(x_1, x_2) = f(x_1, x_2) + g(x_1) + g(x_2), \tag{1.55}$$

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

$$b(x_1, \ldots, x_N) = b_0 + \sum_{j=1}^{n} b_1(x_j) + \frac{1}{2!} \sum_{j\neq k}^{N} b_2(x_j, x_k) + \cdots + b_N(x_1, \ldots, x_N). \tag{1.56}$$

Most dynamical functions of physical interest contain only small number of irreducible dynamical functions, $b_0, b_1, \ldots, b_S$ 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

$$\int \mathrm{d}x_1 \ldots \mathrm{d}x_N \left[\sum_{j=1}^{N} b_1(x_j)\right] F(x_1, \ldots, x_N) = N \int \mathrm{d}x_1 \ldots \mathrm{d}x_N b_1(x_1) F(x_1, \ldots, x_N). \tag{1.57}$$

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

$$f_1(x_1) = N \int \mathrm{d}x_2, \ldots \mathrm{d}x_N F(x_1, x_2, \ldots, x_N). \tag{1.58}$$

We then obtain

$$\int \mathrm{d}x_1 \mathrm{d}x_N \left[\sum_{j=1}^{N} b_1(x_j)\right] F(x_1, \ldots, x_N) = \int \mathrm{d}x_1 b_1(x_1) f_1(x_1). \tag{1.59}$$

In a similar fashion, for the s-particle contribution

$$\begin{aligned}\int \mathrm{d}x_1 \dots \mathrm{d}x_N \left[\frac{1}{s!} \sum_{j_1 \neq j_2 \neq \dots \neq j_s} b_s(x_{j_1}, \dots, x_{j_s})\right] F(x_1, \dots, x_N) \\ = \frac{N!}{(N-s)!s!} \int \mathrm{d}x_1 \dots \mathrm{d}x_N b_s(x_1, \dots, x_s) F(x_1, \dots, x_N) \\ = \frac{1}{s!} \int \mathrm{d}x_1 \dots \mathrm{d}x_s b_s(x_1, \dots, x_s) f_s(x_1, \dots, x_s),\end{aligned} \tag{1.60}$$

where we defined the s-particle reduced distribution function

$$f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!} \int \mathrm{d}x_{s+1} \dots \mathrm{d}x_N F(x_1, \dots, x_N). \tag{1.61}$$

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

$$\int \mathrm{d}x_1 \dots \mathrm{d}x_s f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!}. \tag{1.62}$$

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

$$f_r(x_1, \dots, x_r) = \frac{(N-s)!}{(N-r)!} \int \mathrm{d}x_{r+1} \dots \mathrm{d}x_s f_s(x_1, \dots, x_s) \tag{1.63}$$

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

$$\langle b \rangle = b_0 + \sum_{s=1}^{N} \frac{1}{s!} \int \mathrm{d}x_1 \dots \mathrm{d}x_s b_s(x_1, \dots, x_s) f_s(x_1, \dots, x_s). \tag{1.64}$$

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

1.3.1 Evolution equations for the reduced distributions

Equations for F

$$\partial_t F = \sum_{j=1}^{N} L_j^0 F + \sum_{j<k}^{N} L'_{jk} F. \tag{1.65}$$

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

$$\int \mathrm{d}x_1 \dots \mathrm{d}x_N \left(\sum_{j=1}^{N} L_j^0 + \sum_{j<k}^{N} L'_{jk}\right) F = 0, \tag{1.66}$$

which has to hold for each term separately

$$\int \mathrm{d}x_1 \dots \mathrm{d}x_N L_j^0 F = 0, \qquad \int \mathrm{d}x_1 \dots \mathrm{d}x_N L'_{jk} F = 0. \tag{1.67}$$

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

$$\partial_t f_s(x_1, \dots, x_s) = \frac{N!}{(N-s)!} \int \mathrm{d}x_{s+1} \dots \mathrm{d}x_N \left(\sum_{j=1}^{N} L_j^0 F + \sum_{j<k}^{N} L'_{jk} F\right). \tag{1.68}$$

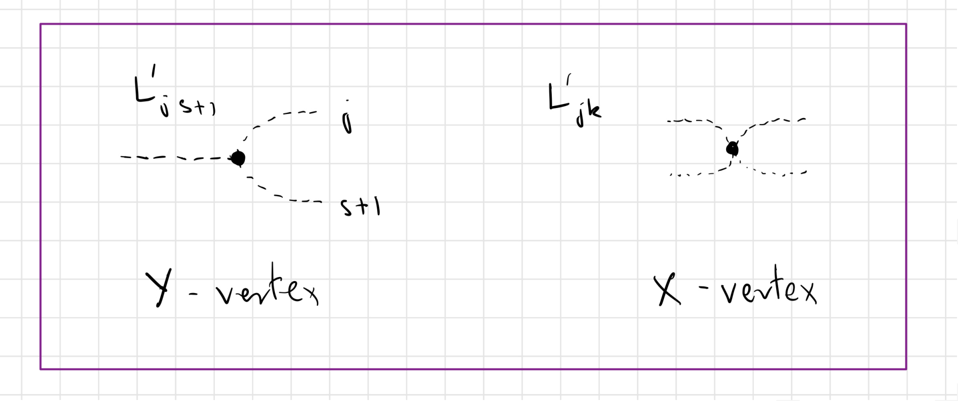


Figure 1.1: The right hand side of the equations for reduced distribution functions can be represented diagrammatically using two types of diagrams. In the Y-vertex the position $(s+1)$ is integrated over.

