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 $\tau_\mathrm{c} \ll$ 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 $d = c_\mathrm{s}\tau_\mathrm{c} \ll$ mean free path $\lambda_\mathrm{mfp} = c_\mathrm{s}\tau \ll$ hydrodynamic lengthscale $L = c_\mathrm{s}T$.

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 $nd^2 = 1/\lambda_\mathrm{mfp}$ fixed.

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

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 (it is not reversible). The Vlasov equation *is* a mean-field theory for the $nd^3 \gg 1$ regime with weak long-range interactions.

Three 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

Three time scales from generic initial conditions: first N-particle, then Boltzmann, then Navier–Stokes are sufficient on successively longer timescales.

Boltzmann equation 1872, Chapman–Enskog expansion 1910s, Bogoliubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy 1935 to 1949.

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 often modelled by Lennard-Jones potentials (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 a bit too soft.

Reality is somewhere between Maxwell molecules and hard spheres.

II. N-PARTICLE HAMILTONIAN MECHANICS

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

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

and Hamilton's equations

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

Rewrite 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, e.g. $\mathcal{F} = t$.

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 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. The ergodic hypothesis says this is the same as taking the average (at a fixed time) over a Gibbs 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 number of 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.

More precisely, 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 $\mathcal{O}(\mathbf{p}, \mathbf{q})$:

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

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.*

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

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

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

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

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

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.

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 only a 2-body interaction potential, heading in the direction 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 contributes 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

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

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 with $nd^3 \to 0$ with $nd^2 = 1/\lambda_{\mathrm{mfp}}$ fixed.

Writing the second member of the hierarchy out in full gives

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

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).

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

$\dfrac{\partial \phi}{\partial \mathbf{q}} \cdot \dfrac{\partial}{\partial \mathbf{p}} \sim \dfrac{1}{\tau_{\mathrm{c}}}$ 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.

f_{s+1}/f_s scales with n, the probability of finding one more particle per unit volume.

However, the integrals on the right hand sides are only nonzero in $O(d^3)$ volumes

The right hand sides thus act on a timescale $\tau = \tau_c/(nd^3) \gg \tau_c$.

The f_1 member of the hierarchy is special though having no τ_c term, a single particle cannot collide with itself, so we keep the f_s "collision" term on its RHS.

We can drop the RHS involving f_3 from the f_2 equation, because it is $nd^3 \ll 1$ smaller than the ϕ term on the LHS.

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 (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

$$\underbrace{\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1}\right]}_{1/T} f_1 = \left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} \equiv \underbrace{\int \mathrm{d}V_2 \frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right) f_2}_{(1/\tau) f_1}. \tag{28}$$

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 special types of solution f_1 that do not evolve on the collisional timescale τ.

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

$$\left[\underbrace{\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{q}_2}}_{\text{notionally } 1/T} - \underbrace{\frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)}_{1/\tau_c}\right] f_2 = 0. \tag{29}$$

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

$$\mathbf{q}_1 = \mathbf{Q} - \frac{1}{2}\mathbf{q}, \quad \mathbf{q}_2 = \mathbf{Q} + \frac{1}{2}\mathbf{q} \tag{30}$$

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

$$\left[\underbrace{\frac{\partial}{\partial t} + \frac{1}{2}\frac{\mathbf{p}_1 + \mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{Q}}}_{1/T} + \underbrace{\frac{\mathbf{p}_2 - \mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}} - \frac{\partial \phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)}_{1/\tau_c}\right] f_2 = 0. \tag{31}$$

We can understand what happens during a collision by treating f_2 as steady on the τ_c timescale (Lagrangian versus Eulerian picture – particles are moving though f_2 is steady). 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 (31) and substituting into (28) gives

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \, \mathrm{d}\mathbf{q}_2 \left(\frac{\mathbf{p}_2 - \mathbf{p}_1}{m}\right) \cdot \frac{\partial}{\partial \mathbf{q}} f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t) \tag{32}$$

Integrating (32) over a sphere of radius 2ℓ satisfying $d \ll \ell \ll \lambda_{\mathrm{mfp}}$ in $\mathbf{q}$ gives

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_S \mathrm{d}S \, \mathbf{n}_S \cdot \mathbf{V} \, f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t), \tag{33}$$

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.)

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

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = G - L \equiv \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t). \tag{34}$$

Boltzmann called these the gain term and the loss term 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 $\mathbf{p}_1'$ and $\mathbf{p}_2'$, so these collisions appear as a loss of particles with momentum $\mathbf{p}_1$. The gain term describes the inverse process under 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 literally "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,

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_1, \mathbf{q}_2, t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{35}$$

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

Two particles with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ before a binary collision will emerge with momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$. Each collision conserves momentum and energy, so

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_1' + \mathbf{p}_2', \tag{36a}$$

$$|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2 = |\mathbf{p}_1'|^2 + |\mathbf{p}_2'|^2. \tag{36b}$$

