I. INTRODUCTION – LENGTH AND TIME SCALES

Kinetic theory: reduced (probabilistic) description for a system of $N \gg 1$ interacting ("colliding") particles derived from their individual equations of motion. Avogadro's number 6×10^{23} particles per mole (one gram of hydrogen).

Timescale *of* collisions $\tau_c \ll$ timescale between collisions $\tau \ll$ hydrodynamic timescale T.

We will find later that the typical particle speed is the sound speed c_s.

Interaction diameter $d = c_s\tau_c \ll$ mean free path $\lambda_{mfp} = c_s\tau \ll$ hydrodynamic lengthscale $L = c_sT$.

Picture with straight line segments, length λ_{mfp}, sharp bends of radius d. (Boltzmann regime, contrast with smoothly curving particle paths in the Vlasov regime for charged particles with long-range Coulomb interactions)

The Boltzmann equation describes the Boltzmann–Grad limit: number density $n \to \infty$, $d \to 0$ with $nd^2 = 1/\lambda_{mfp}$ fixed.

Often useful to think of spheres with diameter d. One unit volume contains n cylinders of volume $(\pi/4)d^2\lambda_{mfp}$.

The Boltzmann–Grad limit implies that the system is dilute ($nd^3 \to 0$).

We will start with a reversible Hamiltonian system, and arrive at the irreversible Boltzmann and Navier–Stokes equations.

The Boltzmann equation is *not* a mean-field theory. The Vlasov equation *is* a mean-field theory for a different parameter regime with $nd^3 \gg 1$, so weak long-range interactions. The Vlasov equation is time-reversible.

We want to connect three different levels of description:

- N-particle Hamiltonian system, 6N ODEs for $\mathbf{p}_i$, $\mathbf{q}_i$ for $i = 1, \ldots, N$
- Boltzmann equation for the 1-particle distribution $f_1(\mathbf{x}, \mathbf{v}, t)$, one integro-differential equation in 6D
- Navier–Stokes equations for $\rho(\mathbf{x}, t)$, $\mathbf{u}(\mathbf{x}, t)$, $T(\mathbf{x}, t)$, five PDEs in 3D

For generic initial conditions, first the N-particle equations are needed, then the Boltzmann equation, and finally the Navier–Stokes equations, become sufficient on successively longer timescales.

Some dates: Boltzmann equation 1872, Chapman–Enskog expansion leading to the Navier–Stokes equations 1916–17, Bogoliubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy 1935 to 1949. The BBGKY hierarchy was initially developed as a step towards a kinetic theory of liquids.

Much of the rigorous mathematical work considers hard spheres. Lanford's 1975 proof shows that the Boltzmann equation describes hard sphere systems for $t \lesssim \tau/5$ (so 20% of particles have collided). The current state of the art is described in the book by Gallagher *et al.* (2014).

Using hard spheres avoids many technical difficulties with long-range interactions and small angle collisions (see later). However, the configuration spaces for hard sphere systems must be restricted to regions where particles do not overlap. This brings in extra boundary terms for the integrals that appear later. These play the same role as the contributions from an interaction potential.

We will consider particles in a general potential, later specialised to pair-wise interactions, to allow for Coulomb and gravitational interactions later in the course.

Atoms are often modelled using the Lennard-Jones potential (e.g. molecular dynamics simulations) with an r^{-12} repulsive potential at short range. So-called "Maxwell molecules" with an r^{-5} repulsive force are theoretically convenient (see later ...) but this potential is a bit too soft.

Reality is somewhere between Maxwell molecules and hard spheres.

II. N-PARTICLE HAMILTONIAN MECHANICS

Consider a system of N particles, position $\mathbf{x}_i$ and velocity $\mathbf{v}_i$ for $i = 1, \ldots, N$, moving in a potential $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$. Introducing canonical coordinates $\mathbf{p}_i = m\mathbf{v}_i$ and $\mathbf{q}_i = \mathbf{x}_i$, and the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \Phi(\mathbf{q}_1, \ldots, \mathbf{q}_N) \tag{1}$$

allows us to express the equations of motion as Hamilton's equations

$$\frac{\mathrm{d}\mathbf{q}_i}{\mathrm{d}t} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}, \quad \frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i}. \tag{2}$$

We can rewrite these in Poisson bracket form as

$$\frac{\mathrm{d}\mathbf{q}_i}{\mathrm{d}t} = \{\mathbf{q}_i, \mathcal{H}\}, \quad \frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} = \{\mathbf{p}_i, \mathcal{H}\}, \tag{3}$$

or more generally for any $\mathcal{F}(\mathbf{q}, \mathbf{p}, t)$ with $\mathbf{p} = (\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and $\mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$,

$$\frac{\mathrm{d}\mathcal{F}}{\mathrm{d}t} = \frac{\partial \mathcal{F}}{\partial t} + \{\mathcal{F}, \mathcal{H}\}, \tag{4}$$

where (note the sign convention)

$$\{\mathcal{A}, \mathcal{B}\} = \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \mathbf{q}_i} \cdot \frac{\partial \mathcal{B}}{\partial \mathbf{p}_i} - \frac{\partial \mathcal{B}}{\partial \mathbf{q}_i} \cdot \frac{\partial \mathcal{A}}{\partial \mathbf{p}_i}. \tag{5}$$

The first term $\partial\mathcal{F}/\partial t$ in (4) accounts for any explicit t-dependence of $\mathcal{F}$, e.g. the function $\mathcal{F}(\mathbf{p}, \mathbf{q}, t) = t$.

III. LIOUVILLE'S THEOREM AND THE N-PARTICLE DISTRIBUTION

Properties we can/want to measure can expressed as a limited set of observables $\mathcal{O}(\mathbf{p}, \mathbf{q})$, e.g. fluid density, velocity, temperature ... (an advantage of N-particle computer simulations is that one can get $\mathbf{p}$ and $\mathbf{q}$).

Actual measurements take place as some kind of average over a finite time interval, and over a finite spatial volume. However, taking averages over small space/time regions, denoted by $[\cdots]$, has the annoying property that the average of an average is different from taking an average once, so $[[f]] \neq [f]$ for a typical function f.

Instead, we consider an average, at a single point, over an ensemble of many such N-particle systems, each reproducing the same value for the observable $\mathcal{O}$, but differing in fine detail.

We represent such an ensemble by a density $\rho(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots \mathbf{q}_N, t)$ in $6N$-dimensional phase space.

We use ρ to define ensemble averages of any function $\mathcal{O}(\mathbf{p},\mathbf{q})$,

$$\langle\mathcal{O}\rangle = \int \mathrm{d}V_1 \ldots \mathrm{d}V_N \, \rho(\mathbf{p},\mathbf{q},t)\mathcal{O}(\mathbf{p},\mathbf{q}), \tag{6}$$

where $\mathrm{d}V_i = \mathrm{d}\mathbf{q}_i\mathrm{d}\mathbf{p}_i$ is the 6-dimensional volume element associated with particle i.

Two ways to look at phase space:

$$(\mathbf{p}_1,\mathbf{q}_1,\mathbf{p}_2,\mathbf{q}_2,\ldots) \qquad\qquad (\mathbf{p},\mathbf{q})$$

Liouville's theorem says that the evolution corresponds to a volume-preserving flow in phase space.

Consider a fixed volume Ω in phase space, with boundary $\partial\Omega$. The fraction of the particles inside Ω is

$$n_\Omega = \int_\Omega \mathrm{d}V \rho(\mathbf{p},\mathbf{q},t), \tag{7}$$

where $\mathrm{d}V = \mathrm{d}V_1 \ldots \mathrm{d}V_N$. Since Ω is fixed,

$$\frac{\mathrm{d}n_\Omega}{\mathrm{d}t} = \int_\Omega \mathrm{d}V \frac{\partial\rho}{\partial t}. \tag{8}$$

Alternatively, the rate of change of n_Ω must equal the flux of particles crossing the boundary $\partial\Omega$,

$$\frac{\mathrm{d}n_\Omega}{\mathrm{d}t} = -\int_{\partial\Omega} \mathrm{d}S(\hat{\mathbf{n}}\cdot\dot{\mathbf{z}})\rho, \tag{9}$$

where $\dot{\mathbf{z}} = (\dot{\mathbf{p}},\dot{\mathbf{q}})$ and $\hat{\mathbf{n}}$ is the unit outward normal on $\partial\Omega$. Applying the divegence theorem,

$$\frac{\mathrm{d}n_\Omega}{\mathrm{d}t} = -\int_\Omega \mathrm{d}V \nabla_{\mathbf{z}}\cdot(\dot{\mathbf{z}}\rho). \tag{10}$$

Since these two expressions must coincide for any fixed volume Ω,

$$\frac{\partial\rho}{\partial t} + \nabla_{\mathbf{z}}\cdot(\dot{\mathbf{z}}\rho) = 0. \tag{11}$$

Writing the $\dot{\mathbf{z}}$ notation out in full,

$$\begin{aligned}
\frac{\partial\rho}{\partial t} + \sum_{i=1}^{N}\left[\frac{\partial}{\partial\mathbf{q}_i}\cdot(\dot{\mathbf{q}}_i\rho) + \frac{\partial}{\partial\mathbf{p}_i}\cdot(\dot{\mathbf{p}}_i\rho)\right] &= 0,\\
\frac{\partial\rho}{\partial t} + \sum_{i=1}^{N}\left[\frac{\partial}{\partial\mathbf{q}_i}\cdot\left(\frac{\partial\mathcal{H}}{\partial\mathbf{p}_i}\rho\right) + \frac{\partial}{\partial\mathbf{p}_i}\cdot\left(-\frac{\partial\mathcal{H}}{\partial\mathbf{q}_i}\rho\right)\right] &= 0,\\
\frac{\partial\rho}{\partial t} + \sum_{i=1}^{N}\left[\frac{\partial\mathcal{H}}{\partial\mathbf{p}_i}\cdot\frac{\partial\rho}{\partial\mathbf{q}_i} - \frac{\partial\mathcal{H}}{\partial\mathbf{q}_i}\cdot\frac{\partial\rho}{\partial\mathbf{p}_i} + \rho\left(\frac{\partial}{\partial\mathbf{q}_i}\cdot\frac{\partial\mathcal{H}}{\partial\mathbf{p}_i} - \frac{\partial}{\partial\mathbf{p}_i}\cdot\frac{\partial\mathcal{H}}{\partial\mathbf{q}_i}\right)\right] &= 0,\\
\frac{\partial\rho}{\partial t} + \{\rho,\mathcal{H}\} &= 0.
\end{aligned}$$

In other words, along any trajectory in phase space:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \{\rho,\mathcal{H}\} = 0.$$

This is closely linked to reversibility: phase space volumes neither expand nor contract as they evolve.

The precise statement of reversibility is that if $\rho(\mathbf{p},\mathbf{q},t)$ is a solution of Liouville's equation, so is $\rho(-\mathbf{p},\mathbf{q},-t)$.

Exercise: derive the classical analogue of Ehrenfest's theorem for the expectation of an observable $\mathcal{O}(\mathbf{p},\mathbf{q})$ with no explicit time-dependence:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathcal{O}\rangle = \langle\{\mathcal{O},\mathcal{H}\}\rangle. \tag{12}$$

IV. REDUCED s-PARTICLE DISTRIBUTION FUNCTIONS

The N-particle distribution $\rho(\mathbf{q}_1,\ldots,\mathbf{q}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N,t)$ offers no simplification (rather the opposite ...) compared with our original system of $6N$ ODEs. We can recover the ODE system by taking ρ to be a product of δ-functions corresponding to the initial conditions,

$$\rho(\mathbf{p},\mathbf{q},t=0) = \delta^3(\mathbf{p}_1-\mathbf{p}_1^{(0)})\delta^3(\mathbf{q}_1-\mathbf{q}_1^{(0)})\cdots\delta^3(\mathbf{p}_N-\mathbf{p}_N^{(0)})\delta^3(\mathbf{q}_N-\mathbf{q}_N^{(0)}). \tag{13}$$

Assuming ρ is normalised to be a probability density function,

$$\int \mathrm{d}V_1\ldots\mathrm{d}V_N\,\rho(\mathbf{p},\mathbf{q},t) = 1, \tag{14}$$

we can define normalised reduced or marginal PDFs in the usual way as

$$\rho_1(\mathbf{p}_1,\mathbf{q}_1,t) = \int \mathrm{d}V_2\ldots\mathrm{d}V_N\,\rho(\mathbf{p}_1,\ldots,\mathbf{p}_N,\mathbf{q}_1,\ldots,\mathbf{q}_N,t), \tag{15a}$$

$$\rho_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2) = \int \mathrm{d}V_3\ldots\mathrm{d}V_N\,\rho(\mathbf{p}_1,\ldots,\mathbf{p}_N,\mathbf{q}_1,\ldots,\mathbf{q}_N,t), \tag{15b}$$

$$\vdots$$

$$\rho_s(\mathbf{p}_1,\ldots,\mathbf{p}_s,\mathbf{q}_1,\ldots,\mathbf{q}_s) = \int \mathrm{d}V_{s+1}\ldots\mathrm{d}V_N\,\rho(\mathbf{p}_1,\ldots,\mathbf{p}_N,\mathbf{q}_1,\ldots,\mathbf{q}_N,t). \tag{15c}$$

These functions are all symmetric under permutations of their arguments if the particles are indistinguishable, *e.g.*

$$\rho_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t) = \rho_2(\mathbf{p}_2,\mathbf{p}_1,\mathbf{q}_2,\mathbf{q}_1,t) \tag{16}$$

on swapping particle 1 with particle 2.