For the first term we have

$$\sum_{j=1}^{N} L_j^0 F = \sum_{j=1}^{s} L_j^0 F + \sum_{j=s+1}^{N} L_j^0 F, \tag{1.69}$$

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

$$\begin{aligned} \partial_t f_s(x_1, \ldots, x_s) - \sum_{j=1}^{s} L_j^0 f_s(x_1, \ldots, x_s) &= \sum_{j<k} L'_{jk} f_s(x_1, \ldots, x_s) \\ &+ \sum_{j=1}^{s} \int \mathrm{d}x_{s+1} L'_{j,s+1} f_{s+1}(x_1, \ldots, x_{s+1}). \end{aligned} \tag{1.70}$$

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

$$\begin{aligned} \partial_t f_1(x_1) - L_1^0 f_1(x_1) &= \int \mathrm{d}x_2 L'_{12} f_2(x_1, x_2), \\ \partial_t f_2(x_1, x_2) - \left(L_1^0 + L_2^0\right) f_2(x_1, x_2) &= L_{12} f_2(x_1, x_2) + \int \mathrm{d}x_3 \left(L'_{13} + L'_{23}\right) f_3(x_1, x_2, x_3). \end{aligned} \tag{1.71}$$

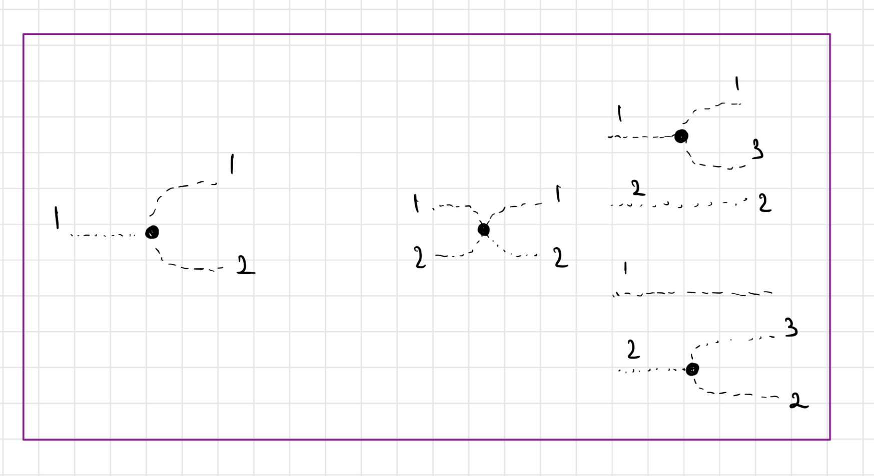


Figure 1.2: Diagrams for the one-body and two-body reduced distribution functions

1.3.2 Correlation functions and their evolution

If the system is uncorrelated at some given time t then

$$f_s(x_1, \ldots, x_s) = \prod_{j=1}^{s} f_1(x_j). \tag{1.72}$$

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

$$f_2(x_1, x_2) = f_1(x_1)f_1(x_2) + g_2(x_1, x_2), \tag{1.73}$$

while for $s = 3$,

$$\begin{aligned} f_3(x_1, x_2, x_3) = f_1(x_1)f_1(x_2)f_1(x_3) + f_1(x_1)g_2(x_2, x_3) + f_1(x_2)g_2(x_1, x_3) \\ +f_1(x_3)g_2(x_1, x_3) + g_3(x_1, x_2, x_3), \end{aligned} \tag{1.74}$$

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

$$\frac{1}{N^2}\int \mathrm{d}x_1\mathrm{d}x_2 f_2(x_1, x_2) = \left(\frac{1}{N}\int \mathrm{d}x_1 f_1(x_1)\right)^2 + \frac{1}{N^2}\int \mathrm{d}x_1\mathrm{d}x_2 g_2(x_1, x_2). \tag{1.75}$$

Using the normalization of the reduced distribution functions we find

$$-\frac{1}{N} = \frac{1}{N^2}\int \mathrm{d}x_1\mathrm{d}x_2 g_2(x_1, x_2), \tag{1.76}$$

which implies that, in the thermodynamic limit,

$$\frac{1}{N^s}\int \mathrm{d}x_1 \ldots \mathrm{d}x_s g_2(x_1, \ldots, x_3) \to 0, \tag{1.77}$$

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

The evolution equations are now

$$\partial_t f(x_1) - L_1^0 f(x_1) = \int \mathrm{d}x_2 \left(L'_{12} f(x_1)f(x_2) + L'_{12} g_2(x_1, x_2)\right), \tag{1.78}$$

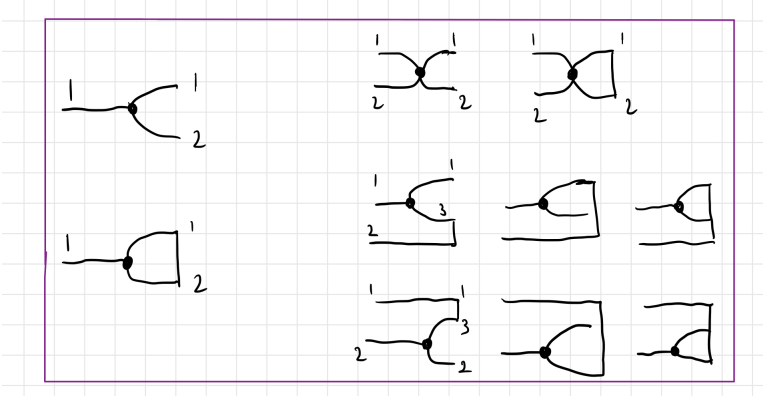


Figure 1.3: Diagrams for the evolution of the connected correlation functions. The horizontal bar implies that the variables enter the same correlator.