The solution may be written as

$$\mathbf{p}_1' = \mathbf{p}_1 - m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}, \quad \mathbf{p}_2' = \mathbf{p}_2 + m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}, \tag{37}$$

where $\mathbf{V} = (\mathbf{p}_2 - \mathbf{p}_1)/m$ is the initial relative velocity, and $\mathbf{n}$ is a unit vector. In other words, the magnitude of the relative velocity is preserved, but its orientation is rotated. This defines an invertible transformation, with inverse

$$\mathbf{p}_1 = \mathbf{p}_1' - m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}', \quad \mathbf{p}_2 = \mathbf{p}_2' + m\,\mathbf{n}\,\mathbf{n}\cdot\mathbf{V}', \tag{38}$$

where $\mathbf{V}' = (\mathbf{p}_2' - \mathbf{p}_1')/m$, and $\mathbf{n}\cdot\mathbf{V}' = -\mathbf{n}\cdot\mathbf{V}$ from (37). In this sense the transformation is its own inverse, so it has unit Jacobian. The transformation is also unchanged by reversing the sign of $\mathbf{n}$.

This lets us find an *inverse collision*, a pair of momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$ that become $\mathbf{p}_1$ and $\mathbf{p}_2$ after a collision. We may thus rewrite (35) as

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_2(\mathbf{p}_1', \mathbf{p}_2', \mathbf{q}_1', \mathbf{q}_2', t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{39}$$

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:

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_+} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1', \mathbf{q}_1', t) f_1(\mathbf{p}_2', \mathbf{q}_2', t) - \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}_S \cdot \mathbf{V}|\, f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_2, t). \tag{40}$$

For hard spheres we can just replace $\mathbf{n}_S$ by $\mathbf{n}$, or by $-\mathbf{n}$ in the first integral, and replace $\mathbf{q}_1'$, $\mathbf{q}_2'$ and $\mathbf{q}_2$ by $\mathbf{q}_1$ as suggested above, to get the Boltzmann equation for hard spheres:

$$\left.\frac{\mathrm{d}f_1}{\mathrm{d}t}\right|_{\mathrm{coll}} = \int \mathrm{d}\mathbf{p}_2 \int_{S_-} \mathrm{d}S\, |\mathbf{n}\cdot\mathbf{V}| \left[f_1(\mathbf{p}_1', \mathbf{q}_1, t) f_1(\mathbf{p}_2', \mathbf{q}_1, t) - f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_1, t) \right] \tag{41}$$

More generally, we can absorb the details of the 2-particle collisions by parametrising each hemisphere using r, ϕ coordinates on the disc D perpendicular to the relative velocity $\mathbf{V}$. We write $\mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, 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,

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

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

$$|\mathbf{V} \cdot \mathbf{n}^{(\mathrm{in})}| \mathrm{d}S^{(\mathrm{in})} = V r \, \mathrm{d}r \, \mathrm{d}\phi = B(\theta, V) \, \mathrm{d}\theta \mathrm{d}\phi = V \sigma(\theta, V) \underbrace{\sin\theta \mathrm{d}\theta \mathrm{d}\phi}_{\mathrm{d}S}, \tag{42}$$

so

$$B(\theta, V) = V r \left| \frac{\partial r}{\partial \theta} \right|, \text{ while } \sigma(\theta, V) = \frac{1}{\sin\theta} \, r \left| \frac{\partial r}{\partial \theta} \right|. \tag{43}$$

The latter has dimensions of area.

The Boltzmann equation for general 2-particle collisions is thus

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{q}_1} = \int \mathrm{d}\mathbf{p}_2 \mathrm{d}\theta \mathrm{d}\phi \, B(V, \theta) \left[f_1(\mathbf{p}_1', \mathbf{q}_1, t) f_1(\mathbf{p}_2', \mathbf{q}_1, t) - f_1(\mathbf{p}_1, \mathbf{q}_1, t) f_1(\mathbf{p}_2, \mathbf{q}_1, t) \right], \tag{44}$$

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 ϕ.

For hard spheres with diameter d, the impact parameter $r = d\cos\theta$, so

$$B(\theta, V) = d^2 \, V \sin\theta \cos\theta.$$

Using $\int \mathrm{d}\mathbf{p}_2 \, f_1(\mathbf{p}_2, \mathbf{q}_1, t) = n(\mathbf{q}_1, t)$, the number density, we get a factor of $nd^2 = 1/\lambda_{\mathrm{mfp}}$, a quantity that remains $O(1)$ in the Boltzmann–Grad limit. The RHS of (44) scales as f_1/τ where $\tau = \lambda_{\mathrm{mfp}}/c_{\mathrm{s}}$ using c_{s} as the scale for V.