In kinetic theory it is more common to work with the s-particle distribution functions f_s. The first of these is defined by

$$\begin{aligned} f_1(\mathbf{p}',\mathbf{q}',t) &= \left\langle \sum_{i=1}^{N} \delta^3(\mathbf{p}'-\mathbf{p}_i)\delta^3(\mathbf{q}'-\mathbf{q}_i) \right\rangle, \\ &= N\int \mathrm{d}V_2\ldots\mathrm{d}V_N\,\rho(\mathbf{p}',\mathbf{p}_2,\ldots,\mathbf{p}_N,\mathbf{q}',\mathbf{q}_2,\ldots,\mathbf{q}_N,t) = N\rho_1(\mathbf{p}',\mathbf{q}',t), \end{aligned}$$

where the factor of N comes from assuming that the particles are indistinguishable. We may thus choose any one of the N pairs $\mathbf{p}_i,\mathbf{q}_i$ to become $\mathbf{p}',\mathbf{q}'$. In general, we define

$$f_s(\mathbf{p}_1,\ldots,\mathbf{p}_s,\mathbf{q}_1,\ldots,\mathbf{q}_s,t) = \frac{N!}{(N-s)!}\,\rho_s(\mathbf{p}_1,\ldots,\mathbf{p}_s,\mathbf{q}_1,\ldots,\mathbf{q}_s,t), \tag{17}$$

since we can pick the first "slot" in N different ways, the second slot in $N-1$ ways, and so on. In other words, there are $N!/(N-s)!$ different ρ that give the same f_s.

This is convenient for two reasons. Firstly, the BBGKY hierarchy for the ρ_s that we derive below will have explicit factors of $N-s$ that are absent in the BBGKY hierarchy for the f_s. Secondly, when particles are uncorrelated we can factor the f_s for $s\geq 2$ into a product of the f_1 distributions.

V. BBGKY HIERARCHY

The evolution equations for the ρ_s and f_s form the Bogoliubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy, published independently between 1935 and 1949.

We assume a 2-body interaction potential, leading towards the idea of a "dilute" monatomic gas, for which only 2-body interactions are significant (as $nd^3 \ll 1$) and consider Hamiltonians of the form

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{1\le i<j\le N} \phi(|\mathbf{q}_i - \mathbf{q}_j|). \tag{18}$$

The ordered sum over $1 \le i < j \le N$ ensures that each interaction between a given pair of particles is included only once.

To compute the evolution of f_s it is convenient to decompose the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}', \tag{19}$$

where the first two terms contain only contributions from particles $1, \ldots, s$ and $s+1, \ldots, N$ respectively:

$$\mathcal{H}_s = \sum_{i=1}^{s} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{1\le i<j\le s} \phi(|\mathbf{q}_i - \mathbf{q}_j|), \tag{20}$$

$$\mathcal{H}_{N-s} = \sum_{i=s+1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{s+1\le i<j\le N} \phi(|\mathbf{q}_i - \mathbf{q}_j|). \tag{21}$$

The two groups of particles are only coupled through the interaction potential

$$\mathcal{H}' = \sum_{i=1}^{s} \sum_{j=s+1}^{N} \phi(|\mathbf{q}_i - \mathbf{q}_j|). \tag{22}$$

Differentiating the definition of ρ_s with respect to time gives

$$\frac{\partial \rho_s}{\partial t} = \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \, \frac{\partial \rho}{\partial t} = -\int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \, \{\rho, \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}'\}, \tag{23}$$

and we will manipulate contributions from $\mathcal{H}_s$, $\mathcal{H}_{N_s}$ and $\mathcal{H}'$ separately.

Since $\mathcal{H}_s$ is independent of the integration variables $\mathbf{p}_{s+1}, \mathbf{q}_{s+1}, \ldots, \mathbf{p}_N, \mathbf{q}_N$ in (23) we can take these integrals inside all the derivatives that define $\{\cdot,\cdot\}$,

$$\int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \, \{\rho, \mathcal{H}_s\} = \left\{ \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \, \rho, \mathcal{H}_s \right\} = \{\rho_s, \mathcal{H}_s\}. \tag{24}$$

The second contribution vanishes because the integrand is an exact divergence in $\mathbf{p}_{s+1}, \mathbf{q}_{s+1}, \ldots, \mathbf{p}_N, \mathbf{q}_N$ space:

$$\begin{aligned}
\int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \, \{\rho, \mathcal{H}_{N-s}\} &= \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{k=1}^{N} \left(\frac{\partial \rho}{\partial \mathbf{q}_k} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \mathbf{p}_k} - \frac{\partial \rho}{\partial \mathbf{p}_k} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \mathbf{q}_k} \right), \\
&= \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{i=s+1}^{N} \left(\frac{\partial \rho}{\partial \mathbf{q}_i} \cdot \frac{\mathbf{p}_i}{m} - \frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \sum_{j=1+1}^{N} \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_j|)}{\partial \mathbf{q}_i} \right), \\
&= \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{i=s+1}^{N} \left\{ \frac{\partial}{\partial \mathbf{q}_i} \cdot \left(\rho \frac{\mathbf{p}_i}{m} \right) - \frac{\partial}{\partial \mathbf{p}_i} \cdot \left(\rho \sum_{j=i+1}^{N} \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_j|)}{\partial \mathbf{q}_i} \right) \right\}, \\
&= 0.
\end{aligned}$$

The remaining interaction term involving $\mathcal{H}'$ is

$$\begin{aligned}
&\int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{k=1}^{N} \left(\frac{\partial \rho}{\partial \mathbf{p}_k} \cdot \frac{\partial \mathcal{H}'}{\partial \mathbf{q}_k} - \frac{\partial \rho}{\partial \mathbf{q}_k} \cdot \frac{\partial \mathcal{H}'}{\partial \mathbf{p}_k} \right) \\
&\qquad = \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \left(\sum_{i=1}^{s} \frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \sum_{j=s+1}^{N} \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_j|)}{\partial \mathbf{q}_i} + \sum_{j=s+1}^{N} \frac{\partial \rho}{\partial \mathbf{p}_j} \cdot \sum_{i=1}^{s} \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_j|)}{\partial \mathbf{q}_j} \right).
\end{aligned} \tag{25}$$

There is no kinetic term $\mathcal{H}'$ so $\partial\mathcal{H}'/\partial\mathbf{p}_i = 0$ for $i = 1, \ldots, N$. The second term in the integrand is an exact divergence in $\mathbf{p}_{s+1}, \ldots, \mathbf{p}_N$, and so integrates to zero. The sum over $j = s+1, \ldots, N$ in the first term contributes $N - s$ identical terms, using the permutation symmetry of ρ, giving

$$\begin{aligned}
&\int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{i=1}^{s} \frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \sum_{j=s+1}^{N} \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_j|)}{\partial \mathbf{q}_i} \\
&\qquad = (N-s) \int \mathrm{d}V_{s+1} \ldots \mathrm{d}V_N \sum_{i=1}^{s} \frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_{s+1}|)}{\partial \mathbf{q}_i}, \\
&\qquad = (N-s) \sum_{i=1}^{s} \int \mathrm{d}V_{s+1} \, \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_{s+1}|)}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \left(\int \mathrm{d}V_{s+2} \ldots \mathrm{d}V_N \, \rho \right), \\
&\qquad = (N-s) \sum_{i=1}^{s} \int \mathrm{d}V_{s+1} \, \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_{s+1}|)}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho_{s+1}}{\partial \mathbf{p}_i}.
\end{aligned}$$

on recognising the definition of ρ_{s+1}.

Assembling the three contributions gives the BBGKY hierarchy:

$$\frac{\partial \rho_s}{\partial t} + \{\rho_s, \mathcal{H}_s\} = (N-s) \sum_{i=1}^{s} \int \mathrm{d}V_{s+1} \, \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_{s+1}|)}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho_{s+1}}{\partial \mathbf{p}_i},$$

or

$$\frac{\partial f_s}{\partial t} + \{f_s, \mathcal{H}_s\} = \sum_{i=1}^{s} \int \mathrm{d}V_{s+1} \, \frac{\partial \phi(|\mathbf{q}_i - \mathbf{q}_{s+1}|)}{\partial \mathbf{q}_i} \cdot \frac{\partial f_{s+1}}{\partial \mathbf{p}_i}.$$

Each left hand side corresponds to f_s or ρ_s evolving independently of the other $N - s$ particles. The right hand sides express interactions with these other particles through the potential, creating a hierarchy in which $\partial_t f_1$ depends on f_2, $\partial_t f_2$ depends on f_3, and so on until we finally reach a closed equation for f_N (back where we started).

The hierarchy is still exact (assuming all the surface terms from integrating by parts decay etc.) and describes time-reversible evolution.

Parallel line of development using hard spheres. No interaction potentials, but the configuration space must be restricted so that particles do not overlap, which brings in boundary terms instead (Grad 1958).

Exercise. Use the first two members of the hierarchy to show that $\langle \mathcal{H} \rangle$ is conserved.

VI. BOLTZMANN EQUATION

We need an argument based on separation of timescales to justify truncating the hierarchy in the Boltzmann–Grad limit $nd^3 \to 0$ with $nd^2 = 1/\lambda_{\mathrm{mfp}}$ fixed.

Writing the second member of the hierarchy out in full gives

$$\begin{aligned}
&\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{q}_2} - \frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \right] f_2 \\
&\qquad = \int \mathrm{d}V_3 \left[\frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_3|)}{\partial \mathbf{q}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} + \frac{\partial \phi(|\mathbf{q}_2 - \mathbf{q}_3|)}{\partial \mathbf{q}_2} \cdot \frac{\partial}{\partial \mathbf{p}_2} \right] f_3, \quad (26)
\end{aligned}$$

after using $\partial\phi(|\mathbf{q}_1 - \mathbf{q}_2|)/\partial\mathbf{q}_1 = -\partial\phi(|\mathbf{q}_1 - \mathbf{q}_2|)/\partial\mathbf{q}_2$. The first member may be rewritten as

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} \right] f_1 = \int \mathrm{d}V_2 \frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) f_2. \quad (27)$$

Motivated by the symmetry of the potential term in the LHS of (26), we have added an exact divergence involving $\partial f_2/\partial \mathbf{p}_2$ that integrates to zero.

Now we estimate the magnitudes of the different terms ...

Each term in square brackets $[\cdots]$ has dimensions of inverse time (frequency).

$\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}$ and $\frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{q}_2}$ are both hydrodynamic (macroscopic) advection times, equivalent to $c_\mathrm{s}\boldsymbol{\nabla}$.

$\frac{\partial\phi}{\partial\mathbf{q}}\cdot\frac{\partial}{\partial\mathbf{p}}\sim\frac{1}{\tau_\mathrm{c}}$ is the inverse *duration* of a collision, the time over which two particles are within d of each other.

This applies to the ϕ term on the LHS of (26) where it multiples f_2.

The ϕ terms on the right hand sides have a different scale, because they act on f_{s+1} instead of f_s.

To see this, we adapt the definition of the marginal probability distributions ρ_2 and ρ_3

$$\rho_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t)=\int\mathrm{d}V_3\,\rho_3(\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3,\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,t), \tag{28}$$

which implies that

$$\frac{1}{N(N-1)}f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t)=\frac{1}{N(N-1)(N-2)}\int\mathrm{d}V_3\,f_3(\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3,\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,t). \tag{29}$$

If we compare the right-hand side of (26) with (29), we have an extra factor due to the potential that is $O(1/\tau_\mathrm{c})$ in magnitude, but only in an $O(d^3)$ volume. The right-hand side of (26) thus scales as

$$\frac{1}{\tau_\mathrm{c}}\frac{d^3}{V}(N-2)f_2\sim\frac{1}{\tau_\mathrm{c}}d^3\frac{N}{V}f_2\sim\frac{nd^3}{\tau_\mathrm{c}}f_2\sim\frac{1}{\tau}f_2, \tag{30}$$

where V is the volume of the spatial domain containing $N\gg1$ particles. The characteristic timescale of the right-hand side of (26) is thus $\tau=\tau_\mathrm{c}/(nd^3)\gg\tau_\mathrm{c}$ since $nd^3\ll1$ in the Boltzmann–Grad limit.

We can thus drop the right-hand side nvolving f_3 from the f_2 equation (26), because it is $\tau_\mathrm{c}/\tau=nd^3\ll1$ smaller than the ϕ term on the left-hand side.

The f_1 member of the hierarchy is special though having no τ_c term on th left-hand side, a single particle cannot collide with itself, so we keep the $O(1/\tau)$ f_2 "collision" term on its right-hand side.

The two-particle distribution f_2 evolves as though no other particles were present, equivalent to neglecting tertiary and higher collisions. It is tempting to replace f_2 with a product of f_1,

$$f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t)=f_1(\mathbf{p}_1,\mathbf{q}_1,t)f_1(\mathbf{p}_2,\mathbf{q}_2,t)$$

but then we would get the Vlasov equation (only valid under different scalings for weak, long-range interactions) instead of the Boltzmann equation. We need to be more clever about how we make this approximation.

Using these scalings, the f_1 equation becomes

$$\underbrace{\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right]}_{1/T}f_1=\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_\mathrm{coll}\equiv\underbrace{\int\mathrm{d}V_2\frac{\partial\phi(|\mathbf{q}_1-\mathbf{q}_2|)}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)f_2}_{(1/\tau)f_1}. \tag{31}$$

Right from the start we seem to have a mismatch of timescales. We will resolve this later in deriving hydrodynamics (for $T\gg\tau$) by showing that we can find a special type of solution for f_1 that does not evolve on the collisional timescale τ.