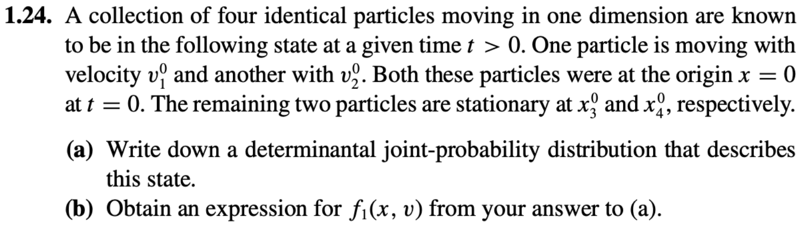
and

$$
\begin{aligned}
\partial_t g_2(x_1, x_2) - (L_1^0 + L_2^0) g_2(x_1, x_2) = {} & L'_{12} f(x_1) f(x_2) + L'_{12} g_2(x_1, x_2) \\
& + \int \mathrm{d}x_3 \left[L'_{13} f(x_1) g_2(x_2, x_3) + L'_{23} f(x_2) g_2(x_1, x_3) \right. \\
& \left. + (L'_{13} + L'_{23}) \left(f(x_3) g_2(x_1, x_2) + g_3(x_1, x_2, x_3) \right) \right] .
\end{aligned}
\tag{1.79}
$$

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

1.3.3 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.

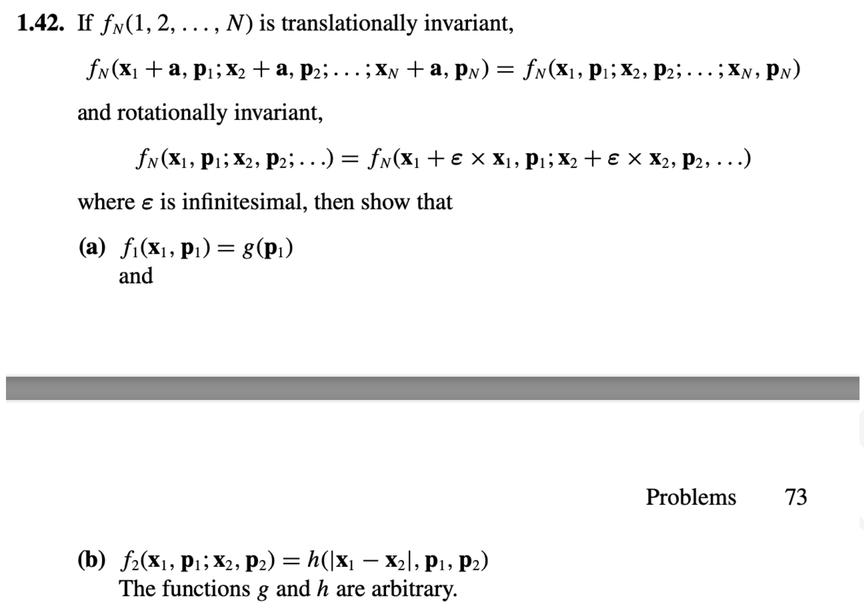
(a) Write down a determinantal joint-probability distribution that describes this state.

(b) Obtain an expression for $f_1(x, v)$ from your answer to (a).

2. Show (1.67) by invoking the form (1.47) of the Liouville operators

3. Derive the equation (1.79) for g_2.

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



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

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

and rotationally invariant,

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

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

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

(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]

1.4 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

$$f(\mathbf{q}, \mathbf{p}; t) = f(\mathbf{q}, m\mathbf{v}; t) = m^3 \hat{f}(\mathbf{q}, \mathbf{v}; t). \tag{1.80}$$

This implies correct normalization

$$N = \int \mathrm{d}\mathbf{p}\mathrm{d}\mathbf{q}\, f(\mathbf{q}, \mathbf{p}; t) = \int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{q}\, \hat{f}(\mathbf{q}, \mathbf{v}; t). \tag{1.81}$$

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

1.4.1 Weakly coupled systems

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

$$V(r) = \lambda v(r) \tag{1.82}$$

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

$$|V(r)| = \mathcal{O}(\lambda), \qquad |H^0| = \mathcal{O}(1). \tag{1.83}$$

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

$$L_j^0 = \mathcal{O}(\lambda^0), \qquad L'_{jk} = \mathcal{O}(\lambda). \tag{1.84}$$

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

$$g_2(\mathbf{q}_1, \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; t) \approx 0, \qquad \text{for} \qquad |\mathbf{q}_1 - \mathbf{q}_2| \gg l_C. \tag{1.85}$$

1.4.2 Derivation of the Vlasov equation and its properties

Note that the simple expansion of the propagator will not work

$$e^{-\lambda t} = 1 - t\lambda + \frac{1}{2}t^2\lambda^2 + \dots, \tag{1.86}$$

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

$$\partial_t f_1(x_1; t - L_1^0 f(x_1;t) = \int \mathrm{d}x_2 L'_{12} \left(f(x_1;t)f(x_2;t) + g_2(x_1, x_2;t)\right). \tag{1.87}$$