More generally, the scattering kernel $B(\theta, V)$ for the power-law potential $\phi(|\mathbf{q}_1 - \mathbf{q}_2|) = k|\mathbf{q}_1 - \mathbf{q}_2|^{1-n}$, with $n \notin \{2, 3\}$, takes the separable form

$$B(\theta, V) = V^\alpha \beta(\theta), \text{ where } \alpha = \frac{n-5}{n-1}. \tag{45}$$

The function $\beta(\theta)$ is defined implicitly by

$$\beta(\theta) = (4k/m)^{1/n-1} b \frac{\mathrm{d}b}{\mathrm{d}\theta}, \tag{46}$$

$$\theta = \int_0^{x_0} \left(1 - x^2 - (x/b)^{n-1}\right)^{-1/2} \mathrm{d}x, \tag{47}$$

$$1 - x_0^2 - (x_0/b)^{n-1} = 0, \tag{48}$$

with the asymptotic behaviours

$$\begin{aligned}&\beta(\theta) = O(\theta) \text{ as } \theta \to 0, \\ &\beta(\theta) = O\left[\left(\frac{\pi}{2} - \theta \right)^{(n+1)/(1-n)} \right] \text{ as } \theta \to \pi/2.\end{aligned}$$

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

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

$$f = f(\mathbf{x}, \mathbf{v}, t), \quad f_\star = f(\mathbf{x}, \mathbf{v}_\star, t), \quad f' = f(\mathbf{x}, \mathbf{v}', t), \quad f_\star' = f(\mathbf{x}, \mathbf{v}_\star', t), \tag{49}$$

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 f, so

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f = C[f,f] = \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'f_\star' - ff_\star\right], \tag{50}$$

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

$$\mathbf{v}' = \mathbf{v} - \mathbf{n}\,\mathbf{n}\cdot(\mathbf{v}_\star - \mathbf{v}), \quad \mathbf{v}_\star' = \mathbf{v}_\star + \mathbf{n}\,\mathbf{n}\cdot(\mathbf{v}_\star - \mathbf{v}), \quad \mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta). \tag{51}$$

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

$$C[f,g] = \frac{1}{2}\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'g_\star' + g'f_\star' - fg_\star - gf_\star\right], \tag{52}$$

and its integral

$$\int \mathrm{d}\mathbf{v}\, C[f,g]\,\psi(\mathbf{v}) = \frac{1}{2}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'g_\star' + g'f_\star' - fg_\star - gf_\star\right]\psi(\mathbf{v}). \tag{53}$$

Interchanging the starred and unstarred variables gives

$$\int \mathrm{d}\mathbf{v}\, C[f,g]\,\psi(\mathbf{v}) = \frac{1}{2}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'g_\star' + g'f_\star' - fg_\star - gf_\star\right]\psi(\mathbf{v}_\star). \tag{54}$$

Using (51) and its inverse to swap between dashed and undashed variables gives

$$\int \mathrm{d}\mathbf{v}\, C[f,g]\,\psi(\mathbf{v}) = \frac{1}{2}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[fg_\star + gf_\star - f'g_\star' - g'f_\star'\right]\psi(\mathbf{v}'), \tag{55}$$

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. We can now interchange the starred and unstarred variables again:

$$\int \mathrm{d}\mathbf{v}\, C[f,g]\,\psi(\mathbf{v}) = \frac{1}{2}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[fg_\star + gf_\star - f'g_\star' - g'f_\star'\right]\psi(\mathbf{v}_\star'). \tag{56}$$

Taking the average of these four equivalent expressions,

$$\int \mathrm{d}\mathbf{v}\, C[f,g]\,\psi(\mathbf{v}) = \frac{1}{8}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'g_\star' + g'f_\star' - fg_\star - gf_\star\right]\left[\psi + \psi_\star - \psi' - \psi_\star'\right], \tag{57}$$

and

$$\int \mathrm{d}\mathbf{v}\, C[f,f]\,\psi(\mathbf{v}) = \frac{1}{4}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'f_\star' - ff_\star\right]\left[\psi + \psi_\star - \psi' - \psi_\star'\right]. \tag{58}$$

The expressions (57) and (58) vanish for all f and g if the function ϕ is such that

$$\psi(\mathbf{v}) + \psi(\mathbf{v}_\star) = \psi(\mathbf{v}') + \psi(\mathbf{v}_\star'). \tag{59}$$

Having constructed the transformation (51) to conserve energy and momentum, the only continuous functions ψ satisfying (59) are linear combinations of the five *collision invariants*

$$1, \quad \mathbf{v} = (v_x, v_y, v_z), \quad |\mathbf{v}|^2. \tag{60}$$

The 1 is linked to binary collisions conserving particle number (see later).

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

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

Putting $\phi = \log f$ into (58) gives

$$\int \mathrm{d}\mathbf{v}\, C[f,f]\,\log f = \frac{1}{4}\int \mathrm{d}\mathbf{v} \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'f_\star' - ff_\star\right]\,\log\left(ff_\star/f'f_\star'\right) \leq 0. \tag{61}$$

The integrand is non-positive since

$$(x-y)\log(y/x) \leq 0 \text{ for all } x, y \in \mathbb{R}^+ \tag{62}$$

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

Equality in (61) thus occurs if and only if $ff_\star = f'f'_\star$. Taking logarithms,

$$\log f + \log f_\star = \log f' + \log f'_\star, \tag{63}$$

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

$$\log f(\mathbf{v}) = a + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2, \tag{64}$$

for constant scalars a and c, and a constant vector $\mathbf{b}$. The constant $c < 0$, so that f is integrable over $\mathbf{v}$ (or at least decays to zero as $|\mathbf{v}| \to \infty$) giving

$$f(\mathbf{v}) = A\,\exp(-\beta|\mathbf{v}-\mathbf{u}|^2), \tag{65}$$

for positive scalars A and β, and a constant vector $\mathbf{u}$. This is the *Maxwell–Boltzmann distribution.* It emerges as a property of Boltzmann's binary collision operator.