Similarly, the simplified equation for f_2 contains two different timescales:

$$\left[\underbrace{\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}+\frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{q}_2}}_{\text{notionally } 1/T}-\underbrace{\frac{\partial\phi(|\mathbf{q}_1-\mathbf{q}_2|)}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)}_{1/\tau_\mathrm{c}}\right]f_2=0. \tag{32}$$

We isolate the fast time scale due to the potential, depending only on $|\mathbf{q}_1-\mathbf{q}_2|$, by writing

$$\mathbf{q}_1=\mathbf{Q}-\frac{1}{2}\mathbf{q},\quad \mathbf{q}_2=\mathbf{Q}+\frac{1}{2}\mathbf{q} \tag{33}$$

in terms of a mean position $\mathbf{Q}=(\mathbf{q}_1+\mathbf{q}_2)/2$ and a separation $\mathbf{q}=\mathbf{q}_2-\mathbf{q}_1$, to get

$$\left[\underbrace{\frac{\partial}{\partial t}+\frac{1}{2}\frac{\mathbf{p}_1+\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{Q}}}_{1/T}+\underbrace{\frac{\mathbf{p}_2-\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}}-\frac{\partial\phi(|\mathbf{q}_1-\mathbf{q}_2|)}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)}_{1/\tau_\mathrm{c}}\right]f_2=0. \tag{34}$$

The different scalings come from thinking of variations with respect to $\mathbf{q}$ being on the $O(d)$ lengthscale of a collision, and variations respect to $\mathbf{Q}$ being on the much larger $O(L)$ macroscopic lengthscale.

We can understand what happens during a collision by treating f_2 as steady on the τ_c timescale. The particles are moving even though f_2 is steady. This comes from the simplified equation (32) which we can write as a two-particle Liouville equation,

$$\frac{\mathrm{d}f_2}{\mathrm{d}t}=\frac{\partial f_2}{\partial t}+\{H_2,f_2\}=0. \tag{35}$$

This says that f_2 is constant along the trajectories of the two-particle system, which decouples from the other particles when scaled appropriately for a binary collision. The scaling argument above also says we can neglect $\partial_t f_2$ and just take $\{H_2,f_2\}=0$. Bogoliubov did this more formally using a forerunner of the method of multiple scales by seeking solutions with a particular functional form for f_2.

Equating the $O(1/\tau_c)$ terms in (34) and substituting into (31) gives

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_\mathrm{coll}=\int\mathrm{d}\mathbf{p}_2\,\mathrm{d}\mathbf{q}_2\left(\frac{\mathbf{p}_2-\mathbf{p}_1}{m}\right)\cdot\frac{\partial}{\partial\mathbf{q}}f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t) \tag{36}$$

Integrating (36) over a sphere of radius 2ℓ satisfying $d\ll\ell\ll\lambda_\mathrm{mfp}$ in $\mathbf{q}$ gives

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_\mathrm{coll}=\int\mathrm{d}\mathbf{p}_2\int_S\mathrm{d}S\,\mathbf{n}_S\cdot\mathbf{V}\,f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t), \tag{37}$$

where $\mathbf{q}=2\ell\mathbf{n}_S$, $\mathbf{V}=(\mathbf{p}_2-\mathbf{p}_1)/m$, $\mathbf{q}_1=\mathbf{Q}-\ell\mathbf{n}_S$, $\mathbf{q}_2=\mathbf{Q}+\ell\mathbf{n}_S$. (Later we will assume that f_1 does not vary on the scale ℓ, so $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{Q}$ become interchangeable.)

Previously when deriving the BBGKY hierarchy we had a fixed system of N particles. We used the divergence theorem extensively, and assumed that all the integrals over very large surfaces vanished. Now we are using the Boltzmann–Grad limit, so we are taking the number of particles to infinite, and the lengthscale d of the region over which binary collisions occur to zero. The surface S of radius 2ℓ is a very large surface compared with the lengthscale d, but not so large that the scaling approximations that led to (34) become invalid. The $O(1/\tau_\mathrm{c})$ balance in (34) shows that the integrand in (36) is vanishingly small unless $|\mathbf{q}_1-\mathbf{q}_2|=O(d)$, so integrating over every surface S large enough to contain this region will give the same result for the integral.

It is useful to decompose the surface integral in (37) into integrals over the two hemispheres S_+ on which $\mathbf{n}_S\cdot\mathbf{V}>0$, and S_- on which $\mathbf{n}_S\cdot\mathbf{V}<0$,

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_\mathrm{coll}=G-L\equiv\int\mathrm{d}\mathbf{p}_2\int_{S_+}\mathrm{d}S\,|\mathbf{n}_S\cdot\mathbf{V}|\,f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t)-\int\mathrm{d}\mathbf{p}_2\int_{S_-}\mathrm{d}S\,|\mathbf{n}_S\cdot\mathbf{V}|\,f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{q}_1,\mathbf{q}_2,t). \tag{38}$$

Boltzmann called these the gain term G and the loss term L respectively.

The loss term describes particles with momentum $\mathbf{p}_1$ colliding with particles with momentum $\mathbf{p}_2$. Each pair of particles emerges from the collision with different momenta $\widetilde{\mathbf{p}}_1$ and $\widetilde{\mathbf{p}}_2$, so these collisions appear as a loss of particles with momentum $\mathbf{p}_1$. The gain term describes the reverse process in which pairs of particles with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ emerge from collisions of pairs of particles with some other initial momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$.

Boltzmann's "stosszahlansatz" or "collision number assumption" assumes that particles moving *towards* each other (so have not yet collided) are uncorrelated, so we may replace f_2 in the loss term with a product of f_1 and f_1,

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\text{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{39}$$

However, we still need to do something about the gain term.

We will do this by finding a pair of particles that have different momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$ before a binary collision, and from which they emerge with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ after the collision.

Each collision conserves momentum and energy, so

$$\mathbf{p}_1' + \mathbf{p}_2' = \mathbf{p}_1 + \mathbf{p}_2, \tag{40a}$$

$$|\mathbf{p}_1'|^2 + |\mathbf{p}_2'|^2 = |\mathbf{p}_1|^2 + |\mathbf{p}_2|^2. \tag{40b}$$

The solution may be written as

$$\mathbf{p}_1 = \mathbf{p}_1' + m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}', \quad \mathbf{p}_2 = \mathbf{p}_2' - m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}', \tag{41}$$

where $\mathbf{V}' = (\mathbf{p}_2' - \mathbf{p}_1')/m$ is the initial relative velocity, and $\mathbf{n}$ is a unit vector. There are four constraints on six degrees of freedom, so we expect the solution to contain two free parameters. We can check that

$$\mathbf{p}_2 - \mathbf{p}_1 = (\,\mathbf{I} - 2\,\mathbf{n}\,\mathbf{n}) \cdot (\mathbf{p}_2' - \mathbf{p}_1')\,, \tag{42}$$

so the relative velocity is reflected in the plane perpendicular to $\mathbf{n}$. This preserves the magnitude of the relative velocity.

This reflection defines an invertible transformation with inverse

$$\mathbf{p}_1' = \mathbf{p}_1 + m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}, \quad \mathbf{p}_2' = \mathbf{p}_2 - m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}, \tag{43}$$

where $\mathbf{V} = (\mathbf{p}_2 - \mathbf{p}_1)/m$ is the relative velocity of separation after the collision, and $\mathbf{n}$ is the same unit vector, with the property that $\mathbf{n}\cdot\mathbf{V} = -\mathbf{n}\cdot\mathbf{V}'$ from (43). In this sense the transformation is its own inverse, so it has unit Jacobian (at least up to sign).

Using this *inverse collision* we can rewrite (39) as

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\text{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1', \mathbf{p}_2', \mathbf{q}_1', \mathbf{q}_2', t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{44}$$

For hard spheres one could work out what $\mathbf{q}_1'$ and $\mathbf{q}_2'$ should be. The first term still contains $|\mathbf{n}_S \cdot \mathbf{V}|$ and an integration over $\mathbf{p}_2$. The dashed variables only appear in the arguments of f_2, but this is enough to let us use Boltzmann's stosszahlansatz again:

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\text{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1', \mathbf{q}_1', t) f_1(\mathbf{p}_2', \mathbf{q}_2', t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{45}$$

More generally, we can absorb the details of the 2-particle collisions by parametrising each hemisphere using r, ψ coordinates on the disc D perpendicular to the relative velocity of separation $\mathbf{V}$. We write $\mathbf{n} = (\sin\theta\cos\psi, \sin\theta\sin\psi, \cos\theta)$, and take the radial coordinate r to be the impact parameter, the distance of closest approach in the absence of interactions, for a trajectory with deflection angle θ. The area element for integrals like those in (45) then transforms as

$$\begin{aligned}
\int_{S_\pm} \mathrm{d}S |\mathbf{n}_S \cdot \mathbf{V}| \cdots &= V \int_D \mathrm{d}r \mathrm{d}\psi\, r \cdots, \\
&= \int_H \mathrm{d}\theta \mathrm{d}\psi\, V r(\theta, V) \left|\frac{\partial r(\theta, V)}{\partial \theta}\right| \cdots, \\
&= \int_H \mathrm{d}\theta \mathrm{d}\psi\, B(\theta, V) \cdots,
\end{aligned}$$

where the last two integrals are over the hemisphere $0 \le \theta \le \pi/2$, $0 \le \psi < 2\pi$.

This defines the *scattering kernel* $B(\theta, V)$, which is related to the differential cross section $\sigma(\theta', V)$ by

$$|\mathbf{V}\cdot\mathbf{n}^{(\text{in})}| \mathrm{d}S^{(\text{in})} = V r\, \mathrm{d}r\, \mathrm{d}\psi = B(\theta, V)\, \mathrm{d}\theta \mathrm{d}\psi = V \sigma(\theta', V) \underbrace{\sin\theta' \mathrm{d}\theta' \mathrm{d}\psi}_{\mathrm{d}S}, \tag{46}$$

so

$$B(\theta, V) = Vr\left|\frac{\partial r}{\partial \theta}\right|, \text{ while } \sigma(\theta', V) = \frac{1}{\sin\theta'}\, r\left|\frac{\partial r}{\partial \theta'}\right|. \tag{47}$$

The latter has dimensions of area. The angle $\theta' = \pi/2 - \theta$, so a small deflection corresponds to $\theta \approx \pi/2$ and $\theta' \approx 0$.

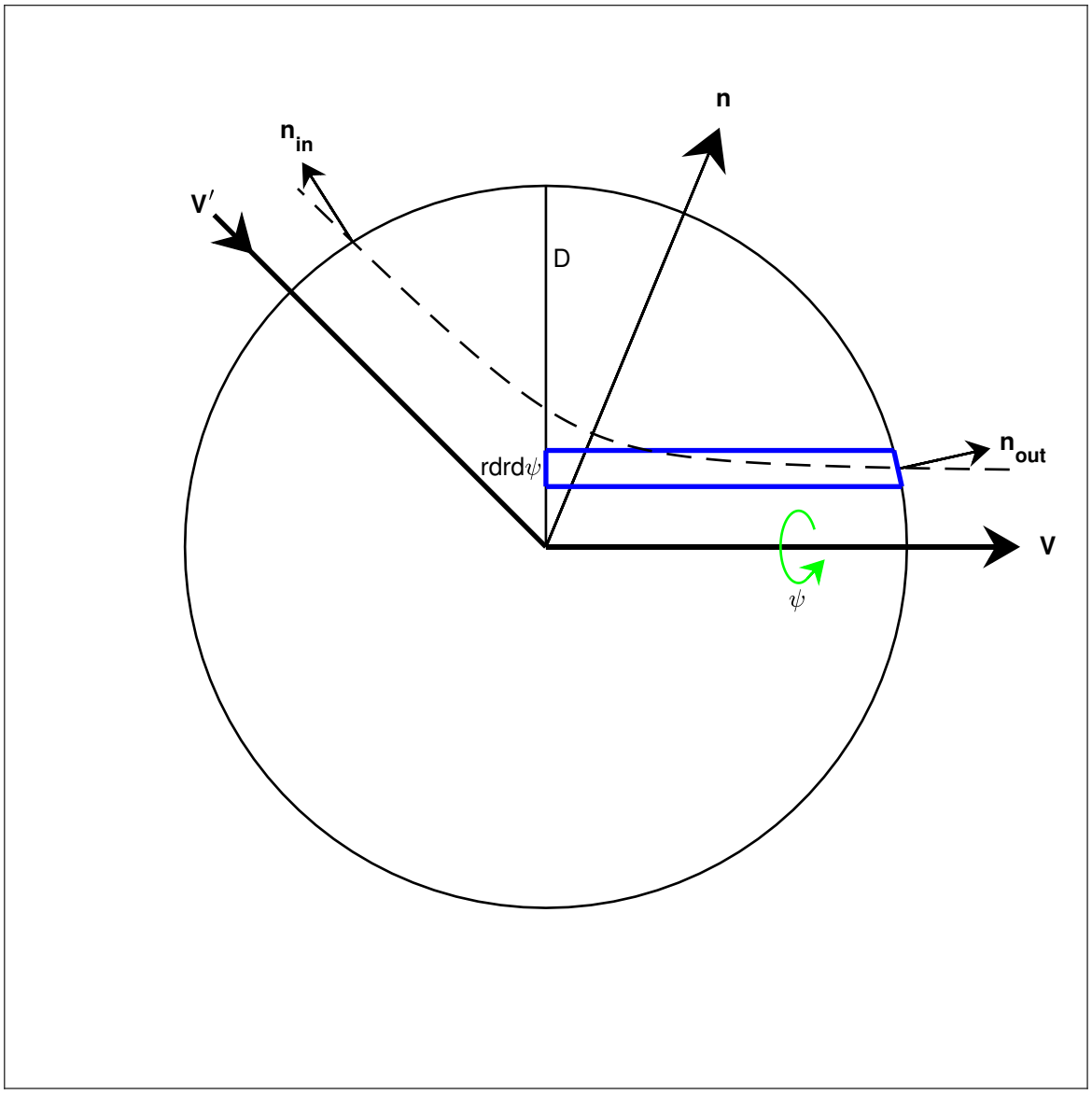
The Boltzmann equation for general 2-particle collisions is thus