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

$$\partial_t f_1(x_1;t) - L_1^0 f(x_1;t) = \int \mathrm{d}x_2 L'_{12} f(x_1;t) f(x_2;t). \tag{1.88}$$

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

$$\begin{aligned}\int \mathrm{d}x_2 L'_{12} f(x_1;t)f(x_2;t) &= \int \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{v}_2 V'(\mathbf{q}_1 - \mathbf{q}_2)(\partial_1 - \partial_2) f(x_1;t)f(x_2;t) \\ &= \int \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{v}_2 V'(\mathbf{q}_1 - \mathbf{q}_2)\partial_1 f(x_1;t)f(x_2;t), \end{aligned} \tag{1.89}$$

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 potenatial at $\mathbf{q}_1$ caused by all the other particles

$$\bar{V}(\mathbf{q}_1;t) = \int \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{v}_2 V(\mathbf{q}_1 - \mathbf{q}_2) f(\mathbf{q}_2, \mathbf{v}_2; t), \tag{1.90}$$

and

$$\partial_t f_1(x_1;t) - L_1^0 f(x_1;t) = \nabla_1 \bar{V}(x_1;t)\partial_1 f_1(x_1;t). \tag{1.91}$$

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.

1.4.3 Landau equation

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

$$\partial_t f(x_1) - L_1^0 f(x_1) = \int \mathrm{d}x_2 L'_{12} \left(f(x_1)f(x_2) + g_2(x_1, x_2)\right), \tag{1.92}$$

$$\partial_t g_2(x_1, x_2) - (L_1^0 + L_2^0) g_2(x_1, x_2) = L'_{12} f(x_1) f(x_2). \tag{1.93}$$

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

$$g_2(x_1, x_2; t) = U_{12}^0(t) g_2(x_1, x_2; 0) + \int_0^t \mathrm{d}\tau U_{12}^0(\tau) L'_{12} f(x_1; t-\tau) f(x_2; t - \tau). \tag{1.94}$$

Let us verify this solution by direct computations. Recall that

$$U_{12}^0(t) = \exp\left(\left(L_1^0 + L_2^0\right) t\right). \tag{1.95}$$

Differentiating the solution, we get

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

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

$$\begin{aligned}
&\int_0^t \mathrm{d}\tau\, U^0_{12}(\tau) L'_{12} \partial_t \left(f(x_1; t-\tau) f(x_2; t-\tau)\right) = -\int_0^t \mathrm{d}\tau\, U^0_{12}(\tau) L'_{12} \partial_\tau \left(f(x_1; t-\tau) f(x_2; t-\tau)\right) \\
&= \int_0^t \mathrm{d}\tau \left(\partial_\tau U^0_{12}(\tau)\right) L'_{12} f(x_1; t-\tau) f(x_2; t-\tau) - (\text{boundary terms}) \\
&= \left(L^0_1 + L^0_2\right) \int_0^t \mathrm{d}\tau\, U^0_{12}(\tau) L'_{12} f(x_1; t-\tau) f(x_2; t-\tau) - (\text{boundary terms}).
\end{aligned}$$

The boundary terms are

$$\text{boundary terms} = U^0_{12}(t) L'_{12} f(x_1; 0) f(x_2; 0) - U^0_{12}(0) L'_{12} f(x_1; t) f(x_2; t), \tag{1.96}$$

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

$$\begin{aligned}
\partial_t g_2(x_1, x_2; t) = \left(L^0_1 + L^0_2\right) &\left(U^0_{12}(t) g_2(x_1, x_2; 0) + \int_0^t \mathrm{d}\tau\, U^0_{12}(\tau) L'_{12} f(x_1; t-\tau) f(x_2; t-\tau)\right) \\
&+ U^0_{12}(\tau) L'_{12} f_1(x_1; t) f_1(x_2; t).
\end{aligned}$$

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

$$\begin{aligned}
\partial_t f(x_1) - L^0_1 f(x_1) = &\int \mathrm{d}x_2 L'_{12} \left(f(x_1) f(x_2) + U^0_{12}(t) g_2(x_1, x_2; 0)\right) \\
&+ \int \mathrm{d}x_2 L'_{12} \int_0^t \mathrm{d}\tau U^0_{12}(\tau) L'_{12} f(x_1; t-\tau) f(x_2; t-\tau).
\end{aligned} \tag{1.97}$$

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 (1.92) we see that is 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 lenght 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)

$$l_C \ll l_{\mathrm{mfp}} \ll l_H \qquad \text{or} \qquad t_C \ll t_R \ll t_H \tag{1.98}$$

Note that the first assumption relies on

$$\frac{l_C}{l_{\mathrm{mfp}}} = \mathcal{O}(\lambda^2) \qquad \frac{t_C}{t_R} = \mathcal{O}(\lambda^2), \tag{1.99}$$

whereas the second tells us the variations of macroscopic variables are of a different length-scale then 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 $t_H \to \infty$). Since we are interested in timescale $t \gg t_C$ then the second term in the eq. (1.97),

$$U^0_{12}(t) g_2(x_1, x_2; 0) = g_2(\mathbf{q}_1 - \mathbf{v}_1 t, \mathbf{q}_2 - \mathbf{v}_2 t, \mathbf{v}_1, \mathbf{v}_2; t) \approx 0, \tag{1.100}$$