Looking ahead a little, it is commom to rewrite this as

$$f(\mathbf{v}) = \frac{n}{(2\pi\theta)^{3/2}}\,\exp(-|\mathbf{v}-\mathbf{u}|^2/(2\theta)), \tag{66}$$

where the constants n, $\mathbf{u}$, θ satisfy

$$n = \int \mathrm{d}\mathbf{v}\, f, \tag{67a}$$

$$\mathbf{u} = (1/n)\int \mathrm{d}\mathbf{v}\,\mathbf{v}\, f, \tag{67b}$$

$$\theta = 1/(3n)\int \mathrm{d}\mathbf{v}\,|\mathbf{v}-\mathbf{u}|^2\, f. \tag{67c}$$

These will turn out to be the fluid number density, velocity, and temperature. The mass density is then $\rho = mn$. 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, and R the gas constant, equal to Boltzmann's constant k_B divided by the molecular mass m.

IX. BOLTZMANN'S H-THEOREM

Suppose $f(\mathbf{x}, \mathbf{v}, t)$ is a solution of Boltzmann's equation

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = C[f, f] \tag{68}$$

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

$$\partial_t H + \boldsymbol{\nabla}\cdot\mathbf{J} = S \leq 0, \tag{69}$$

where

$$H(\mathbf{x}, t) = \int \mathrm{d}\mathbf{v}\, f\log f, \quad \mathbf{J} = \int \mathrm{d}\mathbf{v}\,\mathbf{v}\, f\log f, \quad S = \int \mathrm{d}\mathbf{v}\,\log f\, C[f, f]. \tag{70}$$

Integrating (69) over the spatial domain Ω gives Boltzmann's H-theorem:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} \leq \int_{\partial\Omega} \mathbf{J}\cdot\mathbf{n}\,\mathrm{d}S, \text{ where } \mathcal{H} = \int_\Omega H(\mathbf{x}, t)\,\mathrm{d}\mathbf{x}, \tag{71}$$

and $\mathbf{n}$ is the *inward* normal on $\partial\Omega$. The surface integral vanishes for various special/idealised cases: periodic box, specular reflection boundary conditions, infinite space.

X. RELATIVE ENTROPY

The entropy of f relative to another function $f^{(0)}$ is defined by

$$R[f|f^{(0)}] = \int \mathrm{d}\mathbf{v}\, \Big(f \log(f/f^{(0)}) + f^{(0)} - f \Big) \geq 0. \tag{72}$$

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:

$$R[f|f^{(0)}] = \frac{1}{2} \int \mathrm{d}\mathbf{v}\, \frac{\delta f^2}{f_0} + O(\delta f^3). \tag{73}$$

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

$$f \log(f/f^{(0)}) + f^{(0)} - f \geq \frac{1}{\mathrm{e}} \chi\left(\frac{|f - f^{(0)}|}{f^{(0)}} \right) |f - f^{(0)}|, \text{ where } \chi(z) = \min(1, z), \tag{74}$$

so

$$R[f|f^{(0)}] \geq \frac{1}{\mathrm{e}} \left(\int_L \mathrm{d}\mathbf{v}\, |f - f^{(0)}| + \int_S \mathrm{d}\mathbf{v}\, |f - f^{(0)}|^2 / f^{(0)} \right), \tag{75}$$

where

$$L = \{\mathbf{v} : |f - f^{(0)}| > f^{(0)}\}, \text{ and } S = \{\mathbf{v} : |f - f^{(0)}| < f^{(0)}\}. \tag{76}$$

Using the Cauchy–Schwarz inequality on the second term,

$$\int_S \mathrm{d}\mathbf{v}\, |f - f^{(0)}| \leq \left(\int_S \mathrm{d}\mathbf{v}\, |f - f^{(0)}|^2 / f^{(0)} \right)^{1/2} \left(\int_S \mathrm{d}\mathbf{v}\, f^{(0)} \right)^{1/2} \tag{77}$$

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

$$\int \mathrm{d}\mathbf{v}\, |f - f^{(0)}| = \int_L \mathrm{d}\mathbf{v}\, |f - f^{(0)}| + \int_S \mathrm{d}\mathbf{v}\, |f - f^{(0)}| \to 0. \tag{78}$$

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

$$\begin{aligned} R[f|f^{(0)}] &= \int \mathrm{d}\mathbf{v} f \log f - f \log f^{(0)}, & (79)\\ &= \int \mathrm{d}\mathbf{v} f \log f - f^{(0)} \log f^{(0)} + (f^{(0)} - f) \log f^{(0)}, & (80)\\ &= H[f] - H[f^{(0)}] + \int \mathrm{d}\mathbf{v}\, (f^{(0)} - f)(a + \mathbf{b}\cdot\mathbf{v} + c|\mathbf{v}|^2), & (81)\\ &= H[f] - H[f^{(0)}], & (82) \end{aligned}$$

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 (78).

