2. Kinetic equations in statistical mechanics

Section 1 introduced a hierarchy of descriptions through Brownian motion. The complete Brownian particle–fluid system evolves mechanically. On a temporal resolution much longer than the correlation time of the microscopic force, the detailed molecular impacts are no longer resolved, while the Brownian coordinate and momentum remain dynamical variables. On a still coarser resolution, after the momentum has relaxed, the slower positional dynamics can be described without retaining the instantaneous momentum.

The same structure appears in the statistical mechanics of an interacting many-particle system, but the variables are now distribution functions rather than the state of a single distinguished particle. The microscopic description uses the complete N-particle state and the full N-particle probability density. The kinetic description uses reduced one- and few-particle distributions, especially the one-particle distribution $f_1(\mathbf{r}, \mathbf{p}, t)$. At still longer scales, after local equilibration, the slow variables are macroscopic fields such as local number density $n(\boldsymbol{r}, t)$, flow velocity $\boldsymbol{u}(\boldsymbol{r}, t)$ and temperature $T(\boldsymbol{r}, t)$. This hierarchy of microscopic, kinetic and hydrodynamic stages was formulated systematically in Bogoliubov's 1946 work *Problems of a Dynamical Theory in Statistical Physics*.

The physical time scales can be estimated explicitly for a dilute gas. Let d be the molecular interaction range and v_{th} a typical thermal speed. For a molecular diameter

$$d \sim 3.5 \times 10^{-10}\ \mathrm{m}$$

and

$$v_{\mathrm{th}} \sim 5 \times 10^{2}\ \mathrm{m\,s^{-1}},$$

the duration of a binary encounter is of order

$$\tau_{\mathrm{int}} \sim \mathrm{d}/\mathrm{v_{th}} \sim 7 \times 10^{-13}\ \mathrm{s} \sim 10^{-12}\ \mathrm{s}.$$

The mean-free time is much longer. At room temperature and atmospheric pressure, a representative mean free path in air is

$$\lambda \sim 7 \times 10^{-8}\ \mathrm{m},$$

so

$$\boxed{\tau_{\mathrm{mfp}} \sim \frac{\lambda}{v_{\mathrm{th}}} \sim 1.4 \times 10^{-10}\ \mathrm{s}.}$$

The mean-free time is the microscopic scale that controls local equilibration. Let τ_{loc} denote the relaxation time over which collisions drive the local momentum distribution toward a local Maxwell form. For a dilute gas, $\tau_{loc} \sim \tau_{mfp}$; several collisions may be required, so the two quantities need not be numerically identical. For order-of-magnitude estimates, both are of order 10^{-10} s.

$$onset\ of\ a\ reduced\ regime \quad \neq \quad relaxation\ time\ within\ that\ regime$$

Once $t \gtrsim \tau_{loc}$, the local momentum distribution is approximately Maxwellian and a hydrodynamic description becomes possible. This onset time must be distinguished from the longer macroscopic hydrodynamic evolution time τ_H, over which the fields $\boldsymbol{n}(\boldsymbol{r}, t)$, $\boldsymbol{u}(\boldsymbol{r}, t)$ and $\boldsymbol{T}(\boldsymbol{r}, t)$ vary appreciably. The time τ_H is not a molecular constant; it depends on the macroscopic length L and on the process under consideration. For $L = 1\ mm$, an acoustic traversal time is

$$\tau_{\mathrm{ac}} \sim \frac{L}{c_s} \sim \frac{10^{-3}}{3.4 \times 10^{2}}\ \mathrm{s} \sim 3 \times 10^{-6}\ \mathrm{s},$$

whereas a viscous diffusion time in air, using $\nu \sim 1.5 \times 10^{-5}\ \mathrm{m^2 s^{-1}}$, is

$$\tau_\nu \sim \frac{L^2}{\nu} \sim 7 \times 10^{-2}\ \text{s}.$$

Thus the macroscopic hydrodynamic evolution time is process-dependent, but its separation from the molecular and local-equilibration times is large:

$$\tau_{\text{int}} \sim 10^{-12}\ \text{s} \ll \tau_{\text{loc}} \sim \tau_{\text{mfp}} \sim 10^{-10}\ \text{s} \ll \tau_{\text{H}}$$

with τ_H ranging from microseconds upward for millimetre-scale disturbances, depending on whether the relevant macroscopic process is acoustic, viscous, thermal or diffusive.

These are intrinsic physical times of the system. They must be distinguished from the temporal resolution chosen for a reduced description. The analogue of the first Brownian coarse-graining is a kinetic resolution Δt_{kin} satisfying

$$\tau_{\text{int}} \ll \Delta t_{\text{kin}} \ll \tau_{\text{loc}}$$

On this resolution, the detailed force history during one binary encounter is not resolved. A collision may be represented by the change from incoming to outgoing momenta, while the slower kinetic relaxation of the one-particle distribution remains resolved. After local Maxwellisation, a hydrodynamic description can use a still coarser resolution,

$$\tau_{\text{loc}} \ll \Delta t_{\text{hyd}} \ll \tau_{\text{H}}$$

At this resolution the local-Maxwellisation process itself is no longer resolved. The momentum dependence of the one-particle distribution is already constrained near a local Maxwell form, while the hydrodynamic fields $n(\boldsymbol{r}, t)$ (number density), $\boldsymbol{u}(\boldsymbol{r}, t)$ (hydrodynamics flow field) and $T(\boldsymbol{r}, t)$ (local temprature) continue to evolve on the longer time τ_H.

The reduction from the full N-particle distribution to the reduced distributions $f_1, f_2, \ldots$ must not be confused with this temporal coarse-graining. The reduced distributions are obtained exactly by integrating over particle coordinates. The BBGKY hierarchy that follows from this operation is still an exact consequence of Liouville dynamics. Time-scale separation becomes essential later, when the hierarchy is closed and a kinetic equation for f_1 is obtained.

The present subsection begins before any such reduction or coarse-graining. We first establish the exact microscopic and statistical dynamics of the complete N-particle system.

2.1 N-particle microstates and their time evolution

We begin with the microscopic level of the hierarchy described above. No kinetic approximation is introduced in this subsection, and no temporal coarse-graining is applied to the equations derived below. The purpose is to identify precisely what the complete microscopic state is, how it evolves, and how a probability distribution over complete microscopic states is transported by the same Hamiltonian dynamics.

Microscopic state and phase-space flow

Consider N identical classical particles of mass m. At a given time t, a complete microscopic state is specified by the positions and momenta of all particles,

$$\boxed{\Gamma = (\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N).}$$

The symbol Γ denotes one point in a $6N$-dimensional phase space. If the microscopic state changes with time, the corresponding point moves through phase space and traces a trajectory $\Gamma(t)$.

For a Hamiltonian system,

$$H_N = H_N(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t),$$

the trajectory is determined by Hamilton's equations,

$$\boxed{\dot{\mathbf{r}}_i = \frac{\partial H_N}{\partial \mathbf{p}_i}, \qquad \dot{\mathbf{p}}_i = -\frac{\partial H_N}{\partial \mathbf{r}_i}, \qquad i = 1, \dots, N.}$$

For particles moving in an external potential U_{ext} and interacting through a pair potential Φ, a common Hamiltonian is

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} U_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \Phi(\mathbf{r}_i - \mathbf{r}_j).$$

Hamilton's equations then give

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m},$$

and

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\text{ext}} + \sum_{j \neq i} \mathbf{F}_{ij},$$

where

$$\mathbf{F}_i^{\text{ext}} = -\nabla_i U_{\text{ext}}(\mathbf{r}_i), \qquad \mathbf{F}_{ij} = -\nabla_i \Phi(\mathbf{r}_i - \mathbf{r}_j).$$

The equations of motion assign a $6N$-dimensional velocity vector to every point of phase space. We write this compactly as

$$\boxed{\dot{\Gamma} = \dot{\Gamma}(\Gamma, t).}$$

This notation does not introduce a new dynamical law. It combines all $3N$ equations for the positions and all $3N$ equations for the momenta into one phase-space equation.

Starting from a microscopic state Γ_0 at time t_0,

$$\frac{d\Gamma}{dt} = \dot{\Gamma}(\Gamma, t), \qquad \Gamma(t_0) = \Gamma_0,$$

determines the subsequent trajectory. For a time-independent Hamiltonian, the solution may be written as

$$\boxed{\Gamma(t) = \Phi_{t-t_0}(\Gamma_0).}$$

The map Φ_t is the phase-space flow. For every allowed initial point, it returns the phase-space point reached after an elapsed time t. In particular,

$$\Phi_0(\Gamma_0) = \Gamma_0.$$

For autonomous dynamics the flow satisfies

$$\boxed{\Phi_{t+s} = \Phi_t \circ \Phi_s.}$$

Evolving first for a time s and then for a time t gives the same microscopic state as evolving once for the total time $t + s$. Because the Hamiltonian equations define a unique trajectory both forward and backward in time,

$$\boxed{\Phi_t^{-1} = \Phi_{-t}.}$$

This inverse-flow statement should be distinguished from the operation of time reversal. If the Hamiltonian is invariant under reversal of all momenta, then the trajectory obtained from the state

$$(\mathbf{r}_1, \dots, \mathbf{r}_N, -\mathbf{p}_1, \dots, -\mathbf{p}_N)$$

retraces the original trajectory in the opposite temporal direction. Thus microscopic reversibility concerns the complete N-particle state, not only a selected subset of particle variables.