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

Let us now analyze the last term of (1.97)

$$\int \mathrm{d}x_2 L'_{12} \int_0^t \mathrm{d}\tau U^0_{12}(\tau) L'_{12} f(x_1; t-\tau) f(x_2; t-\tau). \tag{1.101}$$

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

$$f(x_1; t-\tau) \approx U^0_{12}(-\tau) f(x_1, t). \tag{1.102}$$

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

$$\begin{aligned} L'_{12} U^0_{12}(\tau) L'_{12} U^0_{12}(-\tau) &= m^{-2} \left(\nabla_1 V(\mathbf{q}_{12})\right) \cdot \partial_{12}\, U^0_{12}(\tau) \left(\nabla_1 V(\mathbf{q}_{12})\right) \cdot \partial_{12} U^0_{12}(-\tau) \\ &= m^{-2} \left(\nabla_1 V(\mathbf{q}_{12})\right) \cdot \partial_{12} \, \left(\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)\right) \cdot U^0_{12}(\tau) \partial_{12} U^0_{12}(-\tau) \\ &= m^{-2} \partial_{12} \cdot \left(\nabla_1 V(\mathbf{q}_{12})\right) \left(\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)\right) \cdot U^0_{12}(\tau) \partial_{12} U^0_{12}(-\tau). \end{aligned} \tag{1.103}$$

Let us look at the last factor

$$U^0_{12}(\tau) \partial_{12} U^0_{12}(-\tau) = \partial_{12} + \tau \nabla_{12}. \tag{1.104}$$

Therefore

$$L'_{12} U^0_{12}(\tau) L'_{12} U^0_{12}(-\tau) = m^{-2} \partial_{12} \cdot \left(\nabla_1 V(\mathbf{q}_{12})\right) \left(\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)\right) \cdot \left(\partial_{12} + \tau \nabla_{12}\right). \tag{1.105}$$

The memory term of the Master equation is then

$$m^{-2} \int \mathrm{d}x_2 \int_0^t \mathrm{d}\tau \partial_{12} \cdot \left(\nabla_1 V(\mathbf{q}_{12})\right) \left(\nabla_1 V(\mathbf{q}_{12} - \mathbf{v}_{12}\tau)\right) \cdot \left(\partial_{12} + \tau \nabla_{12}\right) f(x_1; t) f(x_2; t). \tag{1.106}$$

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

$$m^{-2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}_2 \int_0^t \mathrm{d}\tau \partial_{12}\cdot\left(\nabla_1 V(\mathbf{r})\right)\left(\nabla_1 V(\mathbf{r}-\mathbf{v}_{12}\tau)\right)\cdot\left(\partial_{12}+\tau\nabla_{12}\right)f(\mathbf{q}_1,\mathbf{v}_1;t)f(\mathbf{q}_1-\mathbf{r},\mathbf{v}_2;t). \tag{1.107}$$

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 $t_C/t_R l_{\mathrm{mfp}}/l_H \sim \lambda^2\lambda$ 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

$$m^{-2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}_2 \int_0^\infty \mathrm{d}\tau \partial_{12}\cdot\left(\nabla_1 V(\mathbf{r})\right)\left(\nabla_1 V(\mathbf{r}-\mathbf{v}_{12}\tau)\right)\cdot\partial_{12}f(\mathbf{q}_1,\mathbf{v}_1;t)f(\mathbf{q}_1,\mathbf{v}_2;t), \tag{1.108}$$

or introducing the Landau tensor

$$m^{-2}\int \mathrm{d}\mathbf{v}_2\,\partial_{12}\cdot\mathbf{G}(\mathbf{v}_1-\mathbf{v}_2)\cdot\partial_{12}f(\mathbf{q}_1,\mathbf{v}_1;t)f(\mathbf{q}_1,\mathbf{v}_2;t), \tag{1.109}$$

where

$$\mathbf{G}(\mathbf{g}) = \int \mathrm{d}\mathbf{r}\int_0^\infty \mathrm{d}\tau\ \left(\nabla_1 V(\mathbf{r})\right)\left(\nabla_1 V(\mathbf{r}-\mathbf{g}\tau)\right). \tag{1.110}$$

Explicit computations give

$$G(\mathbf{g}) = 8\pi^4\int \mathrm{d}\mathbf{k}\delta(\mathbf{k}\cdot\mathbf{g})\tilde{V}^2(k)\mathbf{k}\mathbf{k}, \tag{1.111}$$

or

$$\mathbf{G}_{rs}(\mathbf{g}) = \left(\delta_{rs}-\frac{g_r g_s}{g^2}\right)\frac{B}{g}, \qquad B = 8\pi^5\int_0^\infty \mathrm{d}k\,\tilde{V}^2(k)k^3. \tag{1.112}$$

The Landau equation is then

$$\partial_t f(x_1) - L_1^0 f(x_1) = \mathcal{V}(f,f) + \mathcal{K}^{\mathrm{L}}(f,f), \tag{1.113}$$

where

$$\mathcal{K}^{\mathrm{L}}(f,f) = m^{-2}\int \mathrm{d}\mathbf{v}_2\,\partial_{12}\cdot\mathbf{G}(\mathbf{v}_1-\mathbf{v}_2)\cdot\partial_{12}f(\mathbf{q}_1,\mathbf{v}_1;t)f(\mathbf{q}_1,\mathbf{v}_2;t), \tag{1.114}$$

1.4.4 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.