XI. LINEARISED AND MODEL COLLISION OPERATORS

Recall the symmetric bilinear form of Boltzmann's binary collision operator:

$$C[f,g] = \frac{1}{2}\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta)\left[f'g'_\star + g'f'_\star - fg_\star - gf_\star\right]. \tag{83}$$

For small perturbations around a Maxwellian, $f = f^{(0)} + \epsilon f^{(1)} + \cdots$, we define the linearised Boltzmann collision operator by

$$C[f^{(0)} + \epsilon f^{(1)} + \cdots, f^{(0)} + \epsilon f^{(1)} + \cdots] = \overbrace{C[f^{(0)}, f^{(0)}]}^{=0} + \epsilon\left(C[f^{(0)}, f^{(1)}] + C[f^{(1)}, f^{(0)}]\right) + \cdots, \tag{84}$$

$$= 2C[f^{(0)}, \epsilon f^{(1)}] + O(\epsilon^2). \tag{85}$$

It is more common to write $f^{(1)} = hf^{(0)}$, so $f = f^{(0)}(1+h)$, which defines the operator L by

$$2C[f^{(0)}, hf^{(0)}] = L\,h. \tag{86}$$

We can rewrite $C[f,f]$ as ($\mathbf{x}, t$ arguments suppressed)

$$C[f,f] = -f(\mathbf{v})\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta) f_\star + \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta) f' f'_\star, \tag{87}$$

$$= -\nu(\mathbf{v}) f(\mathbf{v}) + \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta) f' f'_\star, \tag{88}$$

in terms of a collision frequency (recall $V = |\mathbf{v} - \mathbf{v}_\star|$)

$$\nu(\mathbf{v}) = \int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta) f_\star. \tag{89}$$

This is a monotonic function of $|\mathbf{v}|$ for rigid spheres, finite range potentials, and potentials with angular cutoff.

Using this definition of $\nu(\mathbf{v})$ we can write

$$L\,h = K\,h - \nu(\mathbf{v})\,h, \tag{90}$$

where the second term is purely multiplicative. Moreover, the operator K so defined is bounded and completely continuous (for any bounded sequence $\{h_n\}$, $\{Kh_n\}$ contains a convergent subsequence). 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 ∞.

The collision frequency for the hard-sphere scattering kernel $B(\theta, V) = d^2\,V \sin\theta\cos\theta$ is

$$\nu(\xi) = \nu_0\left(e^{-\xi^2} + \sqrt{\pi}(\xi + 1/(2\xi))\,\mathrm{erf}(\xi)\right), \tag{91}$$

where

$$\xi = |\mathbf{v}|/\sqrt{2\pi\theta}, \quad \text{and} \quad \nu_0 = nd^2\sqrt{2\pi\theta} = (6\pi/5)^{1/2}\,c_\mathrm{s}/\lambda_\mathrm{mfp}. \tag{92}$$

The limiting behaviours are

$$\nu(0) = 2\nu_0, \quad \text{and} \quad \nu(\xi) \sim \sqrt{\pi} v_0 \xi \text{ as } \xi \to \infty, \tag{93}$$

using

$$\mathrm{erf}(\xi) = \frac{2}{\sqrt{\pi}}\int_0^\xi e^{-s^2}\mathrm{d}s = \frac{2}{\sqrt{\pi}}\left(\xi - \frac{1}{3}\xi^3 + \cdots\right) \text{ for } \xi \ll 1. \tag{94}$$

The collision frequency for Maxwell molecules is a constant, and L has a discrete spectrum with eigenvalues that can be expressed in terms of Legendre polynomials and the earlier $\beta(\theta)$ function. The eigenfunctions are products of spherical harmonics and Sonine polynomials.

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

We calculated the exact expression

$$C[f,f] = -\underbrace{\nu(\mathbf{v})f(\mathbf{v})}_{\text{loss term}} + \underbrace{\int \mathrm{d}\mathbf{v}_\star \int \mathrm{d}\theta\,\mathrm{d}\phi\, B(V,\theta) f' f'_\star}_{\text{gain term}}. \tag{95}$$

If f is close to a Maxwellian $f^{(0)}$ we can linearise by calculating $\nu(\mathbf{v})$ from this Maxwellian. We can also model the gain term with an expression that ensures $f \to f^{(0)}$ under collisions will preserving the collision invariants n, $\mathbf{u}$, θ. This suggests the Boltzmann–BGKW equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f = -\nu_0\left(f - f^{(0)}\right). \tag{96}$$