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\frac{\partial f_1}{\partial \mathbf{q}_1} = \int \mathrm{d}\mathbf{p}_2 \mathrm{d}\theta \mathrm{d}\psi\, B(V,\theta)\left[f_1(\mathbf{p}_1', \mathbf{q}_1, t) f_1(\mathbf{p}_2', \mathbf{q}_1, t) - f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_1, t)\right], \tag{48}$$

where $V = |\mathbf{p}_1 - \mathbf{p}_2|/m$, and $\mathbf{p}_1'$ and $\mathbf{p}_2'$ are defined functions of $\mathbf{p}_1$, $\mathbf{p}_2$, θ and ψ via (43)

Using $\int \mathrm{d}\mathbf{p}_2\, f_1(\mathbf{p}_2, \mathbf{q}_1, t) = n(\mathbf{q}_1, t)$, the number density, taking $V \sim c_\mathrm{s}$, the sound speed, and noting that the original integrand in (36) was only non-negligible in an $O(d^3)$ volume bounded by an $O(d^2)$ surface, the magnitude of the right-hand side of (48) is

$$c_\mathrm{s} n d^2 f_1 = \frac{1}{\tau} f_1 \text{ where } \tau = \frac{1}{n d^2 c_\mathrm{s}} = \frac{\lambda_\mathrm{mfp}}{c_\mathrm{s}}. \tag{49}$$



A. Calculation of the collision kernel $B(\theta, V)$

The motion of an isolated system of two particles with positions $\mathbf{q}_1$ and $\mathbf{q}_2$ interacting via the potential $\phi(|\mathbf{q}_1 - \mathbf{q}_2|)$ can be reduced in the usual way to a central force problem for the displacement $\mathbf{q} = \mathbf{q}_2 - \mathbf{q}_1$ with the reduced mass $\mu = m/2$. Conservation of the angular momentum vector implies that the motion is confined to a plane. We can introduce polar coordinates R and Φ in this plane. Conservation of energy and angular momentum (now perpendicular to the plane) then lead to

$$\frac{1}{2}\mu\left(\dot{R}^2 + R^2\dot{\Phi}^2\right) + \phi(R) = \frac{1}{2}\mu V^2 + \phi(R_{\rm cut}), \quad R^2\dot{\Phi} = rV. \tag{50}$$

It is common to "cut off" the potential at some large radius, so that $\phi(R) = \phi(R_{\rm cut})$ for $R \geq R_{\rm cut}$. The trajectories are then straight lines for $R \geq R_{\rm cut}$. This eliminates the divergence in the collision kernel that otherwise arises for small deflections.

Eliminating t between these two equations gives an ODE for the trajectory $R(\Phi)$,

$$\frac{\mu}{2}V^2\left(\frac{r^2}{R^4}\left(\frac{\mathrm{d}R}{\mathrm{d}\Phi}\right)^2 + \frac{r^2}{R^2} - 1\right) = \phi(R_{\rm cut}) - \phi(R), \tag{51}$$

which rearranges into

$$\frac{\mathrm{d}R}{\mathrm{d}\Phi} = \pm\sqrt{\frac{2}{\mu}}\frac{1}{rV}R^2\left[\frac{\mu}{2}V^2\left(1 - \frac{r^2}{R^2}\right) - \phi(R) + \phi(R_{\rm cut})\right]^{1/2}. \tag{52}$$

The two signs of the square root give the two halves of the trajectory. The two halves meet at the point of closest approach R_0, where $\mathrm{d}R/\mathrm{d}\Phi = 0$, so R_0 satisfies

$$\frac{\mu}{2}V^2\left(1 - \frac{r^2}{R_0^2}\right) = \phi(R_0) - \phi(R_{\rm cut}). \tag{53}$$

We need the negative square root for $0 \leq \Phi \leq \theta$, as $\mathrm{d}R/\mathrm{d}\Phi \leq 0$ in this half of the trajectory (see figure).

The right hand side of the ODE has no explicit dependence on Φ, so we can separate variables and integrate to find the deflection angle θ as a function of r,

$$\theta = \sqrt{\frac{\mu}{2}}\,rV\int_{R_0}^{R_{\rm cut}}\frac{1}{R^2}\left[\frac{\mu}{2}V^2\left(1 - \frac{r^2}{R^2}\right) - \phi(R) + \phi(R_{\rm cut})\right]^{-1/2}\mathrm{d}R, \tag{54}$$

from the boundary conditions

$$\Phi = \theta \text{ at } R = R_0, \quad \text{and} \quad \Phi \to 0 \text{ as } R \to \infty. \tag{55}$$

B. Power-law potentials

For power-law potentials with no cut-off, so $\phi(R) = kR^{1-n}$ the integral can be tidied up by the substitutions

$$x = \frac{r}{R}, \quad r = \left(\frac{\mu}{2k}\right)^{-1/(n-1)} V^{-2/(n-1)} b \tag{56}$$

to give

$$\theta = \int_0^{x_0} \frac{dx}{\sqrt{1 - x^2 - (x/b)^{n-1}}}, \tag{57}$$

where $x_0 = r/R_0$ satisfies

$$1 - x_0^2 - (x_0/b)^{n-1} = 0. \tag{58}$$

[This is still possible, though slightly messier, with a cut-off. See page 70 of Cercginani 1988.]

From here we get

$$B(\theta, V) = Vr \left|\frac{\partial r}{\partial \theta}\right| = V \left(\frac{\mu}{2k}\right)^{-1/(n-1)} V^{-2/(n-1)} b \frac{\mathrm{d}b}{\mathrm{d}\theta} = V^\alpha \beta(\theta), \tag{59}$$

with

$$\alpha = 1 - \frac{4}{n-1} = \frac{n-5}{n-1}, \quad \beta\theta = \left(\frac{\mu}{2k}\right)^{-1/(n-1)} V^{-2/(n-1)} b \frac{\mathrm{d}b}{\mathrm{d}\theta}. \tag{60}$$

A theoretically important further simplification arises for the "Maxwell molecules" with $n = 5$ and $\alpha = 0$, since B then depends only upon θ.

From the integral we get $b = O(\theta)$ as $\theta \to 0$, and

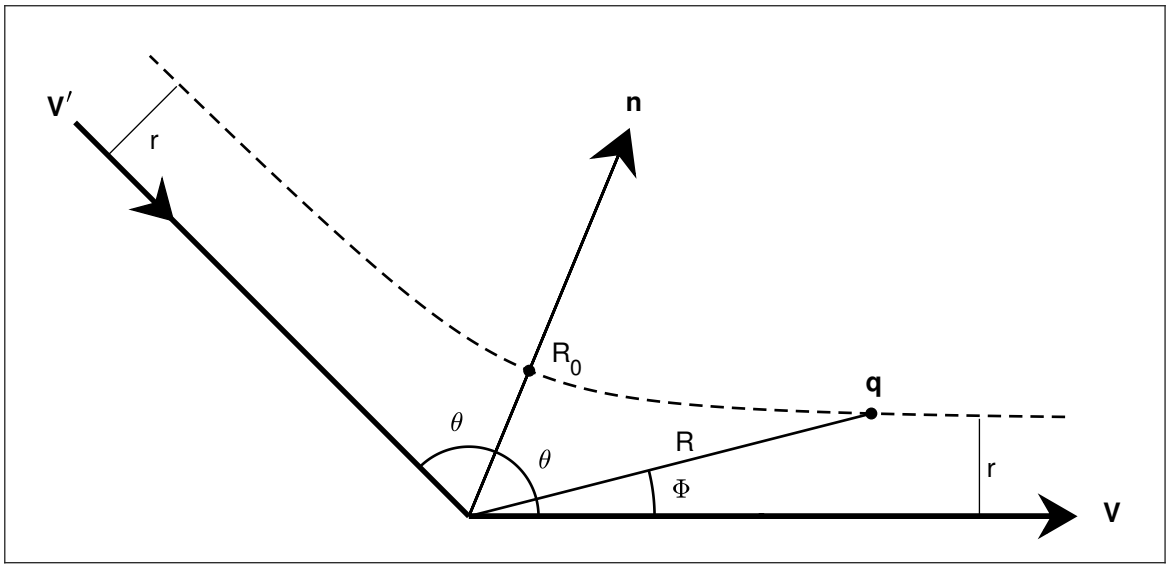
$$\theta = \frac{\pi}{2} + O(b^{1-n}) \text{ as } b \to \infty \tag{61}$$

from expanding the integrand for $x/b \ll 1$ (see page 71 of Cercginani 1988 for details). These two limits give

$$\beta(\theta) = O(\theta) \text{ as } \theta \to 0, \tag{62a}$$

$$\beta(\theta) = O\left[\left(\frac{\pi}{2} - \theta\right)^{-(n+1)/(n-1)}\right] \text{ as } \theta \to \pi/2, \tag{62b}$$

so β diverges for small-angle deflections with θ close to $\pi/2$.



VII. PROPERTIES OF BOLTZMANN'S COLLISION OPERATOR

Change notation to particle velocity $\mathbf{v} = \mathbf{p}/m$, and since we no longer need the 2-particle distribution function, write

$$f = f(\mathbf{x}, \mathbf{v}, t), \quad f_\star = f(\mathbf{x}, \mathbf{v}_\star, t), \quad f' = f(\mathbf{x}, \mathbf{v}', t), \quad f'_\star = f(\mathbf{x}, \mathbf{v}'_\star, t), \tag{63}$$

where $\mathbf{v} = \mathbf{v}_1$, $\mathbf{v}' = \mathbf{v}'_1$, $\mathbf{v}_\star = \mathbf{v}_2$, $\mathbf{v}'_\star = \mathbf{v}'_2$, and absorb factors of m into B, so

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla} f = C[f, f] = \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' f'_\star - f f_\star \right]. \tag{64}$$

The θ and ϕ integral is taken over a hemisphere, and (as before in different notation)

$$\mathbf{v}' = \mathbf{v} - \mathbf{n}\,\mathbf{n} \cdot (\mathbf{v}_\star - \mathbf{v}), \quad \mathbf{v}'_\star = \mathbf{v}_\star + \mathbf{n}\,\mathbf{n} \cdot (\mathbf{v}_\star - \mathbf{v}), \quad \mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta). \tag{65}$$

The $C[f, f]$ notation emphasises the bilinearity of Boltzmann's collision operator. It is useful to consider the more general bilinear expression

$$C[f, g] = \frac{1}{2} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' g'_\star + g' f'_\star - f g_\star - g f_\star \right], \tag{66}$$

and its integral

$$\int \mathrm{d}\mathbf{v} \, C[f, g] \, \psi(\mathbf{v}) = \frac{1}{2} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' g'_\star + g' f'_\star - f g_\star - g f_\star \right] \psi(\mathbf{v}). \tag{67}$$

Interchanging the starred and unstarred variables gives

$$\int \mathrm{d}\mathbf{v} \, C[f, g] \, \psi(\mathbf{v}) = \frac{1}{2} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' g'_\star + g' f'_\star - f g_\star - g f_\star \right] \psi(\mathbf{v}_\star). \tag{68}$$

Using (65) and its inverse to swap between dashed and undashed variables gives

$$\int \mathrm{d}\mathbf{v} \, C[f, g] \, \psi(\mathbf{v}) = \frac{1}{2} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f g_\star + g f_\star - f' g'_\star - g' f'_\star \right] \psi(\mathbf{v}'), \tag{69}$$

using $\mathrm{d}\mathbf{v}' \mathrm{d}\mathbf{v}'_\star = \mathrm{d}\mathbf{v} \mathrm{d}\mathbf{v}_\star$ since the transformation has unit Jacobian, and $|\mathbf{n} \cdot \mathbf{V}| = |\mathbf{n}' \cdot \mathbf{V}|$. We can now interchange the starred and unstarred variables again:

$$\int \mathrm{d}\mathbf{v} \, C[f, g] \, \psi(\mathbf{v}) = \frac{1}{2} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f g_\star + g f_\star - f' g'_\star - g' f'_\star \right] \psi(\mathbf{v}'_\star). \tag{70}$$

Taking the average of these four equivalent expressions gives

$$\int \mathrm{d}\mathbf{v} \, C[f, g] \, \psi(\mathbf{v}) = \frac{1}{8} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' g'_\star + g' f'_\star - f g_\star - g f_\star \right] \left[\psi + \psi_\star - \psi' - \psi'_\star \right], \tag{71}$$

and

$$\int \mathrm{d}\mathbf{v} \, C[f, f] \, \psi(\mathbf{v}) = \frac{1}{4} \int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left[f' f'_\star - f f_\star \right] \left[\psi + \psi_\star - \psi' - \psi'_\star \right]. \tag{72}$$

The expressions (71) and (72) vanish for all f and g if the function ψ is such that

$$\psi(\mathbf{v}) + \psi(\mathbf{v}_\star) = \psi(\mathbf{v}') + \psi(\mathbf{v}'_\star). \tag{73}$$

Having constructed the transformation (65) to conserve energy and momentum, the only continuous functions ψ satisfying (73) are linear combinations of the five *collision invariants*

$$1, \quad \mathbf{v} = (v_x, v_y, v_z), \quad |\mathbf{v}|^2. \tag{74}$$

The 1 is linked to binary collisions conserving particle number (see later) as well as energy and momentum.

VIII. BOLTZMANN'S INEQUALITY, THE MAXWELL–BOLTZMANN DISTRIBUTION

We now investigate which (positive) functions $f(\mathbf{v})$ satisfy $C[f,f]=0$.