The notation $\Gamma(t) = \Phi_{t-t_0}(\Gamma_0)$ therefore represents the solution of Hamilton's equations for every possible initial condition. The collection of all such trajectories forms a flow through phase space.

Why introduce an N-particle distribution function?

If the exact initial point Γ_0 were known, Hamilton's equations would determine one microscopic trajectory completely. A macroscopic system contains an enormous number of microscopic coordinates. For $N \sim 10^{23}$, specifying one initial microstate would require of order 6×10^{23} position and momentum components.

The problem is not only the number of variables. A macroscopic preparation fixes quantities such as particle number, volume, energy, temperature or density, but it does not select one exact point in the $6N$-dimensional phase space. Many microscopic states are compatible with the same preparation.

Statistical mechanics therefore describes the preparation by a probability density over complete microscopic states. We introduce the normalized N-particle distribution

$$\boxed{\rho_N(\Gamma, t).}$$

The quantity

$$\rho_N(\Gamma, t)\, d\Gamma$$

is the probability that the microscopic state lies inside the infinitesimal phase-space volume element

$$\boxed{d\Gamma = \prod_{i=1}^{N} d^3 r_i\, d^3 p_i}$$

around the point Γ. The normalization is

$$\boxed{\int \rho_N(\Gamma, t)\, d\Gamma = 1.}$$

The distribution ρ_N may be interpreted in two equivalent ways. It may represent incomplete specification of the actual microscopic state of one prepared system, or it may describe an ensemble of identically prepared systems whose microscopic initial conditions differ from one realization to another. In both interpretations, ρ_N is a distribution over complete N-particle microstates.

Two objects must therefore be kept distinct:

- $\Gamma(t)$ is one microscopic trajectory in the $6N$-dimensional phase space.
- $\rho_N(\Gamma, t)$ is a probability density defined over the entire phase space.

Hamilton's equations transport each microscopic state along its phase-space trajectory. The remaining task is to determine how the probability density over those trajectories evolves.

Conservation of probability in phase space

Take a fixed region Ω of the $6N$-dimensional phase space. Here Ω does not move with the phase-space flow: its boundary is held at fixed phase-space coordinates while microscopic trajectories may cross it.

The probability that the microscopic state lies inside Ω at time t is

$$P_\Omega(t) = \int_\Omega \rho_N\,(\Gamma, t)\, d\Gamma.$$

Probability can leave or enter this fixed region only when phase-space trajectories cross its boundary $\partial\Omega$. The probability current in phase space is therefore

$$\boxed{\mathbf{J}_\Gamma = \rho_N \dot{\Gamma}.}$$

Here both $\mathbf{J}_\Gamma$ and $\dot{\Gamma}$ are $6N$-dimensional vectors. The outward probability flux through the boundary is

$$\oint_{\partial\Omega} \rho_N \, \dot{\Gamma} \cdot d\mathbf{S}_\Gamma.$$

Hence probability conservation gives

$$\frac{dP_\Omega}{dt} = -\oint_{\partial\Omega} \rho_N \, \dot{\Gamma} \cdot d\mathbf{S}_\Gamma.$$

Using the divergence theorem in $6N$ dimensions,

$$\oint_{\partial\Omega} \rho_N \, \dot{\Gamma} \cdot d\mathbf{S}_\Gamma = \int_\Omega \nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right) d\Gamma,$$

where

$$\nabla_\Gamma = \left(\nabla_{\mathbf{r}_1}, \ldots, \nabla_{\mathbf{r}_N}, \nabla_{\mathbf{p}_1}, \ldots, \nabla_{\mathbf{p}_N}\right).$$

Because Ω itself does not move,

$$\frac{dP_\Omega}{dt} = \int_\Omega \frac{\partial \rho_N}{\partial t} \, d\Gamma.$$

Combining the last three relations,

$$\int_\Omega \left[\frac{\partial \rho_N}{\partial t} + \nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right)\right] d\Gamma = 0.$$

Since the fixed region Ω is arbitrary, the integrand must vanish pointwise:

$$\boxed{\frac{\partial \rho_N}{\partial t} + \nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right) = 0.}$$

This is the continuity equation for probability in phase space. Its structure is the same as the ordinary-space continuity equation

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{v}) = 0,$$

but the flow now takes place in the full $6N$-dimensional phase space.

Hamiltonian phase-space flow is incompressible

The continuity equation derived above is valid for a general deterministic phase-space flow. Hamiltonian dynamics has the additional property that its flow is incompressible in canonical phase space.

The divergence of the phase-space velocity field is

$$\nabla_\Gamma \cdot \dot{\Gamma} = \sum_{i=1}^{N} \left[\nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i\right].$$

Using Hamilton's equations,

$$\nabla_\Gamma \cdot \dot{\Gamma} = \sum_i \left[\nabla_{\mathbf{r}_i} \cdot \frac{\partial H_N}{\partial \mathbf{p}_i} - \nabla_{\mathbf{p}_i} \cdot \frac{\partial H_N}{\partial \mathbf{r}_i}\right].$$

Writing all Cartesian components explicitly,

$$\nabla_\Gamma \cdot \dot{\Gamma} = \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \left[\frac{\partial^2 H_N}{\partial r_{i\alpha}\, \partial p_{i\alpha}} - \frac{\partial^2 H_N}{\partial p_{i\alpha}\, \partial r_{i\alpha}} \right].$$

For a sufficiently smooth Hamiltonian, mixed derivatives commute,

$$\frac{\partial^2 H_N}{\partial r_{i\alpha}\, \partial p_{i\alpha}} = \frac{\partial^2 H_N}{\partial p_{i\alpha}\, \partial r_{i\alpha}},$$

so each pair cancels and

$$\boxed{\nabla_\Gamma \cdot \dot{\Gamma} = 0.}$$

The statement applies to Hamiltonian dynamics expressed in canonical coordinates. It is not a general property of every deterministic mechanical equation. A dissipative phase-space flow can have a nonzero divergence.

Why zero divergence implies conservation of phase-space volume

The equation

$$\nabla_\Gamma \cdot \dot{\Gamma} = 0$$

is a local statement. We now show explicitly how it leads to conservation of the volume of a material region that moves with the Hamiltonian flow.

Let

$$\Gamma(t) = \Phi_t(\Gamma_0)$$

and consider two nearby initial states Γ_0 and $\Gamma_0 + \delta\Gamma_0$. For sufficiently small $\delta\Gamma_0$, their separation at time t is

$$\delta\Gamma(t) \simeq M(t)\, \delta\Gamma_0,$$

where

$$\boxed{M(t) = \frac{\partial \Gamma(t)}{\partial \Gamma_0}}$$

is the $6N \times 6N$ matrix that linearizes the flow around Γ_0.

A small phase-space parallelepiped is formed by $6N$ independent separation vectors. Under the linear transformation M, its volume is multiplied by the determinant of M. We therefore write

$$d\Gamma(t) = J(t)\, d\Gamma(0),$$

with

$$\boxed{J(t) = \det M(t) = \det\left(\frac{\partial \Gamma(t)}{\partial \Gamma_0} \right).}$$

At $t = 0$, the flow map is the identity, so

$$M(0) = I, \qquad J(0) = 1.$$

To determine the evolution of J, write the $6N$ components of the phase-space velocity as $\dot{\Gamma}_a(\Gamma)$, with $a = 1, \ldots, 6N$. The elements of M are

$$M_{ab}(t) = \frac{\partial \Gamma_a(t)}{\partial \Gamma_{0b}}.$$

Differentiate with respect to time:

$$\dot{M}_{ab} = \frac{\partial \dot{\Gamma}_a}{\partial \Gamma_{0b}}.$$

The phase-space velocity depends on the initial condition through the current point $\Gamma(t)$. The chain rule therefore gives

$$\dot{M}_{ab} = \sum_c \frac{\partial \dot{\Gamma}_a}{\partial \Gamma_c} \frac{\partial \Gamma_c}{\partial \Gamma_{0b}}.$$

Define

$$A_{ac} = \frac{\partial \dot{\Gamma}_a}{\partial \Gamma_c}.$$

Then, in matrix form,

$$\boxed{\dot{M} = AM.}$$

Jacobi's formula for the derivative of a determinant gives

$$\frac{dJ}{dt} = J \,\mathrm{Tr}\left(M^{-1}\dot{M}\right),$$

or equivalently

$$\frac{1}{J}\frac{dJ}{dt} = \mathrm{Tr}\left(M^{-1}\dot{M}\right).$$

Using $\dot{M} = AM$,

$$\mathrm{Tr}\left(M^{-1}\dot{M}\right) = \mathrm{Tr}(M^{-1}AM).$$

The trace is invariant under a similarity transformation, therefore

$$\mathrm{Tr}(M^{-1}AM) = \mathrm{Tr}(A).$$

By the definition of A,

$$\mathrm{Tr}(A) = \sum_a \frac{\partial \dot{\Gamma}_a}{\partial \Gamma_a} = \nabla_\Gamma \cdot \dot{\Gamma}.$$

Hence

$$\boxed{\frac{1}{J}\frac{dJ}{dt} = \nabla_\Gamma \cdot \dot{\Gamma}.}$$

For Hamiltonian flow the divergence vanishes, so

$$\frac{dJ}{dt} = 0.$$

Because $J(0) = 1$,

$$\boxed{J(t) = 1.}$$

Therefore

$$\boxed{d\Gamma(t) = d\Gamma(0).}$$

A material region of phase space can stretch, shear and fold as it evolves, but its total $6N$-dimensional volume is unchanged. This is the phase-volume form of Liouville's theorem.