1.5 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

$$\gamma = n l_C^3 \ll 1. \tag{1.115}$$

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

$$L_j^0 = \mathcal{O}(\gamma^0), \qquad L_{jn} = \gamma'. \tag{1.116}$$

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

$$f(x_1) = \mathcal{O}(\gamma), \qquad g_n(x_1, \ldots, x_n) = \mathcal{O}(\gamma^n). \tag{1.117}$$

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

$$\partial_t f(x_1; t) = \int \mathrm{d}x_2 L'_{12} g_2(x_1, x_2; t), \tag{1.118}$$

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

$$\left(\partial_t - L_1^0 - L_2^0 - L'_{12}\right) g_2(x_1, x_2; t) = L'_{12} f(x_1; t) f(x_2; t). \tag{1.119}$$

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

$$\left(\partial_t - L_1^0 - L_2^0 - L'_{12}\right) Y_{12}(t), \tag{1.120}$$

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

$$\partial_t \phi(\mathbf{v}_1; t) = n \int_0^t \mathrm{d}\tau \int \mathrm{d}\mathbf{q}_2 \mathbf{v}_2 L'_{12} Y_{12}(\tau) L'_{12} \phi(\mathbf{v}_1; t-\tau) \phi(\mathbf{v}_2; t-\tau) \tag{1.121}$$

$$+ \frac{1}{n} \int \mathrm{d}\mathbf{q}_2 d\mathbf{v}_2 L'_{12} Y_{12}(t) g_2(\mathbf{q}_1 - \mathbf{q}_2, \mathbf{v}_1, \mathbf{v}_2; 0). \tag{1.122}$$

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

$$\partial_t \phi(\mathbf{v}_1; t) = n \int \mathrm{d}\mathbf{v}_2 J(\mathbf{v}_1, \mathbf{v}_2), \tag{1.123}$$

where

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int \mathrm{d}\mathbf{r} \int_0^\infty \mathrm{d}\tau L'_{12} Y_{12} L'_{12} \phi(\mathbf{v}_1; t) \phi(\mathbf{v}_2; t). \tag{1.124}$$

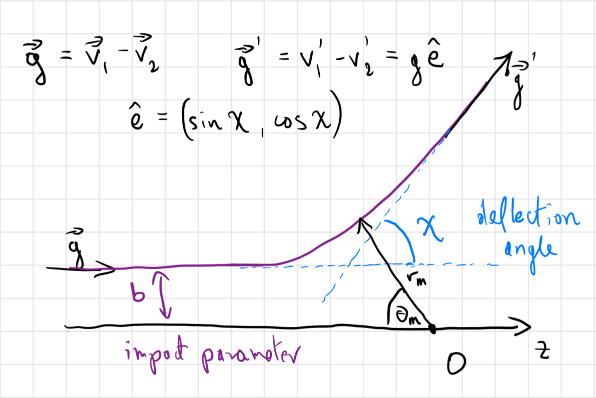


Figure 1.4: ...

It can be shown that

$$J(\mathbf{v}_1, \mathbf{v}_2) = \int_0^{2\pi} \mathrm{d}\phi \int_0^\infty \mathrm{d}b\, bg \left(\phi(\mathbf{v}_1'; t)\phi(\mathbf{v}_2'; t) - \phi(\mathbf{v}_1; t)\phi(\mathbf{v}_2; t)\right), \tag{1.125}$$

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

$$\mathbf{v}_1' + \mathbf{v}_2' = \mathbf{v}_1 + \mathbf{v}_2, \qquad |\mathbf{v}_1'|^2 + |\mathbf{v}_2'|^2 = |\mathbf{v}_1|^2 + |\mathbf{v}_2|^2. \tag{1.126}$$

The geometry of the scattering process is shown in fig. 1.4.

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

$$\left(\partial_t - \mathbf{v} \cdot \nabla\right) \phi(\mathbf{v}; t) = \mathcal{V}(f, f) + \mathcal{K}^{\mathrm{B}}(f, f) \tag{1.127}$$

where

$$\mathcal{K}^{\mathrm{B}}(f, f) = \int \mathrm{d}\mathbf{v}_2 \int_0^{2\pi} \mathrm{d}\phi \int_0^\infty \mathrm{d}b\, bg \left(f(\mathbf{q}, \mathbf{v}_1'; t) f(\mathbf{q}, \mathbf{v}_2'; t) - f(\mathbf{q}, \mathbf{v}_1; t) f(\mathbf{q}, \mathbf{v}_2; t)\right). \tag{1.128}$$

1.5.1 Entropy and stationary states

Consider a homogeneous system and define the following function

$$s(t) = -k_B \int \mathrm{d}\mathbf{v} \phi(\mathbf{v}; t) \ln\left(n\phi(\mathbf{v}; t)\right) + b. \tag{1.129}$$

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

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

We first use the symmetry upon exchanging $\mathbf{v}_1$ with $\mathbf{v}_2$ and later symmetry with exchanging initial with final velocities. Thus $\dot{s}(t) \geqslant 0$ 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

$$\ln \frac{\phi^0(\mathbf{v}_1')\phi^0(\mathbf{v}_2')}{\phi^0(\mathbf{v}_1)\phi^0(\mathbf{v}_2)} = 1, \tag{1.130}$$

which is satisfied by the Maxwell distribution

$$\phi^0(\mathbf{v}) = c \exp\left[-a|\mathbf{v}-\mathbf{u}|^2\right], \tag{1.131}$$