Putting $\psi=\log f$ into (72) gives Boltzmann's inequality

$$\int \mathrm{d}\mathbf{v}\, C[f,f]\,\log f = \frac{1}{4}\int \mathrm{d}\mathbf{v}\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(\theta,V)\left[f'f'_\star - ff_\star\right]\log\left(ff_\star/f'f'_\star\right)\leq 0. \tag{75}$$

The integrand is non-positive since (putting $ff_\star=y$ and $f'f'_\star=x$)

$$(x-y)\big(\log(y)-\log(x)\big)\leq 0 \text{ for all } x,y\in\mathbb{R}^+ \tag{76}$$

with equality if and only if $x=y$.

Equality in (75) thus occurs if and only if $ff_\star=f'f'_\star$. Taking logarithms,

$$\log f+\log f_\star=\log f'+\log f'_\star, \tag{77}$$

so, by the previous result, $\log f$ must be a linear combination of the five collision invariants:

$$\log f(\mathbf{v})=a+\mathbf{b}\cdot\mathbf{v}+c|\mathbf{v}|^2, \tag{78}$$

for constant scalars a and c, and a constant vector $\mathbf{b}$. We need the constant $c<0$, so that f decays to zero as $|\mathbf{v}|\to\infty$. This is the *Maxwell–Boltzmann distribution*. It emerges as a property of Boltzmann's binary collision operator.

Looking ahead a little, it is common to rewrite (78) as

$$f^{(0)}(\mathbf{v})=\frac{n}{(2\pi\Theta)^{3/2}}\,\exp(-|\mathbf{v}-\mathbf{u}|^2/(2\Theta)), \tag{79}$$

where the superscript $^{(0)}$ indicates a Maxwell–Boltzmann distribution. The constants n, $\mathbf{u}$, Θ satisfy

$$n=\int \mathrm{d}\mathbf{v}\, f^{(0)}, \tag{80a}$$

$$\mathbf{u}=(1/n)\int \mathrm{d}\mathbf{v}\,\mathbf{v}\, f^{(0)}, \tag{80b}$$

$$\Theta=1/(3n)\int \mathrm{d}\mathbf{v}\,|\mathbf{v}-\mathbf{u}|^2\, f^{(0)}. \tag{80c}$$

These will turn out to be the fluid number density, velocity, and temperature for any distribution f, not just a Maxwell–Boltzmann distribution. The mass density is $\rho=mn$ if the particle mass is m. The temperature is given in so-called energy units, in which $\Theta^{1/2}$ is the Newtonian (isothermal) sound speed. In more common units $\Theta=RT$, with T in Kelvin. The gas constant $R=k_B/m$ equals Boltzmann's constant k_B divided by m. The energy density is

$$\mathcal{E}=m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}|\mathbf{v}|^2\, f^{(0)}=\frac{1}{2}\rho|\mathbf{u}|^2+\frac{3}{2}\rho\Theta. \tag{81}$$

A spatially homogeneous solution $f(\mathbf{v},t)$ of the Boltzmann equation satisfies

$$\partial_t f=C[f,f]. \tag{82}$$

Multiplying by $1+\log f$ and $\int \mathrm{d}\mathbf{v}$ gives

$$\int \mathrm{d}\mathbf{v}\,(1+\log f)\partial_t f=\int \mathrm{d}\mathbf{v}\,(1+\log f)C[f,f],$$

$$\int \mathrm{d}\mathbf{v}\,\partial_t(f\log f)=\int \mathrm{d}\mathbf{v}\,\log f C[f,f]\leq 0,$$

$$\partial_t\int \mathrm{d}\mathbf{v}\, f\log f\leq 0.$$

The first step on the right hand side uses 1 being a collision invariant. Hence Boltzmann's H-function $H[f]=\int \mathrm{d}\mathbf{v}\, f\log f$ is non-increasing in time. $H[f]$ is the mathematician's convex entropy density for the Boltzmann equation.

Since $H[f]$ is non-increasing in time, and evolution under the spatially homogeneous Boltzmann equation (82) conserves the moments of the collision invariants, it is natural to ask which f minimised $H[f]$ under the constraints of fixed n, $\mathbf{u}$, $\mathcal{E}$, or equivalently fixed mass, momentum, and energy. Using a Lagrange multiplier approach, we minimise

$$F = \int \mathrm{d}\mathbf{v} \left\{ f \log f - (a' + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2) f \right\} = H[f] - (a'n + n\mathbf{b}\cdot\mathbf{u} + 2c\mathcal{E}), \tag{83}$$

and calculate

$$0 = \delta F = \int \mathrm{d}\mathbf{v} \left\{ (1 + \log f) - (a' + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2) \right\} \delta f \tag{84}$$

This gives

$$\log f = \underbrace{(a' - 1)}_{= a} + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2, \tag{85}$$

so we arrive at a Maxwell–Boltzmann distribution again.

We can also show that $H[f] \to H[f^{(0)}]$ implies $\int \mathrm{d}\mathbf{v}\, |f - f^{(0)}| \to 0$ using a related quantity called relative entropy (see later).

IX. BOLTZMANN'S H-THEOREM

Suppose $f(\mathbf{x}, \mathbf{v}, t)$ is a solution of Boltzmann's equation, no longer spatially homogeneous,

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = C[f, f] \tag{86}$$

in a spatial domain Ω. Multiplying by $1 + \log f$ and integrating over $\mathbf{v}$ leads to

$$\partial_t H + \boldsymbol{\nabla}\cdot\mathbf{J} = S \leq 0, \tag{87}$$

using Boltzmann's inequality (75), where

$$H(\mathbf{x}, t) = \int \mathrm{d}\mathbf{v}\, f \log f, \quad \mathbf{J} = \int \mathrm{d}\mathbf{v}\, \mathbf{v}\, f \log f, \quad S = \int \mathrm{d}\mathbf{v}\, \log f\, C[f, f]. \tag{88}$$

Integrating (87) over the spatial domain Ω gives Boltzmann's H-theorem:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} \leq \int_{\partial\Omega} \mathbf{J}\cdot\mathbf{n}\, \mathrm{d}S, \text{ where } \mathcal{H} = \int_\Omega H(\mathbf{x}, t)\, \mathrm{d}\mathbf{x}, \tag{89}$$

and $\mathbf{n}$ is the *inward* normal on $\partial\Omega$. The surface integral vanishes for various special/idealised cases: infinite domains, periodic boxes, and specularly reflecting boundary conditions. The last of these reverses $\mathbf{n}\cdot\mathbf{v}$ under a collision with the boundary, while preserving $\mathbf{n}\times\mathbf{v}$. More formally,

$$f(\mathbf{x}, \mathbf{v}, t) = f(\mathbf{x}, \mathbf{v} - 2\mathbf{n}\mathbf{n}\cdot\mathbf{v}, t) \text{ for } \mathbf{x} \in \partial\Omega \text{ and } \mathbf{v}\cdot\mathbf{n} > 0. \tag{90}$$

This condition gives the distribution of incoming particles with velocity $\mathbf{v}$ in terms of the distribution of outgoing particles with velocity $\mathbf{v} - 2\mathbf{n}\mathbf{n}\cdot\mathbf{v}$ that have been specularly ("mirror") reflected by the boundary.

X. RELATIVE ENTROPY

The entropy of f relative to any other function $f^{(0)}$, not necessarily a Maxwell–Boltzmann distribution, is defined by

$$R[f|f^{(0)}] = \int \mathrm{d}\mathbf{v} \left(f \log(f/f^{(0)}) + f^{(0)} - f \right) \geq 0. \tag{91}$$

The integrand is non-negative, and equal to zero if and only if $f = f^{(0)}$. (Proof: write $f = g f^{(0)}$, so the integrand becomes $f^{(0)}(1 - g + g\log g) \geq 0$.

If $f = f^{(0)} + \delta f$ is close to $f^{(0)}$, the relative entropy gives a positive-definite quadratic measure of the deviation:

$$R[f|f^{(0)}] = \frac{1}{2}\int \mathrm{d}\mathbf{v}\,\frac{\delta f^2}{f_0} + O(\delta f^3). \tag{92}$$

Without assuming $f - f^{(0)}$ is small, one can show that

$$f\log(f/f^{(0)}) + f^{(0)} - f \geq \frac{1}{\mathrm{e}}\min\left(1, \frac{|f-f^{(0)}|}{f^{(0)}}\right)|f - f^{(0)}|, \tag{93}$$

so

$$R[f|f^{(0)}] \geq \frac{1}{\mathrm{e}}\left(\int_L \mathrm{d}\mathbf{v}\,|f-f^{(0)}| + \int_S \mathrm{d}\mathbf{v}\,|f-f^{(0)}|^2/f^{(0)}\right), \tag{94}$$

where

$$L = \{\mathbf{v} : |f - f^{(0)}| > f^{(0)}\}, \text{ and } S = \{\mathbf{v} : |f - f^{(0)}| < f^{(0)}\}. \tag{95}$$

Using the Cauchy–Schwarz inequality on the second term,

$$\int_S \mathrm{d}\mathbf{v}\,|f-f^{(0)}| \leq \left(\int_S \mathrm{d}\mathbf{v}\,|f-f^{(0)}|^2/f^{(0)}\right)^{1/2}\left(\int_S \mathrm{d}\mathbf{v}\,f^{(0)}\right)^{1/2} \tag{96}$$

one can show that $R[f|f^{(0)}] \to 0$ implies

$$\int \mathrm{d}\mathbf{v}\,|f-f^{(0)}| = \int_L \mathrm{d}\mathbf{v}\,|f-f^{(0)}| + \int_S \mathrm{d}\mathbf{v}\,|f-f^{(0)}| \to 0. \tag{97}$$

If, in addition, $f^{(0)}$ is a Maxwell–Boltzmann distribution that shares the same values of n, $\mathbf{u}$, Θ as f,

$$\begin{aligned} R[f|f^{(0)}] &= \int \mathrm{d}\mathbf{v} f\log f - f\log f^{(0)}, \\ &= \int \mathrm{d}\mathbf{v} f\log f - f^{(0)}\log f^{(0)} + (f^{(0)} - f)\log f^{(0)}, \\ &= H[f] - H[f^{(0)}] + \int \mathrm{d}\mathbf{v}\,(f^{(0)} - f)(a + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2), \\ &= H[f] - H[f^{(0)}], \end{aligned} \tag{98}$$

since $\log f^{(0)} = a + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2$ is a collision invariant. The non-negativity of $R[f|f^{(0)}]$ thus implies $H[f] \geq H[f^{(0)}]$. From the previous result, $H[f] \to H[f^{(0)}]$ implies $f \to f^{(0)}$ in the sense of (97).

Establishing how quickly $f \to f^{(0)}$, from some relation between $\partial_t H[f]$ and $H[f] - H[f^{(0)}]$ is generally a hard problem.

XI. LINEARISED COLLISION OPERATOR

We can construct a linearised Boltzmann collision operator by considering a distribution function $f = f^{(0)} + \epsilon f^{(1)}$ that is close to a Maxwell–Boltzmann distribution,

$$f^{(0)} = \frac{n}{(2\pi\Theta)^{3/2}} \exp\left(- \frac{|\mathbf{v}' - \mathbf{u}|^2}{2\Theta} \right). \tag{99}$$

Using the symmetry and bilinearity of $C[\cdot,\cdot]$ gives

$$C[f^{(0)} + \epsilon f^{(1)}, f^{(0)} + \epsilon f^{(1)}] = \underbrace{C[f^{(0)}, f^{(0)}]}_{=0} + 2\,\epsilon\, C[f^{(0)}, f^{(1)}] + \epsilon^2 C[f^{(1)}, f^{(1)}]. \tag{100}$$

The first term vanishes because $f^{(0)}$ is invariant under collision, so $2C[f^{(0)}, f^{(1)}]$ defines a linearised collision operator acting on $f^{(1)}$.

However, we can define a linearised collision operator L with better properties if instead we write $f = f^{(0)}(1 + \epsilon h)$, or $f_1 = f_0 h$, and define L by

$$\begin{aligned}
\mathsf{L}h &= \frac{2}{f^{(0)}} C[f^{(0)}, f^{(0)} h], \\
&= \frac{1}{f^{(0)}} \iiint \mathrm{d}\mathbf{v}_\star \, \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) \left\{ f^{(0)\prime} f_\star^{(0)\prime} \left(h' + h'_\star \right) - f^{(0)} f_\star^{(0)} \left(h + h_\star \right) \right\}, \\
&= \iiint \mathrm{d}\mathbf{v}_\star \, \mathrm{d}\theta \, \mathrm{d}\phi \, B(\theta, V) f_\star^{(0)} \big(h' + h'_\star - h - h_\star \big).
\end{aligned} \tag{101}$$

The last step uses $f^{(0)\prime} f_\star^{(0)\prime} = f^{(0)} f_\star^{(0)}$ because $\mathbf{v}$ and $|\mathbf{v}|^2$ are collision invariants,

$$f^{(0)\prime} f_\star^{(0)\prime} = \frac{n^2}{(2\pi\Theta)^3} \exp\left(- \frac{|\mathbf{v}' - \mathbf{u}|^2 + |\mathbf{v}'_\star - \mathbf{u}|^2}{2\Theta} \right) = \frac{n^2}{(2\pi\Theta)^3} \exp\left(- \frac{|\mathbf{v} - \mathbf{u}|^2 + |\mathbf{v}_\star - \mathbf{u}|^2}{2\Theta} \right) = f^{(0)} f_\star^{(0)}. \tag{102}$$

The factor of $f^{(0)}(\mathbf{x}, \mathbf{v}, t)$ is independent of $\mathbf{v}_\star$, θ and ϕ so it can be taken outside the integrals.

Equation (101) shows that $Lh = 0$ if h is a collision invariant, since then $h' + h'_\star = h + h_\star$.