The fixed region Ω used to derive the continuity equation and the material region used here play different roles. The first is held fixed while probability flows through its boundary. The second moves with the Hamiltonian trajectories and is used to establish conservation of phase-space volume.

Liouville equation for the N-particle distribution

Return to the phase-space continuity equation,

$$\frac{\partial \rho_N}{\partial t} + \nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right) = 0.$$

Expanding the divergence gives

$$\nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right) = \dot{\Gamma} \cdot \nabla_\Gamma \rho_N + \rho_N \nabla_\Gamma \cdot \dot{\Gamma}.$$

Hamiltonian incompressibility gives

$$\nabla_\Gamma \cdot \dot{\Gamma} = 0,$$

so

$$\boxed{\frac{\partial \rho_N}{\partial t} + \dot{\Gamma} \cdot \nabla_\Gamma \rho_N = 0.}$$

The total derivative of ρ_N along a phase-space trajectory is

$$\frac{d\rho_N}{dt} = \frac{\partial \rho_N}{\partial t} + \dot{\Gamma} \cdot \nabla_\Gamma \rho_N.$$

Therefore

$$\boxed{\frac{d\rho_N}{dt} = 0.}$$

Follow one phase-space trajectory $\Gamma(t)$. The value of the probability density carried by that trajectory remains constant. The distribution may deform strongly in phase space because neighbouring trajectories separate, stretch and fold the region occupied by the ensemble, but the fine-grained density is conserved along each Hamiltonian trajectory.

The same equation can be written in Poisson-bracket form. For two phase-space functions $A(\Gamma)$ and $B(\Gamma)$, define

$$\{A, B\} = \sum_{i=1}^{N} \left[\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i}\right].$$

Then the Liouville equation is

$$\boxed{\frac{\partial \rho_N}{\partial t} + \{\rho_N, H_N\} = 0.}$$

For a time-independent Hamiltonian, the solution can be written directly in terms of the phase-space flow. To find the probability density at the phase-space point Γ at time t, follow that point backward under the Hamiltonian flow to the point from which it originated at time t_0:

$$\boxed{\rho_N(\Gamma, t) = \rho_N\left(\Phi_{-(t-t_0)}(\Gamma), t_0\right).}$$

This equation does not mean that the physical trajectory itself runs backward. It is simply the solution of the advection equation: the probability density observed at the current point is the density that was attached to the same material phase-space element at the initial time.

What exactly does the Liouville equation determine?

The microscopic and statistical descriptions answer different questions.

Hamilton's equations, together with the Hamiltonian H_N and one exact initial point Γ_0, determine one microscopic trajectory,

$$\Gamma_0 \to \Gamma(t).$$

The Liouville equation, together with the same Hamiltonian and an initial distribution $\rho_N(\Gamma, t_0)$, determines how the complete probability density over microscopic states evolves,

$$\rho_N(\Gamma, t_0) \to \rho_N(\Gamma, t).$$

The Liouville equation does not specify the microscopic forces by itself. Those forces are contained in the Hamiltonian. It also does not choose one particular microscopic trajectory unless the initial microscopic state is specified.

If the initial microstate is known exactly, it can be represented formally by the distribution

$$\rho_N(\Gamma, t_0) = \delta^{(6N)}(\Gamma - \Gamma_0).$$

The Liouville equation transports this delta distribution along the Hamiltonian trajectory:

$$\boxed{\rho_N(\Gamma, t) = \delta^{(6N)}\left[\Gamma - \Phi_{t-t_0}(\Gamma_0)\right].}$$

Thus the statistical description contains the deterministic trajectory as a limiting case. When the preparation specifies a finite region of possible microstates rather than one exact point, the initial distribution has a finite extent in phase space and the Liouville equation transports the entire distribution.

Given H_N and $\rho_N(\Gamma, t_0)$, the Liouville equation is a closed first-order evolution equation for the full N-particle probability density. Under the usual regularity assumptions, no additional statistical equation is needed to determine its subsequent fine-grained evolution.

At the level of the complete N-particle distribution there is no collision integral, no kinetic closure and no temporal coarse-graining. The evolution is reversible and phase-space volume preserving. The relaxation equations introduced later describe reduced quantities after a hierarchy of variables and time scales has been used.

Liouville dynamics and the problem of relaxation

The Liouville equation gives the exact evolution of the full N-particle distribution,

$$\frac{d\rho_N}{dt} = \frac{\partial \rho_N}{\partial t} + \dot{\Gamma} \cdot \nabla_\Gamma \rho_N = 0.$$

This statement requires a precise interpretation. It does **not** mean that $\rho_N(\Gamma, t)$ is independent of time at a fixed point Γ of phase space. It means that the value of the fine-grained distribution carried by a phase-space element remains constant while that element moves with the Hamiltonian flow:

$$\rho_N(\Gamma(t), t) = \rho_N(\Gamma_0, 0).$$

To examine whether the exact density approaches equilibrium, let $\rho_N^{\mathrm{eq}}(\Gamma)$ be a stationary equilibrium density for the same Hamiltonian. This density also satisfies the Liouville equation and remains constant along each Hamiltonian trajectory. The difference between $\rho_N(\Gamma, t)$ and $\rho_N^{\mathrm{eq}}(\Gamma)$ therefore remains constant along that trajectory. Changing the integration variable from $\Gamma(t)$ to Γ_0, and using conservation of phase-space volume, gives

$$\int d\Gamma \, |\rho_N(\Gamma, t) - \rho_N^{\mathrm{eq}}(\Gamma)| = \int d\Gamma_0 \, |\rho_N(\Gamma_0, 0) - \rho_N^{\mathrm{eq}}(\Gamma_0)|.$$

If the initial distribution differs from equilibrium, this total difference remains positive and unchanged. Hamiltonian evolution moves the regions in which the density exceeds or falls below its equilibrium value, preserving the magnitude of these deviations. Macroscopic relaxation therefore cannot be identified with a decrease of this total difference between the exact densities.

The shapes of these regions nevertheless change. The Hamiltonian flow changes the shape of a material region while preserving its $6N$-dimensional volume. The region can become elongated and develop narrow folds, so that different density values occur over progressively smaller separations in phase space. The deformation can bring phase space elements with different density values

increasingly close together. Each moving element retains its value of ρ_N, so the difference between their densities remains unchanged even as their separation in phase space decreases.

To describe what is resolved at finite phase-space resolution, divide phase space into cells of volume $\Delta\Gamma$. A coarse-grained distribution may be defined by averaging the fine-grained density over one such cell,

$$\overline{\rho}_N(\Gamma, t \mid \Delta\Gamma) = \frac{1}{\Delta\Gamma}\int_{\Delta\Gamma(\Gamma)} \rho_N(\Gamma', t)\, d\Gamma'.$$

Here $\Delta\Gamma(\Gamma)$ denotes a cell centred on the phase-space point Γ. The cell size $\Delta\Gamma$ specifies the phase-space resolution of the description; it is not a new microscopic dynamical variable. When the variations become much finer than the cell size, regions of different density contribute to the same average. A cell average approaches its equilibrium average when the positive and negative deviations from equilibrium increasingly cancel in the integral over that cell. The exact density can still differ from equilibrium at individual points inside the cell. Liouville's equation remains satisfied: each moving phase space element retains its density, while the average over a fixed cell changes as elements with different density values enter and leave it.

The two statements are therefore compatible:

$$\boxed{\frac{d\rho_N}{dt} = 0 \quad \text{along Hamiltonian trajectories}}$$

and

$$\boxed{\overline{\rho}_N(\Gamma, t \mid \Delta\Gamma) \quad \text{may relax at finite resolution.}}$$

The first refers to the exact fine-grained distribution carried by the microscopic flow. The second refers to a description in which phase-space structures below the chosen resolution are not distinguished. Relaxation at this level therefore does not require a violation of the microscopic Hamiltonian equations or of Liouville's theorem.

The same distinction appeared in Brownian motion in a simpler form. There, the full particle-plus-medium dynamics remained mechanical, whereas a description that did not resolve the rapid microscopic degrees of freedom exhibited relaxation of the retained variables. In the present many-particle problem, the exact N-particle distribution plays the role of the fully resolved statistical description; relaxation becomes visible only after one specifies which structures or variables are not resolved by the description.

The phase-space coarse-graining introduced here must also be distinguished from the temporal coarse-graining used later in kinetic and hydrodynamic descriptions. Averaging over a phase-space cell $\Delta\Gamma$ suppresses structures of ρ_N that have become finer than the chosen phase-space resolution. Temporal coarse-graining instead chooses a time-resolution window between separated physical relaxation times. The two operations serve related purposes because both omit unresolved structure, but they are mathematically different.