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

1.5.2 Collision invariants

Let us denote

$$\langle\psi\rangle = \int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{v}\psi(\mathbf{v})f(\mathbf{q},\mathbf{v};t). \tag{1.132}$$

The collision invariant is then a function for which

$$\int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{v}\psi_n(\mathbf{q},\mathbf{v})\mathcal{K}\left(f,f\right) = 0, \tag{1.133}$$

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

$$\begin{aligned}&\int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{v}\psi_n(\mathbf{q},\mathbf{v})\mathcal{K}\left(f,f\right) = \\ &= 2\pi \int \mathrm{d}\mathbf{q} \int \mathrm{d}b\, b \int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\, g\psi(\mathbf{q},\mathbf{v}_1)\left(f(\mathbf{q},\mathbf{v}_1';t)f(\mathbf{q},\mathbf{v}_2';t) - f(\mathbf{q},\mathbf{v}_1;t)f(\mathbf{q},\mathbf{v}_2;t)\right).\end{aligned} \tag{1.134}$$

Consider now the double integral over the velocities

$$\begin{aligned}&\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\, g\psi(\mathbf{q},\mathbf{v}_1)\left[f(\mathbf{q},\mathbf{v}_1';t)f(\mathbf{q},\mathbf{v}_2';t) - f(\mathbf{q},\mathbf{v}_1;t)f(\mathbf{q},\mathbf{v}_2;t)\right] = \\ &= \frac{1}{4}\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\, g\left[\psi(\mathbf{q},\mathbf{v}_1) + \psi(\mathbf{q},\mathbf{v}_2) - \psi(\mathbf{q},\mathbf{v}_1') - \psi(\mathbf{q},\mathbf{v}_1')\right] \times \\ &\times \left[f(\mathbf{q},\mathbf{v}_1';t)f(\mathbf{q},\mathbf{v}_2';t) - f(\mathbf{q},\mathbf{v}_1;t)f(\mathbf{q},\mathbf{v}_2;t)\right]\end{aligned} \tag{1.135}$$

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 velocty, $\psi_n(\mathbf{q},\mathbf{v}) = v_n\psi(\mathbf{q})$ 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.

1.5.3 Hydrodynamic quantities

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

$$B(\mathbf{x},t) = \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{q}\, \beta(\mathbf{v})\delta(\mathbf{x}-\mathbf{q})f(\mathbf{q},\mathbf{v};t). \tag{1.136}$$

This can be interpreted as

$$B(\mathbf{x},t)\int \mathrm{d}\mathbf{v}\,\beta(\mathbf{v})f(\mathbf{v};\mathbf{x},t) \tag{1.137}$$

where we introduce a *local* one-body function

$$f(\mathbf{v};\mathbf{x},t)=\int \mathrm{d}\mathbf{q}\,\delta(\mathbf{x}-\mathbf{q})f(\mathbf{q},\mathbf{v};t). \tag{1.138}$$

Note that know 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 $f(\mathbf{v};\mathbf{x},t)$

$$\left(\partial_t+\mathbf{v}\cdot\nabla\right)f(\mathbf{v};\mathbf{x},t)=\mathcal{K}\left\{f,f\right\}. \tag{1.139}$$

We define the following hydrodynamic fields

- Mass density
$$\rho(\mathbf{x},t)=m\int \mathrm{d}\mathbf{v}f(\mathbf{v};\mathbf{x},t) \tag{1.140}$$
- Momentum density
$$\rho(\mathbf{x},t)\mathbf{u}(\mathbf{x},t)=m\int \mathrm{d}\mathbf{v}\,\mathbf{v}f(\mathbf{v};x,t), \tag{1.141}$$
- (Internal) energy density
$$\rho(\mathbf{x},t)e(\mathbf{x},t)=\frac{1}{2}m\int \mathrm{d}\mathbf{v}|\mathbf{v}-\mathbf{u}|^2f(\mathbf{v};\mathbf{x},t). \tag{1.142}$$

1.5.4 Hydrodynamic equations

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

$$\partial_t\rho(\mathbf{x},t)=-\nabla\cdot\left(\rho\mathbf{u}\right), \tag{1.143}$$

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

$$\begin{aligned}\partial_t\left(\rho u_n\right)&=-m\int \mathrm{d}\mathbf{v}v_nv_s\nabla_sf(\mathbf{v};\mathbf{x},t)=-m\nabla_s\int \mathrm{d}\mathbf{v}v_nv_sf(\mathbf{v};\mathbf{x},t)\\&=-\nabla_s\int \mathrm{d}\mathbf{v}\left(mu_nu_s+m(v_n-u_n)(v_s-u_s)\right)f(\mathbf{v};\mathbf{x},t)\\&=-\nabla_s\left(\rho u_nu_s+P\delta_{ns}+\pi_{ns}\right),\end{aligned} \tag{1.144}$$

where we introduced the hydrostatic pressure

$$P(\mathbf{x},t)=\frac{1}{3}m\int \mathrm{d}\mathbf{v}|\mathbf{v}-\mathbf{u}|^2f(\mathbf{v};\mathbf{x},t), \tag{1.145}$$

and the dissipative pressure tensor is

$$\pi_{rs}(\mathbf{x},t)=m\int \mathrm{d}\mathbf{v}(v_r-u_r)(v_s-u_s)f(\mathbf{v};\mathbf{x},t)-\delta_{rs}P(\mathbf{x},t). \tag{1.146}$$