Using the same approach that we used to derive the symmetrised expression (71) for $C[\cdot,\cdot]$ with two different arguments, we can write

$$\int \mathrm{d}\mathbf{v} f^{(0)} g \, \mathsf{L}h = -\frac{1}{4} \iiiint \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}_\star \, \mathrm{d}\theta \, \mathrm{d}\phi B(\theta, V) f^{(0)} f_\star^{(0)} \big(h' + h'_\star - h - h_\star \big) \big(g' + g'_\star - g - g_\star \big). \tag{103}$$

This expression is unchanged by swapping g and h, so

$$\int \mathrm{d}\mathbf{v} f^{(0)} g \, \mathsf{L} \, h = \int \mathrm{d}\mathbf{v} f^{(0)} h \, \mathsf{L} \, g. \tag{104}$$

This shows that L is a self-adjoint operator with respect to the weighted inner product

$$\langle g, h \rangle = \int \mathrm{d}\mathbf{v} f^{(0)} \, g \, h. \tag{105}$$

The weight function $f^{(0)}$ is the Maxwell–Boltzmann distribution that we linearised around. Putting $g = h$ in (103) gives

$$\langle h, \mathsf{L}h \rangle = -\frac{1}{4} \iiiint \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}_\star \, \mathrm{d}\theta \, \mathrm{d}\phi B(\theta, V) f^{(0)} f_\star^{(0)} \big(h' + h'_\star - h - h_\star \big)^2 \leq 0, \tag{106}$$

since $B(\theta, V) \geq 0$. Equality holds if and only if h is a collision invariant. The linear operator L as defined in (101) is self-adjoint and non-positive definite. We can thus solve the linear equation

$$\mathsf{L}h = r \tag{107}$$

for h if and only if the right-hand side r is orthogonal to the collision invariants, *i.e.* $\langle 1, r \rangle = 0$, $\langle \mathbf{v}, r \rangle = 0$, and $\langle |\mathbf{v}|^2, r \rangle = 0$.

A. The spectrum of the linearised collision operator

With some technical assumptions, we can decompose the linearised collision operator L defined by (101) as

$$\mathsf{L}h = -\nu(\mathbf{v})h + \mathsf{K}h. \tag{108}$$

The first operator is a purely multiplicative operator, called the collision frequency,

$$\nu(\mathbf{v}) = 2\pi \iint \mathrm{d}\mathbf{v}_\star \mathrm{d}\theta B(\theta, |\mathbf{v}-\mathbf{v}_\star|) f_\star^{(0)}. \tag{109}$$

The second operator K can be further decomposed into

$$\mathsf{K}h = \iiint \mathrm{d}\mathbf{v}_\star \,\mathrm{d}\theta \,\mathrm{d}\phi B(\theta, |\mathbf{v}-\mathbf{v}_\star|) f_\star^{(0)} \,(h' + h'_\star) - 2\pi \iint \mathrm{d}\mathbf{v}_\star \,\mathrm{d}\theta \, B(\theta, |\mathbf{v}-\mathbf{v}_\star|) f_\star^{(0)} h_\star. \tag{110}$$

The second term in (110) is a standard linear integral operator with the kernel

$$2\pi f^{(0)}(\mathbf{v}_\star) \int_0^{\pi/2} \mathrm{d}\theta \, B(\theta, |\mathbf{v}-\mathbf{v}_\star|). \tag{111}$$

The first term can be transformed into another standard linear integral operator [see Cercignani 1990 section III.2].

Formally we can always do this, but the separate integrals defining ν and K will typically not converge due to the singularity in B for small-angle deflections with $\theta \approx \pi/2$. The simplest cure is to employ Grad's angular cut-off, and impose $B(\theta, V) = 0$ for $\theta \in [\theta_{\mathrm{cut}}, \pi/2]$ for some θ_{cut} near $\pi/2$. Another approach, as seen earlier, cuts off the inter-particle potential at long distances, so $\phi(R) = \phi(R_{\mathrm{cut}})$ for $R \geq R_{\mathrm{cut}}$.

The spectrum of the linear operator L is the set of values λ for which the linear operator $\mathsf{L} - \lambda\mathsf{I}$ does not have a bounded inverse. In general the spectrum can comprise both discrete values and continuous ranges of values. The latter part is called the continuous spectrum of L.

Given one of the above technical assumptions, the integrals in (110) converge and K is a compact operator. Given any bounded sequence $\{h_n\}$, $\{\mathsf{K}h_n\}$ contains a convergent subsequence. A theorem by Weyl then establishes that the continuous spectrum of L is determined by the multiplicative (and hence self-adjoint) operator $\nu(\mathbf{v})$, so $\lambda = -\nu(\mathbf{v})$. The operator K can only affect the discrete spectrum of L.

B. The collision frequency for hard spheres

We can evaluate the collision frequency ν exactly for hard spheres with scattering kernel $B(\theta, V) = V d^2 \sin\theta\cos\theta$,

$$\nu = 2\pi \iint \mathrm{d}\mathbf{v}_\star \,\mathrm{d}\theta \,|\mathbf{v}-\mathbf{v}_\star| d^2 \sin\theta\cos\theta \frac{n}{(2\pi\Theta)^{3/2}} \exp\left(-\frac{|\mathbf{v}_\star - \mathbf{u}|^2}{2\Theta}\right). \tag{112}$$

Introducing the constant ν_0 and dimensionless "peculiar" velocities $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_\star$ relative to the fluid velocity $\mathbf{u}$,

$$\boldsymbol{\xi} = \frac{\mathbf{v}-\mathbf{u}}{\sqrt{2\Theta}}, \quad \boldsymbol{\xi}_\star = \frac{\mathbf{v}_\star - \mathbf{u}}{\sqrt{2\Theta}}, \quad \nu_0 = nd^2\sqrt{2\pi\Theta}, \tag{113}$$

and evaluating the integral over θ gives

$$\nu = \frac{\nu_0}{\pi} \int \mathrm{d}\boldsymbol{\xi}_\star \,|\boldsymbol{\xi} - \boldsymbol{\xi}_\star| \exp(-|\boldsymbol{\xi}_\star|^2). \tag{114}$$

We now write $\boldsymbol{\xi}_\star = \boldsymbol{\xi} + \boldsymbol{\zeta}$ and express $\boldsymbol{\zeta}$ in spherical polar coordinates so that $|\boldsymbol{\xi} - \boldsymbol{\xi}_\star| = \zeta$, $\boldsymbol{\zeta}\cdot\boldsymbol{\xi} = \zeta\,\xi\cos\varphi$, and

$$|\boldsymbol{\xi}_\star|^2 = |\boldsymbol{\xi}|^2 + 2\,\boldsymbol{\xi}\cdot\boldsymbol{\zeta} + |\boldsymbol{\zeta}|^2 = \xi^2 + 2\,\xi\zeta\cos\varphi + \zeta^2. \tag{115}$$

The Jacobian for spherical polars is $\zeta^2\sin\varphi$, so the integral becomes

$$\begin{aligned}
\nu(\xi) &= 2\nu_0 \int_0^\infty \mathrm{d}\zeta \int_0^\pi \mathrm{d}\varphi \,\zeta^3 \sin\varphi \exp\left(-\xi^2 - 2\xi\zeta\cos\varphi - \zeta^2\right), \\
&= \nu_0 \int_0^\infty \mathrm{d}\zeta \,\frac{\zeta^2}{\xi} \left\{\exp(-(\xi-\zeta)^2) - \exp(-(\xi+\zeta)^2)\right\}, \\
&= \nu_0 \left(e^{-\xi^2} + \sqrt{\pi}(\xi + 1/(2\xi))\,\mathrm{erf}(\xi)\right).
\end{aligned} \tag{116}$$

The error function is

$$\operatorname{erf}(\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-s^2} \mathrm{d}s = \frac{2}{\sqrt{\pi}} \left(\xi - \frac{1}{3}\xi^3 + \cdots \right) \text{ for } \xi \ll 1, \tag{117}$$

and $\operatorname{erf}(\xi) \to 1$ as $\xi \to \infty$. The limiting behaviours of ν for large and small ξ are thus

$$\nu(\xi) \sim 2\,\nu_0 \left(1 + \xi^2/3\right) \text{ as } \xi \to 0, \quad \text{and} \quad \nu(\xi) \sim \sqrt{\pi} v_0\, \xi \text{ as } \xi \to \infty. \tag{118}$$

C. The collision frequency for power-law potentials

The power-law potentials have the scattering kernel

$$B(\theta, V) = V^\alpha \beta(\theta), \text{ where } \alpha = \frac{n-5}{n-1}. \tag{119}$$

If we introduce a Grad-type angular cut-off to tame β as $\theta \to \pi/2$, we can define

$$\beta_0 = 2\pi \int_0^{\pi/2} \mathrm{d}\theta\, \beta(\theta) \tag{120}$$

The angular cut-off is needed for this integral to converge. The collision frequency then becomes

$$\nu(\mathbf{v}) = \beta_0 \int \mathrm{d}\mathbf{v}_\star f_\star^{(0)} |\mathbf{v}_\star - \mathbf{v}|^\alpha. \tag{121}$$

In particular, the collision frequency is a constant, $\nu(\mathbf{v}) = n\beta_0$, for Maxwell molecules with $\alpha = 0$. Another special case is the limit $n \to \infty$ giving $\alpha = 1$ and the previous case of hard spheres with $\beta_0 = \pi d^2$ and no angular cut-off needed.

More generally, making the same change of variables to $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_\star$ as above, the collision frequency again becomes a function of $\xi = |\boldsymbol{\xi}|$. The following integral is invariant under rotations of $\boldsymbol{\xi}$, because we can apply the same rotation to $\boldsymbol{\xi}_\star$,

$$\nu(\xi) = n\beta_0 \pi^{-3/2} (2\Theta)^{\alpha/2} \int \mathrm{d}\boldsymbol{\xi}_\star\, |\boldsymbol{\xi}_\star - \boldsymbol{\xi}|^\alpha \exp\left(-|\boldsymbol{\xi}_\star|^2\right). \tag{122}$$

The derivative of the collision frequency is

$$\frac{\mathrm{d}\nu}{\mathrm{d}\xi} = \frac{\boldsymbol{\xi}}{\xi} \cdot \frac{\mathrm{d}\nu}{\mathrm{d}\boldsymbol{\xi}} = -\frac{\alpha}{\xi} n\beta_0 \pi^{-3/2} (2\Theta)^{\alpha/2} \int \mathrm{d}\boldsymbol{\xi}_\star \exp\left(-|\boldsymbol{\xi}_\star|^2\right) \boldsymbol{\xi} \cdot (\boldsymbol{\xi}_\star - \boldsymbol{\xi}) |\boldsymbol{\xi}_\star - \boldsymbol{\xi}|^{\alpha-2}. \tag{123}$$

By writing $|\boldsymbol{\xi}_\star|^2 = |\boldsymbol{\xi}|^2 + |\boldsymbol{\xi}_\star - \boldsymbol{\xi}|^2 + 2\,\boldsymbol{\xi} \cdot (\boldsymbol{\xi}_\star - \boldsymbol{\xi})$ we can deduce that the positive contribution from the half-space with $\boldsymbol{\xi} \cdot (\boldsymbol{\xi}_\star - \boldsymbol{\xi}) > 0$ is smaller in modulus than the negative contribution from $\boldsymbol{\xi} \cdot (\boldsymbol{\xi}_\star - \boldsymbol{\xi}) < 0$. The integral is thus negative, so $\mathrm{d}\nu/\mathrm{d}\xi$ has the same sign as α.

The collision frequency $\nu(\xi)$ is thus a monotonically increasing function of ξ for $\alpha > 0$, and a monotonically decreasing function of ξ for $\alpha < 0$.

The linearised Boltzmann collision operator L for cut-off power-law potentials then has a continuous spectrum:

$$-\lambda = \nu(\xi) \geq \nu(0) > 0, \quad (n > 5) \quad \text{hard potentials} \tag{124}$$

$$-\lambda = \nu(\xi) \text{ with } 0 < \nu(\xi) \leq \nu(0), \quad (n < 5) \quad \text{soft potentials} \tag{125}$$

For soft potentials $-L$ has a continous spectrum from 0 to $\nu(0)$. For hard potentials $-L$ has five isolated eigenvalues at 0, from the collision invariants, and a continuous spectrum from $\nu(0)$ to ∞. We will return to this when deriving hydrodynamics.

The Maxwell molecules (inverse fifth power repulsive force) are the dividing case between hard and soft potentials. The collision frequency $\nu(\mathbf{v})$ is then a constant, since $B(\theta, V)$ is independent of $V = |\mathbf{v} - \mathbf{v}_\star|$. The operator L has a discrete spectrum with eigenvalues that can be expressed using the earlier $\beta(\theta)$ function. The eigenfunctions are products of spherical harmonics and Sonine polynomials.

D. The Bhatnagar–Gross–Krook–Welander model collision operator

We calculated the exact expression (without needing to linearise)

$$C[f,f] = -\underbrace{\nu(\mathbf{v}) f(\mathbf{v})}_{\text{loss term}} + \underbrace{\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\, \mathrm{d}\phi\, B(\theta,V) f' f'_\star}_{\text{gain term}}. \tag{126}$$

If f is close to a Maxwell–Boltzmann distribution $f^{(0)}$ we can linearise the loss term by calculating $\nu(\mathbf{v})$ from this Maxwell–Boltzmann distribution. We can also replace $\nu(\mathbf{v})$ with a constant ν_0, which is true for Maxwell molecules, and otherwise a model.

We now want to model the gain term with an expression that ensures $f \to f^{(0)}$ under collisions while preserving the conserved quantitites n, $\mathbf{u}$, Θ. This suggests the Boltzmann–BGKW equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f = -\nu_0 \left(f - f^{(0)} \right), \tag{127}$$

where $\nu_0 = 1/\tau$ in the previous notation.