One further distinction is needed before introducing kinetic equations. The phase-space coarse-graining above is **not** the same operation as constructing reduced distribution functions. The one-particle distribution

$$f_1(1, t) = N\int d2 \cdots dN\, \rho_N(1,2, \ldots, N, t)$$

is obtained by integrating over the coordinates and momenta of the remaining $N - 1$ particles. This is an exact marginalisation of the full distribution, not an averaging over a finite phase-space cell. The same statement applies to $f_2, f_3, \ldots$.

Consequently, the hierarchy of reduced distributions obtained from the Liouville equation is still exact. No irreversible collision term has yet been introduced. The kinetic approximation enters only later, when physical assumptions about separated relaxation times and the evolution of

interparticle correlations allow this exact hierarchy to be closed in terms of a smaller set of distributions.

From the exact N-particle description to kinetic theory

The full distribution $\rho_N(\Gamma, t)$ is exact but depends on $6N$ phase-space variables. For a macroscopic system it is not a useful object for direct calculation or measurement. The hierarchy of relaxation processes also indicates that the slower stages of the evolution should not require the full microscopic information.

The first reduction is made by integrating over particles that are not explicitly retained. The one-particle distribution will be defined schematically as

$$f_1(1,t) = N\int d2 \cdots dN\, \rho_N(1,2,\dots,N,t),$$

and the two-particle distribution as

$$f_2(1,2,t) = N(N-1)\int d3 \cdots dN\, \rho_N(1,2,\dots,N,t).$$

These definitions reduce the number of explicit particle variables, but they do not yet introduce irreversibility or time coarse-graining. When the Liouville equation is integrated in the same way, the exact equation for f_1 contains f_2, the exact equation for f_2 contains f_3, and so on. This is the BBGKY hierarchy.

The physical time-scale separation introduced at the beginning of Section 2 enters at the next step. For gas, let τ_{loc} denote the local-equilibration time. It is of the order of the mean free-flight time, $\tau_{loc} \sim \tau_{mfp}$, while the duration of an individual interaction satisfies

$$\tau_{\mathrm{int}} \ll \tau_{\mathrm{loc}}$$

A kinetic temporal resolution satisfying

$$\tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}$$

does not resolve the detailed force history inside an individual collision. The collision can be represented by its net scattering effect on the incoming momenta. At the same time, the slower change of the one-particle distribution remains resolved. This is the many-particle analogue of choosing a Brownian resolution long compared with the microscopic force-correlation time but short compared with momentum relaxation.

After local Maxwellisation, $t \gtrsim \tau_{loc}$, a further coarse description becomes possible:

$$\tau_{\mathrm{loc}} \ll \Delta t_{\mathrm{hyd}} \ll \tau_{\mathrm{H}}$$

At this resolution the fast relaxation of the detailed momentum dependence is no longer resolved. The one-particle distribution f_1 is approximately local-Maxwellian, while its low-order moments remain slow. The natural variables are then the hydrodynamic fields

$$n(\mathbf{r},t), \qquad \mathbf{u}(\mathbf{r},t), \qquad T(\mathbf{r},t).$$

The corresponding spatial coarse-graining must satisfy

$$\lambda_{\mathrm{mfp}} \ll \Delta x_{\mathrm{hyd}} \ll \mathrm{L}$$

where λ_{mfp} is the mean free path and L is the characteristic macroscopic length over which the hydrodynamic fields vary.

The resulting hierarchy of descriptions is therefore

$$\boxed{\rho_N(\Gamma,t) \;\rightarrow\; \{f_1, f_2, \dots\} \;\rightarrow\; f_1 \;\rightarrow\; \{n, \mathbf{u}, T\}.}$$

The first arrow is an exact reduction by integration over particle variables. The second requires a physical closure of the BBGKY hierarchy and produces a kinetic equation. The third becomes possible after local equilibration on the time τ_{loc} and uses the separation between that local-relaxation scale and the much slower hydrodynamic evolution time τ_H.

Section 2.2 will first identify the exact structure of the equation for the one-particle distribution. Section 2.3 will then derive the BBGKY hierarchy and make the closure problem explicit. Only after that exact structure is established will the Boltzmann and Vlasov equations be introduced as different physical reductions of the many-particle dynamics.

Summary of Section 2.1

A complete microscopic state of an N-particle Hamiltonian system is one point

$$\Gamma = (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$$

in a $6N$-dimensional phase space. Hamilton's equations generate the phase-space flow

$$\Gamma(t) = \Phi_{t-t_0}(\Gamma_0).$$

A preparation that does not specify one exact microscopic point is described by the normalized N-particle probability density $\rho_N(\Gamma, t)$. Conservation of probability in a fixed phase-space region gives

$$\frac{\partial \rho_N}{\partial t} + \nabla_\Gamma \cdot \left(\rho_N \dot{\Gamma}\right) = 0.$$

Hamiltonian flow is incompressible,

$$\nabla_\Gamma \cdot \dot{\Gamma} = 0,$$

and therefore preserves material phase-space volume,

$$d\Gamma(t) = d\Gamma(0).$$

The probability density satisfies the Liouville equation,

$$\boxed{\frac{d\rho_N}{dt} = 0,}$$

or equivalently

$$\boxed{\frac{\partial \rho_N}{\partial t} + \{\rho_N, H_N\} = 0.}$$

This is an exact, closed and reversible statistical description once the Hamiltonian and the initial N-particle distribution are specified. No kinetic approximation has entered.

The next stage is to derive exact equations for reduced one- and few-particle distributions. The need for a kinetic approximation appears only when one asks for a closed equation for the slower variables, especially f_1. The hierarchy of intrinsic times

$$\tau_{\text{int}} \ll \tau_{\text{loc}} \ll \tau_{\text{H}}$$

with $\tau_{loc} \sim \tau_{mfp}$, together with the corresponding choice of kinetic and hydrodynamic resolutions, provides the physical basis for those later reductions.

2.2 General structure of a kinetic equation for the one-particle distribution function

Section 2.1 described the complete N-particle system by the normalized distribution $\rho_N(\Gamma, t)$ in the full $6N$-dimensional phase space. That description is exact, but most observables of interest do not require the simultaneous specification of all N particles. We now make the first exact reduction of the many-particle description.

The reduction introduced here must be distinguished from the phase-space coarse-graining discussed at the end of Section 2.1. We do not average ρ_N over a finite cell of phase space, and we

do not introduce a temporal resolution window. Instead, we integrate over particle variables that are not retained explicitly. This operation is an exact marginalisation of the full distribution.

Exact reduction to the one-particle distribution

For compactness, denote the one-particle phase-space coordinates of particle i by

$$\boxed{i \equiv (\mathbf{r}_i, \mathbf{p}_i), \qquad di \equiv d^3 r_i \, d^3 p_i.}$$

The one-particle distribution is defined by

$$\boxed{f_1(1,t) = N \int d2 \cdots dN \, \rho_N(1,2,\dots,N,t).}$$

The factor N is chosen so that f_1 counts particles rather than being normalized to unity. Since

$$\int d1 \cdots dN \, \rho_N(1,\dots,N,t) = 1,$$

we have

$$\boxed{\int d1 \, f_1(1,t) = N.}$$

Therefore

$$f_1(\mathbf{r},\mathbf{p},t) \, d^3 r \, d^3 p$$

is the mean number of particles whose positions lie inside $d^3 r$ around $\mathbf{r}$ and whose momenta lie inside $d^3 p$ around $\mathbf{p}$ at time t. If a probability density for one randomly selected particle were required instead, it would be f_1/N.

The operation

$$\rho_N \to f_1$$

contains no kinetic approximation. The function f_1 is an exact marginal of ρ_N. The operation is nevertheless not invertible: knowledge of f_1 does not determine the full N-particle distribution and does not determine the interparticle correlations contained in it. This loss of information about correlations is a consequence of retaining only one-particle variables, not of any kinetic closure.

Physical information contained in f_1

Many local macroscopic quantities are moments of the one-particle distribution.

The local number density is

$$\boxed{n(\mathbf{r},t) = \int d^3 p \, f_1(\mathbf{r},\mathbf{p},t).}$$

The local mean velocity $\mathbf{u}(\mathbf{r},t)$ is defined by

$$\boxed{n(\mathbf{r},t) \, \mathbf{u}(\mathbf{r},t) = \int d^3 p \, \frac{\mathbf{p}}{m} \, f_1(\mathbf{r},\mathbf{p},t).}$$

Introduce the peculiar velocity, the particle velocity measured relative to the local mean flow,

$$\boxed{\mathbf{c} = \frac{\mathbf{p}}{m} - \mathbf{u}(\mathbf{r},t).}$$

The kinetic part of the internal-energy density is

$$\varepsilon_{\text{kin}}(\mathbf{r},t) = \int d^3 p \, \frac{mc^2}{2} \, f_1(\mathbf{r},\mathbf{p},t).$$

For a locally isotropic monatomic gas this defines the kinetic temperature through

$$\boxed{\frac{3}{2} n k_B T = \int d^3 p \, \frac{mc^2}{2} \, f_1.}$$

The kinetic pressure tensor and the kinetic heat flux are also moments of f_1,

$$P_{\alpha\beta}^{\mathrm{kin}} = m\int d^3p\, c_\alpha c_\beta f_1,$$

$$\mathbf{q}^{\mathrm{kin}} = \int d^3p\, \frac{mc^2}{2}\, \mathbf{c}\, f_1.$$

Thus f_1 determines the local density, mean flow, kinetic temperature and kinetic transport fluxes. Quantities that depend explicitly on the simultaneous state of two or more particles cannot, in general, be reconstructed from f_1 alone. The exact description of those quantities, and the hierarchy of reduced many-particle distributions that they require, begins in Section 2.3.