Replacing $\nu(\mathbf{v})$ by the constant ν_0, and determining the n, $\mathbf{u}$, θ in the $f^{(0)}$ from the conditions

$$n = \int \mathrm{d}\mathbf{v}\, f, \tag{97a}$$

$$\mathbf{u} = (1/n)\int \mathrm{d}\mathbf{v}\,\mathbf{v}\, f, \tag{97b}$$

$$\theta = 1/(3n)\int \mathrm{d}\mathbf{v}\,|\mathbf{v}-\mathbf{u}|^2 f. \tag{97c}$$

ensures that this model collision operator satisfies both the H-theorem and the five conservation properties

$$\int \mathrm{d}\mathbf{v}\, f^{(0)} = \int \mathrm{d}\mathbf{v}\, f, \tag{98a}$$

$$\int \mathrm{d}\mathbf{v}\,\mathbf{v} f^{(0)} = \int \mathrm{d}\mathbf{v}\,\mathbf{v} f, \tag{98b}$$

$$\int \mathrm{d}\mathbf{v}\,|\mathbf{v}|^2 f^{(0)} = \int \mathrm{d}\mathbf{v}\,|\mathbf{v}|^2 f. \tag{98c}$$

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.

XII. DERIVATION OF HYDRODYNAMICS

Multiplying the Boltzmann equation

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = C[f,f], \tag{99}$$

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

$$\partial_t\rho + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}) = 0, \quad \partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} = 0, \quad \partial_t\mathcal{E} + \boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{F}} = 0, \tag{100}$$

for the mass, momentum, and energy densities

$$\rho(\mathbf{x},t) = m\int \mathrm{d}\mathbf{v}\, f(\mathbf{x},\mathbf{v},t), \quad \rho\mathbf{u} = m\int \mathrm{d}\mathbf{v}\,\mathbf{v} f(\mathbf{x},\mathbf{v},t), \quad \mathcal{E} = m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}|\mathbf{v}|^2 f(\mathbf{x},\mathbf{v},t). \tag{101}$$

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

$$\boldsymbol{\Pi} = m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\mathbf{v} f(\mathbf{x},\mathbf{v},t), \quad \boldsymbol{\mathcal{F}} = m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}\mathbf{v}|\mathbf{v}|^2 f(\mathbf{x},\mathbf{v},t). \tag{102}$$

The right hand sides of (100) 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 $\mathbf{v}$,

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

$$m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\partial_t f + m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\mathbf{v}\cdot\boldsymbol{\nabla} f = m\int \mathrm{d}\mathbf{v}\,\mathbf{v}C[f,f],$$

$$\partial_t\left(m\int \mathrm{d}\mathbf{v}\,\mathbf{v} f\right) + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\mathbf{v} f\right) = 0.$$

The three conservation laws (100) 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

$$\mathcal{E} = \frac{1}{2}\mathrm{Tr}\,\boldsymbol{\Pi} \tag{103}$$

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, $\rho\mathbf{u}$, $\mathcal{E}$, are distinguished by evolving on collisional timescales:

$$\partial_t\boldsymbol{\Pi} + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}\mathbf{v}\mathbf{v}\mathbf{v}f(\mathbf{x},\mathbf{v},t)\right) = m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\mathbf{v}C[f,f] \neq 0, \text{ etc.} \tag{104}$$

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.

The momentum conservation equation thus becomes

$$\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}\mathbf{u} + \mathsf{P}) = 0, \tag{105}$$

in terms of the pressure tensor

$$\mathsf{P} = m\int \mathrm{d}\mathbf{v}\,(\mathbf{v}-\mathbf{u})(\mathbf{v}-\mathbf{u})f(\mathbf{x},\mathbf{v},t). \tag{106}$$

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

$$\mathsf{P}^{(0)} = m\int \mathrm{d}\mathbf{v}\,(\mathbf{v}-\mathbf{u})(\mathbf{v}-\mathbf{u})\frac{n}{(2\pi\theta)^{3/2}}\,\exp\left(-\frac{|\mathbf{v}-\mathbf{u}|^2}{2\theta}\right) = \rho\theta\mathsf{I}. \tag{107}$$

The Maxwellian is a function of peculiar velocity, and working solely with velocity differences (as in Boltzmann's collision operator) ensures Galilean invariance.

Putting $\mathsf{P} = \mathsf{P}^{(0)} = \rho\theta\mathsf{I}$ into (105) gives

$$\partial_t(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}\mathbf{u}) + \boldsymbol{\nabla}p = 0. \tag{108}$$

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

$$\rho\frac{\mathrm{D}\mathbf{u}}{\mathrm{D}t} \equiv \rho\left(\partial_t\mathbf{u} + \mathbf{u}\cdot\boldsymbol{\nabla}\mathbf{u}\right) = -\boldsymbol{\nabla}p. \tag{109}$$