Note the ideal gas relations

$$P(\mathbf{x},t)=n(x,t)T(\mathbf{x},t),\qquad \rho(\mathbf{x},t)e(\mathbf{x},t)=\frac{3}{2}n(\mathbf{x},t)T(\mathbf{x},t). \tag{1.147}$$

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

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

$$\partial_t \rho e = -\nabla \cdot (\rho e \mathbf{u} + \mathbf{q}) - P \nabla \cdot u - \pi : \nabla \mathbf{u}. \tag{1.148}$$

with the heat flux

$$q_r(\mathbf{x}, t) = \frac{1}{2} m \int \mathrm{d}\mathbf{v} (v_r - u_r) |\mathbf{v} - \mathbf{u}|^2 f(\mathbf{v}; \mathbf{x}, t). \tag{1.149}$$

1.5.5 Exercises

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

$$\mathbf{v}_1' = \frac{1}{2} (\mathbf{v}_1 + \mathbf{v}_2 + g\mathbf{e}) \, , \qquad \mathbf{v}_2' = \frac{1}{2} (\mathbf{v}_1 + \mathbf{v}_2 - g\mathbf{e}) \, , \tag{1.150}$$

   where **e** is an unit vector in an arbitrary direction.

2. Derive the balance equation for the energy.

3. Write down the linearized Boltzmann equation

1.6 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

$$H_{\text{2body}} = \frac{m\mathbf{v}_1^2}{2} + \frac{m\mathbf{v}_2^2}{2} + V(\mathbf{q}_1 - \mathbf{q}_2). \tag{1.151}$$

We introduce the center of mass and relative coordinates and velocities

$$\begin{aligned} \mathbf{Q}_G &= \frac{\mathbf{q}_1 + \mathbf{q}_2}{2}, \qquad & \mathbf{r} &= \mathbf{q}_1 - \mathbf{q}_2, \\ \mathbf{V}_G &= \frac{\mathbf{v}_1 + \mathbf{v}_2}{2}, \qquad & \mathbf{g} &= \mathbf{v}_1 - \mathbf{v}_2. \end{aligned} \tag{1.152}$$

The Hamiltonian becomes

$$H_{\text{2body}} = \frac{m|\mathbf{V}_G|^2}{2} + \frac{\mu|\mathbf{g}|^2}{2} + V(|\mathbf{r}|), \tag{1.153}$$

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

$$E = \frac{\mu}{2}\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2\right] + V(r) = \text{constant}, \tag{1.154}$$

wheres the angular momentum L is

$$L = \mu r^2 \left(\frac{d\theta}{dt}\right) = \text{constant}, \tag{1.155}$$

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)

$$E = \frac{\mu g_0^2}{2}, \qquad L = \mu g_0 b, \qquad g_0 = |\mathbf{g}_0|. \tag{1.156}$$

From expressions for the two conservation laws we find

$$\frac{dr}{dt} = \pm\left[\frac{2}{\mu}\left(E - V(r) - \frac{L^2}{2\mu r^2}\right)\right]^{1/2}. \tag{1.157}$$

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

$$\mathrm{d}\theta = \frac{L}{\mu r^2 (dr/dt)}\mathrm{d}r, \tag{1.158}$$

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

$$E - V(r_{\min}) - \frac{L^2}{2\mu r_{\min}^2} = 0. \tag{1.159}$$

Integrating the differential trajectory we obtain

$$\theta = -L \int_{\infty}^{r_{\min}} \frac{\mathrm{d}r}{\mu r^2 \left[\frac{2}{\mu}\left(E - V(r) - \frac{L^2}{2\mu r^2}\right)\right]^{1/2}}. \tag{1.160}$$

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

$$\chi = |\pi - 2\theta|. \tag{1.161}$$

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

1.6.1 Cross section

1.6.2 Exercise

1. Compute the scattering cross-section for the hard-sphere model (see Balescu eq. (7.45))

1.A Hamiltonian dynamics

We recall here basic informations on the Hamiltonian dynamics. The equations of motion are The Hamiltonian determines the law of evolution. These are Hamilton's equations of motion

$$\frac{dq_j(t)}{dt} = \{q_j, H\} = \frac{\partial H(q,p)}{\partial p_j}, \qquad \frac{dp_j(t)}{dt} = \{p_j, H\} = -\frac{\partial H(q,p)}{\partial q_j} \tag{1.162}$$

with Poisson bracket

$$\{f, g\} = \sum_{j=1}^{F} \left(\frac{\partial f}{\partial q_j} \frac{\partial g}{\partial p_j} - \frac{\partial f}{\partial p_j} \frac{\partial g}{\partial q_j} \right) \tag{1.163}$$

Straightforward computations give

$$\{q_j, p_k\} = \delta_{j,k}, \qquad \{q_j, q_k\} = \{p_j, p_k\} = 0. \tag{1.164}$$

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

$$\{q'_j, p'_k\} = \delta_{j,k}, \qquad \{q'_j, q'_k\} = \{p'_j, p'_k\} = 0. \tag{1.165}$$

Important results of Hamiltonian dynamics that we use are: time evolution is a canonical transformation and volume element of the phase space ($\mathrm{d}q\mathrm{d}p$) is invariant under any canonical transformation.

Chapter 2

Quantum dynamics