Collisionless evolution of the one-particle distribution

We first determine the evolution of f_1 when the particles do not interact with one another. This step isolates the part of a kinetic equation that comes from one-particle Hamiltonian motion.

Write the Hamiltonian as

$$H_N = H_0 + H_{\mathrm{int}},$$

with

$$H_0 = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + U_{\mathrm{ext}}(\mathbf{r}_i, t)\right].$$

For the moment set

$$H_{\mathrm{int}} = 0.$$

The Liouville equation then becomes

$$\frac{\partial \rho_N}{\partial t} + \sum_{i=1}^{N}\left[\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i}\rho_N + \mathbf{F}_i^{\mathrm{ext}}\cdot\nabla_{\mathbf{p}_i}\rho_N\right] = 0,$$

where

$$\mathbf{F}_i^{\mathrm{ext}} = -\nabla_{\mathbf{r}_i} U_{\mathrm{ext}}(\mathbf{r}_i, t).$$

Multiply this equation by N and integrate over the variables of particles $2, \dots, N$. The time derivative gives

$$N\int d2\cdots dN\, \frac{\partial \rho_N}{\partial t} = \frac{\partial f_1}{\partial t}.$$

The terms containing the variables of particle 1 give

$$N\int d2\cdots dN\, \frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1}\rho_N = \frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1} f_1,$$

and

$$N\int d2\cdots dN\, \mathbf{F}_1^{\mathrm{ext}}\cdot\nabla_{\mathbf{p}_1}\rho_N = \mathbf{F}_1^{\mathrm{ext}}\cdot\nabla_{\mathbf{p}_1} f_1.$$

For each $i = 2, \dots, N$, the corresponding terms vanish after integration because they are total divergences in the variables being integrated out. For example,

$$\int d^3r_i\, \frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i}\rho_N$$

is a boundary term in coordinate space, and

$$\int d^3p_i\, \mathbf{F}_i^{\mathrm{ext}}\cdot\nabla_{\mathbf{p}_i}\rho_N$$

is a boundary term in momentum space. We assume boundary conditions for which these contributions vanish.

The one-particle distribution therefore satisfies

$$\boxed{\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f_1 + \mathbf{F}^{\text{ext}} \cdot \nabla_{\mathbf{p}} f_1 = 0.}$$

This is the collisionless one-particle Liouville equation. It contains three distinct processes: local change of f_1, streaming through coordinate space, and acceleration through momentum space by the external force.

It is convenient to define the one-particle streaming operator

$$\boxed{\mathcal{L}_1 \equiv \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} + \mathbf{F}^{\text{ext}} \cdot \nabla_{\mathbf{p}}.}$$

Then collisionless evolution is simply

$$\boxed{\mathcal{L}_1 f_1 = 0.}$$

This equation transports the one-particle distribution through phase space but contains no mechanism by which interparticle encounters can change the population of a given one-particle phase-space element.

General structure of the kinetic equation

A real gas contains interparticle interactions. On the one-particle level their effect is represented by an additional term that changes the population of one-particle phase-space elements. We therefore write the general kinetic structure as

$$\boxed{\mathcal{L}_1 f_1 = \mathcal{I}_1(\mathbf{r}, \mathbf{p}, t),}$$

or explicitly,

$$\boxed{\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f_1 + \mathbf{F}^{\text{ext}} \cdot \nabla_{\mathbf{p}} f_1 = \mathcal{I}_1.}$$

At this stage $\mathcal{I}_1$ is a notation for the change of the one-particle distribution caused by interactions. It has not yet been derived from the N-particle dynamics, and it should not be assumed to be a functional of f_1 alone.

For a small one-particle phase-space element $d^3r\, d^3p$,

$$\mathcal{I}_1(\mathbf{r}, \mathbf{p}, t)\, d^3r\, d^3p$$

is the net rate at which interactions change the mean number of particles in that element. For a local binary-collision description this is the difference between particles scattered into and particles scattered out of the momentum element at position $\mathbf{r}$.

There is no universal form of $\mathcal{I}_1$. Its structure depends on the interaction mechanism and on the level of description. In the Boltzmann equation it becomes a binary-collision integral. In a mean-field description the collective interaction is more naturally incorporated into an effective force on the left-hand side, leading to a Vlasov-type equation. Other physical mechanisms lead to other kinetic operators.

For a number-conserving local collision term,

$$\boxed{\int d^3p\, \mathcal{I}_1(\mathbf{r}, \mathbf{p}, t) = 0.}$$

If the collision term describes elastic collisions among identical particles and the interaction contribution has been assigned entirely to $\mathcal{I}_1$, consistency with local conservation of momentum and kinetic energy requires the corresponding collisional moments to vanish,

$$\int d^3p\, \mathbf{p}\, \mathcal{I}_1 = 0,$$

$$\int d^3p\, \frac{p^2}{2m}\, \mathcal{I}_1 = 0.$$

These constraints do not determine the collision term. They state what any admissible local elastic-collision model must preserve.

A simple relaxation-time model

Before deriving the microscopic interaction term, it is useful to see the simplest closed model that has the required tendency toward local equilibrium. Let

$$f_{\mathrm{LE}}(\mathbf{r},\mathbf{p},t) = n(\mathbf{r},t)\left(\frac{1}{2\pi m k_B T(\mathbf{r},t)}\right)^{3/2} \exp\left[-\frac{(\mathbf{p}-m\mathbf{u}(\mathbf{r},t))^2}{2mk_BT(\mathbf{r},t)}\right]$$

be the local Maxwell distribution constructed from the same local density, mean velocity and temperature as f_1.

The relaxation-time approximation replaces the interaction term by

$$\boxed{\mathcal{J}_1^{(R)} = -\frac{f_1 - f_{\mathrm{LE}}}{\tau_R}.}$$

The parameter τ_R is a model relaxation time. It is not a new stage in the time-scale hierarchy. For a dilute gas close to local equilibrium its order is set by the collisional relaxation scale,

$$\boxed{\tau_R \sim \tau_{\mathrm{loc}} \sim \tau_{\mathrm{mfp}}.}$$

Because f_{LE} is constructed with the same n, $\mathbf{u}$ and T as f_1, the differences of their first three collision invariants vanish:

$$\int d^3p\,(f_1 - f_{\mathrm{LE}}) = 0,$$
$$\int d^3p\,\mathbf{p}\,(f_1 - f_{\mathrm{LE}}) = 0,$$
$$\int d^3p\,\frac{p^2}{2m}(f_1 - f_{\mathrm{LE}}) = 0.$$

The relaxation model therefore preserves particle number, momentum and kinetic energy under the assumptions stated above.

For a spatially uniform system without an external force, and with a time-independent equilibrium distribution f_{eq}, the model reduces to

$$\frac{\partial f_1}{\partial t} = -\frac{f_1 - f_{\mathrm{eq}}}{\tau_R}.$$

Hence

$$\boxed{f_1(t) - f_{\mathrm{eq}} = \left[f_1(0) - f_{\mathrm{eq}}\right]\exp(-t/\tau_R).}$$

This exponential law is a phenomenological representation of relaxation near equilibrium. It does not derive the microscopic collision dynamics. Its usefulness is that it makes explicit what a closed kinetic equation must accomplish: streaming and external forces transport f_1 through one-particle phase space, while interactions drive its non-equilibrium part toward the appropriate local equilibrium form.

Where the time-scale separation enters

The exact marginalisation

$$\rho_N \to f_1$$

and the collisionless equation $\mathcal{L}_1 f_1 = 0$ do not require temporal coarse-graining. The kinetic description of collisions does.

For the dilute-gas hierarchy fixed in Section 2.1,

$$\boxed{\tau_{\mathrm{int}} \ll \tau_{\mathrm{loc}} \ll \tau_H, \qquad \tau_{\mathrm{loc}} \sim \tau_{\mathrm{mfp}}.}$$

A kinetic temporal resolution is chosen such that

$$\boxed{\tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}.}$$

The detailed continuous force history during one molecular encounter is then unresolved, while the slower change of the one-particle distribution remains resolved. Interactions can therefore be represented by their accumulated effect on f_1 rather than by following the internal mechanical trajectory of every binary encounter.

The relaxation-time model above represents this slow kinetic relaxation with a single parameter τ_R of order τ_{loc}. A microscopic kinetic theory must instead determine the interaction term from the underlying many-particle dynamics and specify which correlations are retained or neglected.

After local Maxwellisation, a hydrodynamic description becomes possible. The subsequent hydrodynamic resolution satisfies

$$\tau_{\mathrm{loc}} \ll \Delta t_{\mathrm{hyd}} \ll \tau_H,$$

with the corresponding spatial condition

$$\lambda_{\mathrm{mfp}} \ll \Delta x_{\mathrm{hyd}} \ll L.$$

At that stage the detailed momentum dependence of f_1 is fast relative to the macroscopic evolution, while its low-order moments n, $\mathbf{u}$ and T remain slow.