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

$$\mathcal{E} = \frac{1}{2}\mathrm{Tr}\,\mathsf{P} = \frac{1}{2}\mathrm{Tr}\,(\rho\mathbf{u}\mathbf{u} + \rho\theta\mathsf{I}) = \frac{1}{2}\rho|\mathbf{u}|^2 + \frac{3}{2}\rho\theta, \tag{110}$$

while 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

$$\mathbf{q}(\mathbf{x},t) = m\frac{1}{2}\int \mathrm{d}\mathbf{v}\,\mathbf{w}|\mathbf{w}|^2 f(\mathbf{x},\mathbf{v},t). \tag{111}$$

This gives the energy equation

$$\partial_t\left(\frac{1}{2}\rho|\mathbf{u}|^2 + \frac{3}{2}\rho\theta\right) + \boldsymbol{\nabla}\cdot\left(\frac{1}{2}\rho\mathbf{u}|\mathbf{u}|^2 + \frac{3}{2}\mathbf{u}\rho\theta + \mathsf{P}\cdot\mathbf{u} + \mathbf{q}\right) = 0, \tag{112}$$

or

$$\frac{3}{2}\rho\frac{\mathrm{D}\theta}{\mathrm{D}t} + \mathsf{P} : \boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\cdot\mathbf{q} = 0. \tag{113}$$

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

$$\frac{3}{2}\rho\frac{\mathrm{D}\theta}{\mathrm{D}t} + \rho\theta\boldsymbol{\nabla}\cdot\mathbf{u} = 0. \tag{114}$$

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

$$\rho\theta\frac{\mathrm{D}s}{\mathrm{D}t} + (\mathsf{P} - \rho\theta\mathsf{I}) : \boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\cdot\mathbf{q} = 0, \tag{115}$$

for the gas-dynamic entropy $s = (3/2)\log(\theta\rho^{-2/3})$ from evaluating Boltzmann's H-function for a Maxwellian. The entropy following a fluid element thus changes only through non-equilibrium effects.

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 $\boldsymbol{\Pi}$,

$$\partial_t\boldsymbol{\Pi} + \boldsymbol{\nabla}\cdot\left(m\int \mathrm{d}\mathbf{v}\,\frac{1}{2}\mathbf{v}\mathbf{v}\mathbf{v}f(\mathbf{x},\mathbf{v},t)\right) = m\int \mathrm{d}\mathbf{v}\,\mathbf{v}\mathbf{v}C[f,f] \neq 0 \tag{116}$$

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

$$\partial_t\left(\rho u_i u_j + P_{ij}\right) + \frac{\partial}{\partial x_k}\left(Q_{ijk} + u_i P_{jk} + u_j P_{ki} + u_k P_{ij} + \rho u_i u_j u_k\right) = m\int \mathrm{d}\mathbf{v}\,v_i v_j C[f,f], \tag{117}$$

where

$$Q_{ijk} = m\int \mathrm{d}\mathbf{v}\,(v_i - w_i)(v_j - w_j)(v_k - w_k)f. \tag{118}$$

We can evaluate the first time derivative on the LHS,

$$\begin{aligned}\partial_t\left(\rho u_i u_j\right) &= u_i\partial_t\left(\rho u_j\right) + u_j\partial_t\left(\rho u_i\right) - u_i u_j\partial_t\rho,\\ &= -u_i\partial_k\left(\rho u_j u_k + P_{jk}\right) - u_j\partial_k\left(\rho u_i u_k + P_{ik}\right) + u_i u_j\partial_k(\rho u_k).\end{aligned} \tag{119}$$

Subtracting gives

$$\partial_t P_{ij} + \partial_k\left(u_k P_{ij} + Q_{ijk}\right) + P_{ik}\frac{\partial u_j}{\partial x_k} + P_{kj}\frac{\partial u_i}{\partial x_k} = m\int \mathrm{d}\mathbf{v}\, w_i w_j C[f,f]. \tag{120}$$

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 term are collision invariants.

Replacing $C[f,f]$ by the BGKW collision operator gives

$$m\int \mathrm{d}\mathbf{v}\, w_i w_j \left(-\nu\left(f - f^{(0)}\right)\right) = -\frac{1}{\tau}\left(\mathsf{P} - \mathsf{P}^{(0)}\right), \tag{121}$$

with $\tau = 1/\nu$. 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

$$\partial_t P_{ij} + \partial_k\left(u_k P_{ij} + Q_{ijk}\right) + P_{ik}\frac{\partial u_j}{\partial x_k} + P_{kj}\frac{\partial u_i}{\partial x_k} = -\frac{1}{\tau}\left(P_{ij} - P_{ij}^{(0)}\right). \tag{122}$$

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

$$\partial_t T_{ij} + \partial_k\left(u_k T_{ij} - Q_{ijk} + \frac{2}{3}q_k\delta_{ij}\right) - \rho\theta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right) + T_{ik}\frac{\partial u_j}{\partial x_k} + T_{kj}\frac{\partial u_i}{\partial x_k} - \frac{2}{3}(\mathsf{T} : \boldsymbol{\nabla}\mathbf{u})\delta_{ij} = -\frac{1}{\tau}T_{ij}, \tag{123}$$

where $q_k = \frac{1}{2}Q_{iik}$ is the contraction of Q on two indices.