Recall that a Maxwell–Boltzmann distribution is

$$f^{(0)}(\mathbf{v}) = \frac{n}{(2\pi\Theta)^{3/2}} \exp(-|\mathbf{v}-\mathbf{u}|^2/(2\Theta)), \tag{128}$$

If we determine the five parameters n, $\mathbf{u}$, Θ in $f^{(0)}$ from the conditions

$$n = \int \mathrm{d}\mathbf{v}\, f, \tag{129a}$$

$$\mathbf{u} = (1/n) \int \mathrm{d}\mathbf{v}\, \mathbf{v}\, f, \tag{129b}$$

$$\Theta = 1/(3n) \int \mathrm{d}\mathbf{v}\, |\mathbf{v}-\mathbf{u}|^2\, f, \tag{129c}$$

the BGKW model collision operator satisfies both the H-theorem and the five conservation properties

$$\int \mathrm{d}\mathbf{v}\, f^{(0)} = \int \mathrm{d}\mathbf{v}\, f, \tag{130a}$$

$$\int \mathrm{d}\mathbf{v}\, \mathbf{v} f^{(0)} = \int \mathrm{d}\mathbf{v}\, \mathbf{v} f, \tag{130b}$$

$$\int \mathrm{d}\mathbf{v}\, |\mathbf{v}|^2 f^{(0)} = \int \mathrm{d}\mathbf{v}\, |\mathbf{v}|^2 f. \tag{130c}$$

Although the RHS $-\nu_0 \left(f - f^{(0)} \right)$ looks linear in f, there are unpleasant (worse than quadratic) nonlinearities concealed in the dependence of $f^{(0)}$ on f via n, $\mathbf{u}$, Θ, notably division and exponentiation.

XII. DERIVATION OF HYDRODYNAMICS

Multiplying the Boltzmann equation

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = C[f,f], \tag{131}$$

by one of the five collision invariants 1, $\mathbf{v}$, $\frac{1}{2}|\mathbf{v}|^2$ and integrating over $\mathbf{v}$ gives the conservation laws

$$\partial_t \rho + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}) = 0, \quad \partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} = 0, \quad \partial_t \mathcal{E} + \boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{F}} = 0, \tag{132}$$

for the mass, momentum, and energy densities

$$\rho(\mathbf{x},t) = m\int \mathrm{d}\mathbf{v}\, f(\mathbf{x},\mathbf{v},t), \quad \rho\mathbf{u} = m\int \mathrm{d}\mathbf{v}\, \mathbf{v} f(\mathbf{x},\mathbf{v},t), \quad \mathcal{E} = \frac{1}{2}\rho|\mathbf{u}|^2 + \frac{3}{2}\rho\Theta = m\int \mathrm{d}\mathbf{v}\, \frac{1}{2}|\mathbf{v}|^2 f(\mathbf{x},\mathbf{v},t). \tag{133}$$

The quantities ρ, $\mathbf{u}$, Θ are uniquely determined by these moments, and *vice versa*. We will find later that the fluid pressure is $\rho\Theta$, so Θ is the temperature in so-called "energy units" in which $\Theta^{1/2}$ is the Newtonian speed of sound (the

speed at which small-amplitude density perturbations would propagate if the gas were held at a precisely constant temperature). By using Θ in these units we avoid the need to introduce a gas constant R, or Boltzmann's constant k_B, to convert a temperature in Kelvin into an energy density.

The momentum flux $\boldsymbol{\Pi}$ and energy flux $\boldsymbol{\mathcal{F}}$ are given by further moments of f,

$$\boldsymbol{\Pi} = m \int \mathrm{d}\mathbf{v}\, \mathbf{v}\mathbf{v} f(\mathbf{x},\mathbf{v},t), \quad \boldsymbol{\mathcal{F}} = m \int \mathrm{d}\mathbf{v}\, \frac{1}{2}\mathbf{v}|\mathbf{v}|^2 f(\mathbf{x},\mathbf{v},t). \tag{134}$$

The right hand sides of (132) vanish precisely because 1, $\mathbf{v}$, $\frac{1}{2}|\mathbf{v}|^2$ are collision invariants. As $\mathbf{x}$, $\mathbf{v}$, t are independent variables, we can take ∂_t and ∇ outside integrals over $\mathbf{v}$, *e.g.*

$$\begin{aligned}
\mathbf{v}\partial_t f + \mathbf{v}\mathbf{v}\cdot\boldsymbol{\nabla} f &= \mathbf{v} C[f,f], \\
m\int \mathrm{d}\mathbf{v}\, \mathbf{v}\partial_t f + m\int \mathrm{d}\mathbf{v}\, \mathbf{v}\mathbf{v}\cdot\boldsymbol{\nabla} f &= m\int \mathrm{d}\mathbf{v}\, \mathbf{v} C[f,f], \\
\partial_t\left(m\int \mathrm{d}\mathbf{v}\, \mathbf{v} f\right) + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\, \mathbf{v}\mathbf{v} f\right) &= 0, \\
\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} &= 0.
\end{aligned}$$

The three conservation laws (132) are exact deductions from the Boltzmann equation, but they are not closed because we do not know how to evaluate the momentum flux $\boldsymbol{\Pi}$ or the energy flux $\boldsymbol{\mathcal{F}}$. All we know is the consistency relation

$$\mathcal{E} = \frac{1}{2}\mathrm{Tr}\,\boldsymbol{\Pi} \tag{135}$$

which holds for monatomic gases (only). In "rational mechanics" terminology, we have the conservation laws, but we do not have any constitutive relations to close them by expressing $\boldsymbol{\Pi}$ and $\boldsymbol{\mathcal{F}}$ in terms of ρ, $\mathbf{u}$, Θ and their (spatial) derivatives.

However, the fluxes $\boldsymbol{\Pi}$ and $\boldsymbol{\mathcal{F}}$, along with all moments other than ρ, $\mathbf{u}$, Θ, are distinguished by evolving on collisional timescales:

$$\partial_t\boldsymbol{\Pi} + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\, \frac{1}{2}\mathbf{v}\mathbf{v}\mathbf{v} f(\mathbf{x},\mathbf{v},t)\right) = m\int \mathrm{d}\mathbf{v}\, \mathbf{v}\mathbf{v} C[f,f] \neq 0, \text{ etc.} \tag{136}$$

This suggests we can look for special hydrodynamic solutions that evolve on a slow hydrodynamic timescale T much longer than the natural timescale τ of the collision term on the right hand side.

A. Peculiar velocity

Instead of the above moments with respect to the particle velocity $\mathbf{v}$, it is common to consider moments with respect to the so-called peculiar velocity $\mathbf{w} = \mathbf{v} - \mathbf{u}(\mathbf{x},t)$,

$$\begin{aligned}
\boldsymbol{\Pi} &= m\int \mathrm{d}\mathbf{v}\, \mathbf{v}\mathbf{v} f(\mathbf{x},\mathbf{v},t), \\
&= m\int \mathrm{d}\mathbf{v}\, (\mathbf{u}+\mathbf{w})(\mathbf{u}+\mathbf{w}) f(\mathbf{x},\mathbf{v},t), \\
&= m\int \mathrm{d}\mathbf{v}\, (\mathbf{u}\mathbf{u}+\mathbf{u}\mathbf{w}+\mathbf{w}\mathbf{u}+\mathbf{w}\mathbf{w}) f(\mathbf{x},\mathbf{v},t), \\
&= m\int \mathrm{d}\mathbf{v}\, \mathbf{u}\mathbf{u} f(\mathbf{x},\mathbf{v},t) + m\int \mathrm{d}\mathbf{v}\, \mathbf{w}\mathbf{w} f(\mathbf{x},\mathbf{v},t), \\
&= \rho\mathbf{u}\mathbf{u} + \mathsf{P}.
\end{aligned}$$

All terms with precisely one $\mathbf{w}$ vanish, because $\int \mathrm{d}\mathbf{v}\, \mathbf{w} f = 0$ by construction. Beware that $\mathbf{x}$, $\mathbf{v}$, t are independent variables, but $\mathbf{x}$, $\mathbf{w}$, t are not. Taking moments with respect to $\mathbf{w}$ does not commute with ∂_t or $\boldsymbol{\nabla}$.

The momentum conservation equation thus becomes

$$\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}\mathbf{u} + \mathsf{P}) = 0, \tag{137}$$

in terms of the pressure tensor

$$\mathsf{P} = m\int \mathrm{d}\mathbf{v}\, (\mathbf{v}-\mathbf{u})(\mathbf{v}-\mathbf{u}) f(\mathbf{x},\mathbf{v},t). \tag{138}$$

Evaluating for a Maxwellian (indicated by the superscript $^{(0)}$) gives

$$\mathsf{P}^{(0)} = m \int \mathrm{d}\mathbf{w}\, \mathbf{w}\mathbf{w} \frac{n}{(2\pi\Theta)^{3/2}} \exp\left(-\frac{|\mathbf{w}|^2}{2\Theta}\right) = \rho\Theta\mathsf{I}. \tag{139}$$

The Maxwellian is a function of peculiar velocity, and working solely with velocity differences (as in Boltzmann's collision operator) ensures Galilean invariance. The integral in (139) contains no preferred direction, so it defines an isotropic second-rank tensor, a scalar multiple of I. Taking the trace of both sides determines the scalar multiplier.

Putting $\mathsf{P} = \mathsf{P}^{(0)} = \rho\Theta\mathsf{I}$ into (137) gives

$$\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}\mathbf{u}) + \boldsymbol{\nabla}p = 0. \tag{140}$$

Using the continuity equation $\partial_t\rho = -\boldsymbol{\nabla}\cdot(\rho\mathbf{u})$, we get Euler's equation with pressure $p = \rho\Theta$,

$$\rho\frac{\mathrm{D}\mathbf{u}}{\mathrm{D}t} \equiv \rho\left(\partial_t\mathbf{u} + \mathbf{u}\cdot\boldsymbol{\nabla}\mathbf{u}\right) = -\boldsymbol{\nabla}p. \tag{141}$$

Similarly, the energy density splits into a sum of fluid kinetic and internal energies,

$$\mathcal{E} = \frac{1}{2}\mathrm{Tr}\,\boldsymbol{\Pi} = \int \mathrm{d}\mathbf{v}\,\frac{1}{2}m|\mathbf{v}|^2 = \int \mathrm{d}\mathbf{v}\,\frac{1}{2}m|\mathbf{u}|^2 + \int \mathrm{d}\mathbf{v}\,\frac{1}{2}m|\mathbf{w}|^2 = \frac{1}{2}\rho|\mathbf{u}|^2 + \frac{3}{2}\rho\Theta, \tag{142}$$

on putting $\mathbf{v} = \mathbf{u} + \mathbf{w}$. The cross-term involving $\mathbf{w}\cdot\mathbf{u}$ vanishes because $\int \mathrm{d}\mathbf{v}\,\mathbf{w}f = 0$ by construction.

The energy density contains only kinetic energy: bulk motion with the fluid velocity $\mathbf{u}$, plus additional kinetic energy attributed to the peculiar velocity $\mathbf{w} = \mathbf{v} - \mathbf{u}$. There is no contribution from the potential energy ϕ that we started with in the original N-particle Hamiltonian. This contribution vanishes under the Boltzmann–Grad limit.

The energy flux becomes

$$\begin{aligned}
\boldsymbol{\mathcal{F}} &= m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}(\mathbf{u}+\mathbf{w})|\mathbf{u}+\mathbf{w}|^2 f, \\
&= m\int \mathrm{d}\mathbf{v}\,\left(\frac{1}{2}\mathbf{u}|\mathbf{u}|^2 + \frac{1}{2}\mathbf{u}|\mathbf{w}|^2 + \mathbf{w}\mathbf{w}\cdot\mathbf{u} + \frac{1}{2}\mathbf{w}|\mathbf{w}|^2\right) f, \\
&= \frac{1}{2}\rho\mathbf{u}|\mathbf{u}|^2 + \frac{3}{2}\mathbf{u}\rho\Theta + \mathsf{P}\cdot\mathbf{u} + \mathbf{q},
\end{aligned}$$

with heat flux

$$\mathbf{q}(\mathbf{x},t) = m\frac{1}{2}\int \mathrm{d}\mathbf{v}\,\mathbf{w}|\mathbf{w}|^2 f(\mathbf{x},\mathbf{v},t). \tag{143}$$

This gives the energy equation

$$\partial_t\left(\frac{1}{2}\rho|\mathbf{u}|^2 + \frac{3}{2}\rho\Theta\right) + \boldsymbol{\nabla}\cdot\left(\frac{1}{2}\rho\mathbf{u}|\mathbf{u}|^2 + \frac{3}{2}\mathbf{u}\rho\Theta + \mathsf{P}\cdot\mathbf{u} + \mathbf{q}\right) = 0, \tag{144}$$

or

$$\frac{3}{2}\rho\frac{\mathrm{D}\Theta}{\mathrm{D}t} + \mathsf{P} : \boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\cdot\mathbf{q} = 0. \tag{145}$$

The Euler form with $\mathsf{P}^{(0)} = \rho\Theta\mathsf{I}$ and $\mathbf{q}^{(0)} = 0$ is

$$\frac{3}{2}\rho\frac{\mathrm{D}\Theta}{\mathrm{D}t} + \rho\Theta\boldsymbol{\nabla}\cdot\mathbf{u} = 0. \tag{146}$$

So if collisions are very fast, $\tau \ll T$, we can imagine putting $f(\mathbf{x},\mathbf{v},t) = f^{(0)}\big(\rho(\mathbf{x},t), \mathbf{u}(\mathbf{x},t), \Theta(\mathbf{x},t)\big)$ to evaluate P and $\mathbf{q}$ from a local Maxwellian. This gives a closed system of conservation laws that coincide with the Euler equations.