Why Section 2.3 is needed

The general kinetic equation

$$\mathcal{L}_1 f_1 = \mathcal{J}_1$$

has identified where interparticle interactions enter the one-particle description, but it has not determined $\mathcal{J}_1$ from the exact N-particle dynamics. The relaxation-time expression is one possible phenomenological closure, not a microscopic derivation.

Section 2.3 returns to the exact Liouville equation with the interparticle interaction restored. It introduces the reduced two-, three- and higher-particle distributions and derives the BBGKY hierarchy. The first equation of that hierarchy shows explicitly which two-particle information is required to determine the exact evolution of f_1. The hierarchy itself remains exact and reversible. Kinetic approximations such as the Boltzmann or mean-field closures enter only after this exact structure has been established.

The division between the present subsection and Section 2.3 is therefore precise:

Section 2.2:	one-particle variables and the general structure of a kinetic equation,
Section 2.3:	exact many-particle origin of the interaction term and the closure problem.

2.3 BBGKY hierarchy and the closure problem

The **Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy** consists of coupled evolution equations for the one particle, two particle and higher distribution functions.

Section 2.2 introduced the one-particle distribution $f_1(1,t)$ and wrote its general kinetic equation in the form

$$\mathcal{L}_1 f_1 = \mathcal{J}_1.$$

The streaming operator $\mathcal{L}_1$ was obtained directly from one-particle Hamiltonian motion, whereas the interaction term $\mathcal{I}_1$ was left unspecified. We now restore the interparticle interaction in the full N-particle Liouville equation and determine the exact origin of this term.

The result is not yet a closed kinetic equation for f_1. The exact evolution of f_1 requires the two-particle distribution f_2; the evolution of f_2 requires the three-particle distribution f_3; and the same structure continues up to the full N-particle distribution. This chain of exact coupled equations is the BBGKY hierarchy.

Reduced s-particle distribution functions

We use the compact notation introduced in Section 2.2,

$$i \equiv (\mathbf{r}_i, \mathbf{p}_i), \qquad di \equiv d^3 r_i \, d^3 p_i.$$

The full N-particle probability density is normalized according to

$$\int d1 \cdots dN \, \rho_N(1, \dots, N, t) = 1.$$

For $1 \le s \le N$, define the reduced s-particle distribution by

$$\boxed{f_s(1, \dots, s, t) = \frac{N!}{(N-s)!} \int d(s+1) \cdots dN \, \rho_N(1, \dots, N, t).}$$

The combinatorial factor is chosen so that f_s counts ordered s-tuples of particles. Its normalization is

$$\boxed{\int d1 \cdots ds \, f_s(1, \dots, s, t) = \frac{N!}{(N-s)!}.}$$

Thus

$$f_s(1, \dots, s, t) \, d1 \cdots ds$$

is the mean number of ordered s-tuples whose one-particle states lie in the corresponding phase-space elements. In particular,

$$\int d1 \, f_1(1, t) = N,$$

and

$$\int d1 \, d2 \, f_2(1,2, t) = N(N-1).$$

Successive members of the hierarchy satisfy an exact consistency relation. Integrating f_{s+1} over the state of particle $s+1$ gives

$$\boxed{\int d(s+1) \, f_{s+1}(1, \dots, s+1, t) = (N-s) f_s(1, \dots, s, t).}$$

For $s = N$ no variables remain to be integrated out, and

$$f_N(1, \dots, N, t) = N! \; \rho_N(1, \dots, N, t).$$

The complete set $f_1, f_2, \dots, f_N$ is equivalent to the original N-particle distribution because, as the preceding equation shows, its highest member is exactly N! times the original N-particle density. All lower reduced distributions are then obtained by integration. If only a particular f_s is retained and higher members are discarded, the reduced description no longer contains the full N-particle statistics.

First equation of the hierarchy

Consider the Hamiltonian

$$H_N = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + U_{\text{ext}}(\mathbf{r}_i, t) \right] + \frac{1}{2} \sum_{i \neq j} \Phi\left(\mathbf{r}_i - \mathbf{r}_j\right),$$

and define

$$\mathbf{F}_i^{\text{ext}} = -\nabla_{\mathbf{r}_i} U_{\text{ext}}(\mathbf{r}_i, t), \qquad \mathbf{F}_{ij} = -\nabla_{\mathbf{r}_i} \Phi\big(\mathbf{r}_i - \mathbf{r}_j\big).$$

For a pair potential, Newton's third law gives

$$\mathbf{F}_{ji} = -\mathbf{F}_{ij}.$$

The Liouville equation is

$$\frac{\partial \rho_N}{\partial t} + \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \nabla_{\mathbf{r}_i} \rho_N + \sum_{i=1}^{N} \left(\mathbf{F}_i^{\text{ext}} + \sum_{j \neq i} \mathbf{F}_{ij} \right) \cdot \nabla_{\mathbf{p}_i} \rho_N = 0.$$

To obtain the equation for f_1, multiply this equation by N and integrate over $d2 \cdots dN$. The time derivative, streaming term and external-force term for particle 1 give the one-particle streaming operator already derived in Section 2.2,

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} + \mathbf{F}_1^{\text{ext}} \cdot \nabla_{\mathbf{p}_1} \right] f_1(1, t).$$

Terms that contain derivatives with respect to the variables of particles 2, … , N are integrated over those same variables. For example, a momentum derivative with respect to particle 2 becomes a boundary term after integration over the full momentum space of particle 2; it vanishes when the full N-particle density tends to zero sufficiently rapidly as the magnitude of particle 2's momentum tends to infinity. Spatial derivative terms vanish for periodic boundaries, or when there is no probability flux through the system boundary. The same argument applies to every integrated particle.

The new contribution comes from the force exerted on particle 1 by all other particles,

$$N \sum_{j=2}^{N} \int d2 \cdots dN \, \mathbf{F}_{1j} \cdot \nabla_{\mathbf{p}_1} \rho_N.$$

We assume that the N-particle distribution is symmetric under exchange of particle labels, as appropriate for identical classical particles. After relabelling the dummy integration variables, the term with j = 2 therefore has the same value as the terms with j = 3, ..., N. There are $N - 1$ equal contributions, hence

$$N(N-1) \int d2 \cdots dN \, \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} \rho_N.$$

Using the definition of f_2,

$$f_2(1,2,t) = N(N-1) \int d3 \cdots dN \, \rho_N,$$

we obtain the exact first BBGKY equation,

$$\boxed{\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} + \mathbf{F}_1^{\text{ext}} \cdot \nabla_{\mathbf{p}_1} \right] f_1(1, t) = -\int d2 \, \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} f_2(1,2,t).}$$

Comparison with the general kinetic equation of Section 2.2 identifies the exact interaction term as

$$\boxed{\mathcal{J}_1(1, t) = -\int d2 \, \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} f_2(1,2,t).}$$

This expression is exact. It is not the Boltzmann collision integral. The interaction term depends on the simultaneous statistical state of a pair of particles, represented by f_2.

Why the one-particle distribution is not closed

The appearance of f_2 has a direct physical origin. The instantaneous force acting on a particle at state $1 = (\mathbf{r}_1, \mathbf{p}_1)$ depends on where the other particles are. Knowledge of $f_1(1, t)$ specifies the

population of one-particle states, but it does not specify how the state of particle 1 is correlated with the state of a second particle.

The function

$$f_2(1,2,t)$$

is the mean number of ordered particle pairs for which one particle lies near state 1 and the second lies near state 2. It therefore specifies how the occurrence of one-particle state 1 is statistically related to the occurrence of one-particle state 2. The exact rate at which interactions change f_1 cannot, in general, be calculated from f_1 alone.

To determine f_2, we must derive its own evolution equation.

Equation for the two-particle distribution

Multiply the Liouville equation by $N(N-1)$ and integrate over $d3\cdots dN$. The streaming and external-force terms of particles 1 and 2 remain explicit. Their mutual interaction also remains explicit because neither particle is integrated out.

The force between particles 1 and 2 contributes

$$\mathbf{F}_{12}\cdot\nabla_{\mathbf{p}_1}f_2+\mathbf{F}_{21}\cdot\nabla_{\mathbf{p}_2}f_2.$$

Since $\mathbf{F}_{21}=-\mathbf{F}_{12}$, this becomes

$$\mathbf{F}_{12}\cdot\left(\nabla_{\mathbf{p}_1}-\nabla_{\mathbf{p}_2}\right)f_2.$$

Particle 1 interacts not only with particle 2 but also with particles 3, ..., N, and the same is true for particle 2. After the states of particles 3, ..., N are integrated out, the force exerted by one additional particle requires the simultaneous distribution of particles 1, 2 and that third particle. This is f_3. Define the complete two-particle Liouville operator

$$\boxed{\mathcal{L}_2=\frac{\partial}{\partial t}+\sum_{i=1}^{2}\left[\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i}+\mathbf{F}_i^{\text{ext}}\cdot\nabla_{\mathbf{p}_i}\right]+\mathbf{F}_{12}\cdot\left(\nabla_{\mathbf{p}_1}-\nabla_{\mathbf{p}_2}\right).}$$

The exact equation for f_2 can then be written without suppressing any force contribution,

$$\boxed{\mathcal{L}_2 f_2(1,2,t)=-\int d3\left[\mathbf{F}_{13}\cdot\nabla_{\mathbf{p}_1}+\mathbf{F}_{23}\cdot\nabla_{\mathbf{p}_2}\right]f_3(1,2,3,t).}$$

Thus the two-particle distribution is not closed either: its exact evolution requires the three-particle distribution.