[[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

$$\mathsf{T} = \mathsf{T}^{(0)} + \tau\mathsf{T}^{(1)} + \cdots, \mathsf{Q} = \mathsf{Q}^{(0)} + \tau\mathsf{Q}^{(1)} + \cdots \tag{124}$$

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

$$T_{ij}^{(1)} = \tau\rho\theta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right), \tag{125}$$

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).

Applying the same approach of formulating an evolution equation for $\mathbf{q}$ and substituting the leading order approximation for the non-conserved moments gives

$$\mathbf{q}^{(1)} = -\frac{5}{2}\tau\rho\theta\boldsymbol{\nabla}\theta, \tag{126}$$

which is Fourier's law with a kinetic theorist's Prandtl number of unity, due to the 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.

XIV. THE MULTIPLE-SCALES CHAPMAN–ENSKOG EXPANSION

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 $\epsilon\tau$,

$$\partial_t f + \mathbf{v}\cdot\boldsymbol{\nabla} f = -\frac{1}{\epsilon\tau}\left(f - f^{(0)}\right), \tag{127}$$

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

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots . \tag{128}$$

However, this leads to a disordered expansion as $\epsilon f^{(1)}$ becomes comparable to $f^{(0)}$ after long times when $t \sim 1/\epsilon$, which is when we would expect viscous effects to be significant.

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

$$\partial_t = \partial_{t_0} + \epsilon \partial_{t_1} + \epsilon^2 \partial_{t_2} + \cdots . \tag{129}$$

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, *e.g.* we can represent ϵt with $f_0(t_1)$ or with $f_1(t_0)$.

We restore uniqueness of the expansion by imposing the solvability conditions

$$\int \mathrm{d}\mathbf{v} f^{(n)} = 0, \quad \int \mathrm{d}\mathbf{v}\, \mathbf{v} f^{(n)} = 0, \quad \int \mathrm{d}\mathbf{v}\, \frac{1}{2}|\mathbf{v}|^2 f^{(n)} = 0, \text{ for } n \geq 1, \tag{130}$$

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 (127), these would be exactly the conditions we would need to solve linear systems of the form $C[f^{(0)}, f^{(n)}] = \text{RHS}$. The RHS and the solution $f^{(n)}$ must both be orthogonal to the kernel 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 (127) gives

$$\left(\partial_{t_0} + \epsilon\partial_{t_1} + \epsilon^2\partial_{t_2} + \cdots\right)\left(f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots\right) + \mathbf{v}\cdot\boldsymbol{\nabla}\left(f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \cdots\right) = -\frac{1}{\tau}\left(f^{(1)} + \epsilon f^{(2)} + \cdots\right). \tag{131}$$

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

$$\partial_{t_0} f^{(0)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(0)} = -\frac{1}{\tau} f^{(1)}, \tag{132a}$$

$$\partial_{t_1} f^{(0)} + \partial_{t_0} f^{(1)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(1)} = -\frac{1}{\tau} f^{(2)}. \tag{132b}$$

Taking the five conserved moments of (132a) gives the Euler equations

$$\partial_{t_0}\rho + \boldsymbol{\nabla}\cdot(\rho\mathbf{u}) = 0, \quad \partial_{t_0}(\rho\mathbf{u}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi}^{(0)} = 0, \quad \partial_{t_0}\theta + \mathbf{u}\cdot\boldsymbol{\nabla}\theta + \frac{2}{3}\theta\boldsymbol{\nabla}\cdot\mathbf{u} = 0. \tag{133}$$

No superscripts are needed on ρ, $\mathbf{u}$, θ due to the solvability conditions. We can now use (132a) again to solve for $f^{(1)}$:

$$f^{(1)} = -\tau\left(\partial_{t_0} f^{(0)} + \mathbf{v}\cdot\boldsymbol{\nabla} f^{(0)}\right). \tag{134}$$

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

$$f^{(0)} = \frac{\rho/m}{(2\pi\theta)^{3/2}} \exp\left(-\frac{|\mathbf{v}-\mathbf{u}|^2}{2\theta}\right), \tag{135}$$

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 (132a) instead of just $-1/\tau$.

Finally, substituting the resulting expression for $f^{(1)}$ into (132b) 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

$$\partial_t(\rho\mathbf{u}) = \left(\partial_{t_0} + \epsilon\partial_{t_1}\right)(\rho\mathbf{u}) = -\boldsymbol{\nabla}\cdot\left(\boldsymbol{\Pi}^{(0)} + \epsilon\boldsymbol{\Pi}^{(1)}\right), \tag{136}$$

and similarly

$$(\partial_{t_0} + \epsilon\partial_{t_1})\,\theta + \mathbf{u}\cdot\boldsymbol{\nabla}\theta + \frac{2}{3}\theta\boldsymbol{\nabla}\cdot\mathbf{u} + \frac{2}{3}\frac{1}{\rho}\boldsymbol{\nabla}\cdot\mathbf{q}^{(1)} = 0, \tag{137}$$

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.