Another equation we can write is

$$\rho\Theta\frac{\mathrm{D}s}{\mathrm{D}t} + (\mathsf{P} - \rho\Theta\mathsf{I}) : \boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\cdot\mathbf{q} = 0, \tag{147}$$

for the gas-dynamic entropy density $s = (3/2)\log(\Theta\rho^{-2/3})$ given by evaluating Boltzmann's H-function for a Maxwellian,

$$f^{(0)} = \frac{\rho/m}{(2\pi\Theta)^{3/2}} \exp\left(-\frac{|\mathbf{v}-\mathbf{u}|^2}{2\Theta}\right) \implies$$

$$\int \mathrm{d}\mathbf{v}\, f^{(0)}\log f^{(0)} = -\frac{3}{2}\rho\left[\log\Theta - \frac{2}{3}\log\rho + 1 + \frac{2}{3}\log m + \log(2\pi)\right] = -\rho s + \rho\times\text{constant}. \tag{148}$$

The entropy following a fluid element thus changes only through non-equilibrium effects, when $\mathsf{P} \neq \rho\Theta\mathsf{I}$ and/or $\mathbf{q} \neq \mathbf{0}$.

XIII. BEYOND THE EULER EQUATIONS

To go beyond the Euler equations we need to formulate evolution equations for P and $\mathbf{q}$. Transforming the evolution equation for $\mathbf{\Pi}$,

$$\partial_t \mathbf{\Pi} + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\,\mathbf{vvv} f(\mathbf{x},\mathbf{v},t)\right) = m\int \mathrm{d}\mathbf{v}\,\mathbf{vv} C[f,f] \neq 0 \tag{149}$$

into moments of the peculiar velocity gives (in summation convention)

$$\partial_t\left(\rho u_i u_j + P_{ij}\right) + \frac{\partial}{\partial x_k}\left(Q_{ijk} + u_i P_{jk} + u_j P_{ki} + u_k P_{ij} + \rho u_i u_j u_k\right) = m\int \mathrm{d}\mathbf{v}\, v_i v_j C[f,f], \tag{150}$$

where

$$Q_{ijk} = m\int \mathrm{d}\mathbf{v}\,(v_i - u_i)(v_j - u_j)(v_k - u_k) f. \tag{151}$$

We can evaluate the first time derivative on the LHS,

$$\begin{aligned}\partial_t\left(\rho u_i u_j\right) &= u_i\partial_t\left(\rho u_j\right) + u_j\partial_t\left(\rho u_i\right) - u_i u_j \partial_t\rho,\\ &= -u_i\partial_k\left(\rho u_j u_k + P_{jk}\right) - u_j\partial_k\left(\rho u_i u_k + P_{ik}\right) + u_i u_j \partial_k(\rho u_k).\end{aligned} \tag{152}$$

Subtracting gives

$$\partial_t P_{ij} + \partial_k\left(u_k P_{ij} + Q_{ijk}\right) + P_{ik}\frac{\partial u_j}{\partial x_k} + P_{kj}\frac{\partial u_i}{\partial x_k} = m\int \mathrm{d}\mathbf{v}\, w_i w_j C[f,f]. \tag{153}$$

We have simplified the collision term using $v_i v_j = (w_i + u_i)(w_j + u_j) = w_i w_j + u_i w_j + w_i u_j + u_i u_j$. All except the first of these four terms is a collision invariant.

Replacing $C[f,f]$ by the BGKW collision operator on the RHS of (149) gives

$$m\int \mathrm{d}\mathbf{v}\, w_i w_j \left(-\nu_0\left(f - f^{(0)}\right)\right) = -\frac{1}{\tau}\left(\mathsf{P} - \mathsf{P}^{(0)}\right) \tag{154}$$

with $\tau = 1/\nu_0$. This is also true for the linearised Boltzmann collision operator for Maxwell molecules, from which we can calculate τ in terms of the mean free path. Overall, we get

$$\partial_t P_{ij} + \partial_k\left(u_k P_{ij} + Q_{ijk}\right) + P_{ik}\frac{\partial u_j}{\partial x_k} + P_{kj}\frac{\partial u_i}{\partial x_k} = -\frac{1}{\tau}\left(P_{ij} - P_{ij}^{(0)}\right). \tag{155}$$

We can deal with the troublesome time derivative $\partial_t P_{ij}$ by writing $\mathsf{P} = \mathsf{P}^{(0)} - \mathsf{T} = \rho\Theta\mathsf{I} - \mathsf{T}$ in terms of the deviatoric stress T (the minus sign is conventional) to obtain

$$\partial_t T_{ij} + \partial_k\left(u_k T_{ij} - Q_{ijk} + \frac{1}{3}Q_{llk}\delta_{ij}\right) - \rho\Theta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right) + T_{ik}\frac{\partial u_j}{\partial x_k} + T_{kj}\frac{\partial u_i}{\partial x_k} - \frac{2}{3}(\mathsf{T}:\boldsymbol{\nabla}\mathbf{u})\delta_{ij} = -\frac{1}{\tau}T_{ij}. \tag{156}$$

[[Note: we will see something very similar for the deviatoric stress in viscoelastic liquids next term.]]

Now, if we expand the non-conserved moments (and only the non-conserved moments) as

$$\mathsf{T} = \mathsf{T}^{(0)} + \tau\mathsf{T}^{(1)} + \cdots, \mathsf{Q} = \mathsf{Q}^{(0)} + \tau\mathsf{Q}^{(1)} + \cdots \tag{157}$$

and substitute the leading order approximations $\mathsf{T} = \mathsf{T}^{(0)} = 0$ and $\mathsf{Q} = \mathsf{Q}^{(0)} = 0$ into the left hand side we get

$$\tau T_{ij}^{(1)} = \tau\rho\Theta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right), \tag{158}$$

which is the Navier–Stokes viscous stress with shear viscosity $\mu = \tau\rho\Theta$ and no bulk viscosity. The trace of the right hand side vanishes because collisions conserve energy. This is not true for polyatomic gases, as collisions can transfer energy into internal rotational and vibrational degrees of freedom.

Applying the same approach of formulating an evolution equation for the heat flux vector $\mathbf{q}$ defined by $q_k = \frac{1}{2}Q_{iik}$, and substituting the leading order approximation for the non-conserved moments gives

$$\tau\mathbf{q}^{(1)} = -\frac{5}{2}\tau\rho\Theta\boldsymbol{\nabla}\Theta, \tag{159}$$

which is Fourier's law $\mathbf{q} = -\kappa\boldsymbol{\nabla}\Theta$ with thermal conductivity $\kappa = (5/2)\tau\rho\Theta$. In these units the specific heat at constant pressure $c_p = 5/2$, so the thermal *diffusivity* $K = \kappa/(\rho c_p) = \tau\Theta$ is the same as the kinematic viscosity $\nu = \mu/\rho = \tau\Theta$. The kinetic theorist's Prandtl number ν/K is unity, which is due to our use of the BGKW collision operator.

Real monatomic gases have a Prandtl number close to 2/3 since the heat flux, being a higher moment, is carried more predominantly by faster particles that collide more quickly than slower particles. One gets a Prandtl number of 2/3 using the linearised Boltzmann collision operator for Maxwell molecules.

XIV. THE MULTIPLE-SCALES CHAPMAN–ENSKOG EXPANSION

The multiple-scales version of the Chapman–Enskog expansion is a systematic approach for finding closed evolution equations for the five conserved moments ρ, $\mathbf{u}$, Θ. Starting with the Boltzmann–BGKW equation for simplicity, we rescale the collision time from τ to $\epsilon\tau$,

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = -\frac{1}{\epsilon\tau}\left(f - f^{(0)}\right), \tag{160}$$

and expand the distribution function f as a power series in ϵ:

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots . \tag{161}$$

If we just do this we get the Hilbert expansion. It becomes disordered after long times when $t \sim 1/\epsilon$, since $\epsilon f^{(1)}$ then becomes comparable to $f^{(0)}$. This is the timescale on which we would expect viscous effects to become significant. Moreover, at each order we get the Euler, or Oseen, fluid equations with forcing terms from lower orders. We never get anything that looks like the Navier–Stokes equations.

To avoid this disordering we use a further multiple-scales expansion of the time derivative. We introduce multiple time variables $t_0 = t$, $t_1 = \epsilon t$, $t_2 = \epsilon^2 t$, and treat f as a function $f(\mathbf{x}, \mathbf{v}, t_0, t_1, t_2, \ldots)$ with t_0, t_1, t_2 etc. treated as independent variables. This is equivalent to expanding the time derivative as

$$\partial_t = \partial_{t_0} + \epsilon\partial_{t_1} + \epsilon^2\partial_{t_2} + \cdots . \tag{162}$$

The different t_m represent natural timescales for different phenomena: t_0 for advection, t_1 for viscous diffusion etc.

However, by expanding both f and t we can represent the same function through different expansions. For example, we can represent $f(t) = \epsilon t$ as either $f_0(t_0, t_1, \ldots) = t_1$ or $f_1(t_0, t_1, \ldots) = t_0$.

To restore uniqueness of the expansion we impose the solvability conditions

$$\int \mathrm{d}\mathbf{v} f^{(n)} = 0, \quad \int \mathrm{d}\mathbf{v}\,\mathbf{v} f^{(n)} = 0, \quad \int \mathrm{d}\mathbf{v}\,\frac{1}{2}|\mathbf{v}|^2 f^{(n)} = 0, \text{ for } n \geq 1, \tag{163}$$

so $f^{(1)}$ and higher do not contribute to the mass, momentum, and energy densities. If we had put the linearised Boltzmann collision operator for Maxwell molecules on the right hand side of (160), these would be exactly the conditions we would need to solve linear systems of the form $\mathsf{L}h = r$. The right-hand side r and the solution h must both be orthogonal to the kernel of L that is spanned by the collision invariants.

It also turns out that these are the right conditions to prevent the appearance of "secular terms" proportional to t_0, t_1, etc. in the expansion. Normally one would find these conditions later as part of the solution, but this conventional to approach to the method of multiple scales relies upon finding the complete closed form solution of the equations at each order. This is not possible when the leading order equations are the Euler equations ...

Substituting the dual expansion into (160) gives

$$\begin{aligned}\left(\partial_{t_0} + \epsilon\partial_{t_1} + \epsilon^2\partial_{t_2} + \cdots\right)\left(f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots\right)& \\ + \mathbf{v}\cdot\boldsymbol{\nabla}\left(f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots\right) &= -\frac{1}{\tau}\left(f^{(1)} + \epsilon f^{(2)} + \cdots\right).\end{aligned} \tag{164}$$

This system balances at $O(\epsilon^{-1})$ because we took $f^{(0)}$ to be a Maxwell–Boltmann distribution.

Collecting terms at the next two orders gives

$$\partial_{t_0} f^{(0)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(0)} = -\frac{1}{\tau} f^{(1)}, \tag{165a}$$

$$\partial_{t_1} f^{(0)} + \partial_{t_0} f^{(1)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(1)} = -\frac{1}{\tau} f^{(2)}. \tag{165b}$$

Taking the five conserved moments of (165a) gives the Euler equations

$$\partial_{t_0}\rho + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}) = 0, \quad \partial_{t_0}(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi}^{(0)} = 0, \quad \partial_{t_0}\Theta + \mathbf{u}\cdot\boldsymbol{\nabla}\Theta + \frac{2}{3}\Theta\boldsymbol{\nabla}\cdot\mathbf{u} = 0. \tag{166}$$

No superscripts are needed on ρ, $\mathbf{u}$, Θ due to the solvability conditions. We can now use (165a) again to solve for $f^{(1)}$:

$$f^{(1)} = -\tau\left(\partial_{t_0} f^{(0)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(0)}\right). \tag{167}$$

We can evaluate the right hand side in terms of ρ, $\mathbf{u}$, Θ and their *spatial* derivatives since

$$f^{(0)} = \frac{\rho/m}{(2\pi\Theta)^{3/2}}\,\exp\left(-\frac{|\mathbf{v}-\mathbf{u}|^2}{2\Theta}\right), \tag{168}$$

and we know $\partial_{t_0}\rho$, $\partial_{t_0}\mathbf{u}$, and $\partial_{t_0}\Theta$ from the Euler equations. At this point we would need the solvability conditions if we had an integral operator on the right hand side of (165a) instead of just $-1/\tau$.

Finally, substituting the resulting expression for $f^{(1)}$ into (165b) and taking the five conserved moments gives $\partial_{t_1}\rho = 0$, evolution under the Navier–Stokes viscous stress for $\partial_{t_1}\mathbf{u}$, and evolution under Fourier's law for $\partial_{t_1}\Theta$. Truncating at this order and reassembling gives

$$\partial_t(\rho\mathbf{u}) = (\partial_{t_0} + \epsilon\partial_{t_1})(\rho\mathbf{u}) = -\boldsymbol{\nabla}\cdot\left(\boldsymbol{\Pi}^{(0)} + \epsilon\boldsymbol{\Pi}^{(1)}\right), \tag{169}$$

and similarly

$$(\partial_{t_0} + \epsilon\partial_{t_1})\,\Theta + \mathbf{u}\cdot\boldsymbol{\nabla}\Theta + \frac{2}{3}\Theta\boldsymbol{\nabla}\cdot\mathbf{u} + \frac{2}{3}\frac{1}{\rho}\boldsymbol{\nabla}\cdot\mathbf{q}^{(1)} = 0, \tag{170}$$

so we recover the compressible Navier–Stokes–Fourier equations for an ideal monatomic gas with $\gamma = 5/3$, no bulk viscosity, and kinetic theorist's Prandtl number again equal to unity from the use of the BGKW collision operator.