General BBGKY hierarchy

Repeating the same reduction for an arbitrary s gives the hierarchy

$$\boxed{\mathcal{L}_s f_s=-\sum_{i=1}^{s}\int d(s+1)\,\mathbf{F}_{i,s+1}\cdot\nabla_{\mathbf{p}_i}f_{s+1},\qquad 1\le s<N.}$$

To display every contribution explicitly, separate this operator into a one-particle part and a retained pair-interaction part,

$$\boxed{\mathcal{L}_s=\mathcal{L}_s^{(0)}+\mathcal{L}_s^{(\text{pair})}.}$$

The one-particle part is

$$\boxed{\mathcal{L}_s^{(0)}=\frac{\partial}{\partial t}+\sum_{i=1}^{s}\left[\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i}+\mathbf{F}_i^{\text{ext}}\cdot\nabla_{\mathbf{p}_i}\right],}$$

and the mutual interactions among the retained particles are

$$\boxed{\mathcal{L}_s^{(\mathrm{pair})} = \sum_{1\le i<j\le s} \mathbf{F}_{ij}\cdot\left(\nabla_{\mathbf{p}_i} - \nabla_{\mathbf{p}_j}\right).}$$

The first operator contains explicit time dependence, one-particle streaming and acceleration by external forces. The second contains all pair interactions among the s particles whose states are retained explicitly. Each retained particle also interacts with all N-s particles whose states have been integrated out. Because these unretained particles are identical and the N-particle distribution is permutation symmetric, their combined contribution can be written as one integral over the state labelled s+1; the factor N-s is already contained in the normalization of f_{s+1}.

The hierarchy has the structure

$$\boxed{f_1 \leftarrow f_2, \qquad f_2 \leftarrow f_3, \qquad \ldots, \qquad f_{N-1} \leftarrow f_N.}$$

The arrows in this expression indicate dependence of one evolution equation on the next distribution. They do not represent a sequence in physical time.

The hierarchy terminates at $f_N = N!\,\rho_N$. If every equation is retained, the description remains exact and contains the same information as the original Liouville equation.

What the hierarchy has achieved

The BBGKY construction has reorganized the N-particle dynamics according to the number of particles that are described explicitly. It has not yet produced a closed equation for f_1.

Three properties must be kept separate.

First, the reduction

$$\rho_N \to f_s$$

is an exact procedure. No time averaging and no finite phase-space cell have been introduced.

Second, the complete hierarchy remains reversible because it is derived exactly from the Liouville equation. No irreversible collision law has yet been introduced.

Third, a kinetic equation for f_1 requires a closure: the influence of f_2 must be expressed using the variables retained at the one-particle level. The physical content of a kinetic approximation lies in this closure step.

Pair correlations and statistical independence

Suppose, as a reference case, that the states of two distinct particles are statistically independent. The probability density for one randomly selected particle is f_1/N. The joint probability density for two independently selected distinct particles is the product of the two one-particle probabilities. Since there are N(N-1) ordered pairs of distinct particles, the corresponding ordered-pair distribution is

$$N(N-1)\frac{f_1(1,t)}{N}\frac{f_1(2,t)}{N} = \frac{N-1}{N} f_1(1,t) f_1(2,t).$$

The factor (N-1)/N appears because the one-particle distribution is normalized to N, whereas the two-particle distribution is normalized to N(N-1), the number of ordered pairs of distinct particles. This factor follows from the chosen normalization; it is not an additional physical correlation.

It is therefore useful to write the exact two-particle distribution as

$$\boxed{f_2(1,2,t) = \frac{N-1}{N} f_1(1,t) f_1(2,t) + g_2(1,2,t),}$$

where g_2 is the two-particle correlation function. It measures the difference between the actual pair distribution and the pair distribution that would result from statistically independent particles. With the normalizations defined above, it satisfies

$$\boxed{\int d2\, g_2(1,2,t) = 0.}$$

The integral identity above is only a normalization condition. It does not imply that the two-particle correlation function vanishes for each pair of states. Positive and negative deviations from the independent-particle reference distribution can cancel when the state of particle 2 is integrated over.

Statistical independence is the much stronger pointwise condition $g_2 = 0$ for every pair of one-particle states 1 and 2. In that case the exact factorized pair distribution is the one written above. For a system containing N particles, and in the macroscopic limit $N \gg 1$,

$$\frac{N-1}{N} \simeq 1,$$

the normalization factor approaches unity, and the independent-particle pair distribution is commonly written as

$$f_2(1,2,t) \simeq f_1(1,t) f_1(2,t).$$

For an interacting system, this factorisation is generally not exact. Interactions can make f_2 differ from the independent-particle product, and that difference is represented by g_2.

Weakening of correlations and the closure problem

For a dilute system with short-range or effectively screened interactions, away from a critical point, correlations produced by a local interaction decay as the particle separation increases. If two particles are separated by a distance much larger than the characteristic correlation length ℓ_{corr}, their joint distribution approaches the statistically independent form,

$$\boxed{|\mathbf{r}_1 - \mathbf{r}_2| \gg \ell_{\mathrm{corr}} \quad \Rightarrow \quad f_2(1,2,t) \to \frac{N-1}{N} f_1(1,t) f_1(2,t).}$$

This is a boundary condition on the correlations, not a statement that f_2 factorises at all separations. Particles that are interacting, or that have recently interacted, can be strongly correlated.

Immediately after a nonequilibrium state is prepared, the two-particle, three-particle, and higher reduced distributions can contain correlations fixed independently by the initial preparation. Bogoliubov's kinetic hypothesis assumes that this separate memory of the initial higher-order correlations disappears on a microscopic correlation time. At later times the higher distributions still contain correlations, but those correlations are determined primarily by the current, more slowly evolving one-particle distribution. One then writes schematically,

$$\boxed{f_s(1,\ldots,s,t) \simeq \mathcal{F}_s[\, f_1(t)\,], \qquad s \geq 2,}$$

where the functional $\mathcal{F}_s$ depends on the interaction regime and on the approximation being used. This relation is not a consequence of the exact BBGKY hierarchy. It is an additional kinetic assumption used to close the hierarchy.

Relation to the time-scale hierarchy

The time scales introduced in Sections 1 and 2.1 clarify when such a closure can be useful. For a dilute gas with short-range interactions,

$$\boxed{\tau_{\mathrm{int}} \ll \tau_{\mathrm{loc}} \ll \tau_H, \qquad \tau_{\mathrm{loc}} \sim \tau_{\mathrm{mfp}}.}$$

A binary encounter lasts only for the microscopic interaction time τ_{int}. The mean interval between successive encounters of a given particle is the much longer mean-free-flight time introduced in Section 2.1, and local relaxation of the one-particle distribution occurs on the comparable kinetic scale τ_{loc}. The separation

$$\tau_{\mathrm{int}} \ll \tau_{\mathrm{loc}}$$

means that a temporal resolution chosen between these two scales does not resolve the continuous force and detailed trajectory during a short encounter. The encounter can instead be represented by the relation between the incoming and outgoing momenta, while the slower evolution of f_1 remains resolved.

The exact BBGKY equations themselves do not require any temporal coarse-graining. Temporal coarse-graining enters only when a kinetic closure is introduced: instead of evolving the higher reduced distributions with independent initial data, the approximation expresses their relevant correlations through the current one-particle distribution and no longer resolves structures that evolve on times shorter than the chosen kinetic resolution. In the notation fixed in Section 2.1, the kinetic resolution satisfies

$$\boxed{\tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}.}$$

This is the many-particle analogue of the first temporal coarse-graining used for Brownian motion in Section 1.

Two routes from BBGKY

The decomposition

$$f_2 = \frac{N-1}{N} f_1 f_1 + g_2$$

shows why different interaction regimes lead to different kinetic equations.

For long-range interactions, the force exerted by many particles can remain important even when pair correlations are weak. Substituting the factorised part of f_2 into the first BBGKY equation replaces the exact pair-force term by an average over the states of the other particles: the pair force is integrated against their one-particle distribution, and the resulting average force acts on particle 1. This is a self-consistent mean field because the same one-particle distribution determines both the force and the particles that evolve in that force. Neglecting the correlation correction g_2 at leading order produces a Vlasov-type kinetic equation. The detailed derivation will be given later.

For a dilute gas with short-range interactions, the important change of momentum occurs during isolated binary encounters. The pair correlation generated during an encounter cannot be discarded. The Boltzmann closure instead assumes statistical independence for the *incoming* particles before a collision, follows the binary encounter, and allows the outgoing particles to be correlated. Molecular chaos is therefore a condition imposed on the distribution of pre-collision pairs. It is not the statement that $f_2 = f_1 f_1$ throughout the collision.

The two limiting routes can therefore be written separately as

$$\boxed{\text{long-range collective interactions} \;\rightarrow\; \text{mean-field closure} \;\rightarrow\; \text{Vlasov equation},}$$

and

$$\boxed{\text{short-range binary encounters} \;\rightarrow\; \text{binary-collision closure} \;\rightarrow\; \text{Boltzmann equation}.}$$

Both begin from the same exact BBGKY hierarchy. The hierarchy is therefore the exact bridge between microscopic Hamiltonian dynamics and the kinetic equations developed in the following subsections. The next step is to specify the physical assumptions appropriate to a dilute gas and derive the Boltzmann collision term from binary encounters.

2.4 The Boltzmann kinetic equation

Section 2.3 established that the exact evolution of the one particle distribution depends on the pair distribution. With the notation defined there, the first BBGKY equation reads

$$\mathcal{L}_1 f_1(1,t) = \mathcal{J}_1(1,t) = -\int d2\, \mathrm{F}_{12} \cdot \nabla_{\mathrm{p}_1} f_2(1,2,t). \tag{2.4.1}$$

The operator $\mathcal{L}_1$ contains the time derivative, streaming and acceleration by the external force. The integral on the right describes the effect of interparticle forces. Since F_{12} is appreciable during a collision, this integral requires the pair distribution at the separations where the two particles interact.

For a dilute gas, we can calculate the effect of collisions by following the mean number of particles in a small momentum element. A collision removes a particle from that element if its momentum changes to a value outside it. Another collision adds a particle if its final momentum lies inside the element. The difference between these two rates is the collision integral.

This calculation requires both the mechanics of scattering and the statistics of particles before they collide. The two particle scattering problem determines the momentum changes for specified initial momenta and an impact parameter. The distribution of particles before the collision determines how frequently those initial states occur together. We shall combine these two ingredients to obtain the loss and gain rates.

We first perform the counting for a spatially uniform gas without an external force. After deriving the collision integral, we shall state the conditions under which the same calculation applies locally to a nonuniform gas. The subsequent Bogoliubov derivation will examine the physical basis of the assumption about pair statistics used in collision counting.

Diluteness and the separation of collision times

Consider identical classical particles of mass m, interacting through the short-range central potential $\Phi(|\mathrm{r}_1 - \mathrm{r}_2|)$. The interaction range is d, as in Section 2.1. We consider elastic, unbound collisions, after which the two particles separate again.

Let n be the number density. The mean volume per particle is $1/n$; its cube root defines the characteristic distance a between particles. The dilute condition is therefore

$$a = n^{-1/3}, \qquad nd^3 = \left(\frac{d}{a}\right)^3 \ll 1. \tag{2.4.2}$$

For the dilute gas states considered here, the mean number of additional particles in a volume of order d^3 is of order nd^3. Thus the force acting during a typical collision is predominantly the force between the two colliding particles. This permits us to calculate their momentum changes using isolated two particle mechanics. The statistical distribution of the two particles before the collision will be specified separately.

The length scales also determine the relevant times. Let v_{th} be a typical thermal speed and λ_{mfp} the mean free path. A collision lasts for a time of order d/v_{th}, whereas the mean interval between successive collisions of one particle is of order $\lambda_{\mathrm{mfp}}/v_{\mathrm{th}}$.

As defined in the preceding sections, τ_{loc} is the time over which collisions relax the local momentum distribution, and τ_H is the longer time of hydrodynamic evolution. The counting interval Δt_{kin} is chosen between the collision duration and the collisional relaxation time:

$$\begin{gathered} \tau_{\mathrm{int}} \sim \frac{d}{v_{\mathrm{th}}}, \quad \tau_{\mathrm{mfp}} \sim \frac{\lambda_{\mathrm{mfp}}}{v_{\mathrm{th}}}, \\ \tau_{\mathrm{int}} \ll \tau_{\mathrm{loc}} \ll \tau_H, \quad \tau_{\mathrm{loc}} \sim \tau_{\mathrm{mfp}}, \\ \tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}. \end{gathered} \tag{2.4.3}$$

The lower bound allows a typical collision to be represented by its complete change from initial to final momenta. The upper bound allows the momentum distribution to be treated as approximately constant when calculating the collision rate over this interval.

For a numerical illustration, take $n \simeq 3 \times 10^{25}\,\mathrm{m}^{-3}$, together with the representative values introduced in Section 2.1: $d \simeq 3.5 \times 10^{-10}\,\mathrm{m}$, $v_{\mathrm{th}} \simeq 5 \times 10^{2}\,\mathrm{m\,s}^{-1}$, and $\lambda_{\mathrm{mfp}} \simeq 7 \times 10^{-8}\,\mathrm{m}$. These give:

Quantity	Estimate
Characteristic particle separation a	$3.2 \times 10^{-9}\,\mathrm{m}$
Mean number nd^3 in an interaction volume	1.3×10^{-3}
Collision duration τ_{int}	$7 \times 10^{-13}\,\mathrm{s}$
Mean interval τ_{mfp} between collisions	$1.4 \times 10^{-10}\,\mathrm{s}$

Thus $d \ll a \ll \lambda_{\mathrm{mfp}}$, and the mean interval between collisions is about two hundred times the collision duration. For example, during a counting interval $\Delta t_{\mathrm{kin}} \sim 10^{-11}\,\mathrm{s}$, the mean number of collisions of one particle is approximately $\Delta t_{\mathrm{kin}}/\tau_{\mathrm{mfp}} \simeq 0.07$. A typical collision is completed within this interval, while only a small fraction of the particles undergo a collision.

At the same time, collisions are numerous when counted over a gas volume containing many particles. A cube of side λ_{mfp} contains approximately $n\lambda_{\mathrm{mfp}}^3 \simeq 10^4$ particles. During the same counting interval, these particles undergo about 4×10^2 binary collisions. This estimate follows by multiplying the particle number by the mean number of collisions per particle and dividing by two, since each binary collision involves two particles.

The collision count therefore averages over many completed collisions, although only a small fraction of the particle population changes momentum. Since $\Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}$, many counting intervals fit within one relaxation time. Successive counts can consequently follow the collisional evolution of f_1, treating it as approximately constant during each interval.

The correlations generated during an individual collision develop on the much shorter time τ_{int}. Numerous collisions are completed during Δt_{kin}, while f_1 changes little. This separation motivates Bogoliubov's kinetic hypothesis: after a short initial relaxation, the pair, three particle and higher distributions adjust rapidly to forms determined by the slowly evolving f_1. Their subsequent evolution then follows that of f_1, including the correlations continually generated by collisions.

The numerical estimates establish the separation between collision duration and collisional relaxation. The loss of independent dependence on the initial higher correlations is the additional physical assumption in Bogoliubov's hypothesis. We shall examine that assumption in the derivation from BBGKY.

We first determine the momentum changes and incident geometry of one elastic binary collision.

Two particle scattering and the cross section

Consider a collision that adds a particle to the momentum population around p_1. Denote the momenta of the two particles after this collision by $\mathrm{p}_1, \mathrm{p}_2$, and their momenta before it by $\mathrm{p}_1', \mathrm{p}_2'$. Thus, in the gain contribution, the primed momenta are the incoming momenta that produce the specified final states. The loss contribution will concern collisions starting with p_1.

These momenta are measured at separations where the pair potential is negligible. For an isolated elastic collision, conservation of total momentum and energy gives

$$\begin{aligned} \mathrm{p}_1' + \mathrm{p}_2' &= \mathrm{p}_1 + \mathrm{p}_2, \\ \frac{\mathrm{p}_1'^2}{2m} + \frac{\mathrm{p}_2'^2}{2m} &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m}. \end{aligned} \tag{2.4.4}$$

The mutual forces give equal and opposite momentum changes to the two particles. Their total momentum therefore remains constant, and their centre of mass moves uniformly. The interaction depends on their relative position, which we denote by $\mathrm{R} = \mathrm{r}_2 - \mathrm{r}_1$, through the potential $\Phi(|\mathrm{R}|)$. The scattering problem can consequently be reduced to their relative motion.

We therefore separate the conserved total momentum from the relative velocity. For the unprimed separated state, define

$$\mathrm{P} = \mathrm{p}_1 + \mathrm{p}_2, \qquad \mathrm{g} = \frac{\mathrm{p}_2 - \mathrm{p}_1}{m}, \qquad g = |\mathrm{g}|. \tag{2.4.5}$$

The centre of mass has velocity $\mathrm{P}/(2m)$. The vector g is the velocity of particle 2 relative to particle 1, consistent with our definition of R: at this separated state, $\dot{\mathrm{R}} = \mathrm{g}$.

Solving the sum and difference of the momenta in (2.4.5) gives

$$\mathrm{p}_1 = \frac{\mathrm{P}}{2} - \frac{m\mathrm{g}}{2}, \qquad \mathrm{p}_2 = \frac{\mathrm{P}}{2} + \frac{m\mathrm{g}}{2}. \tag{2.4.6}$$

Substituting these expressions into the kinetic energy, the terms proportional to $\mathrm{P} \cdot \mathrm{g}$ cancel, leaving

$$\frac{p_1^2}{2m} + \frac{p_2^2}{2m} = \frac{P^2}{4m} + \frac{mg^2}{4}. \tag{2.4.7}$$

Define the corresponding incoming quantities by $\mathrm{P}' = \mathrm{p}_1' + \mathrm{p}_2'$ and $\mathrm{g}' = (\mathrm{p}_2' - \mathrm{p}_1')/m$, with $g' = |\mathrm{g}'|$. Equation (2.4.4), together with the energy decomposition (2.4.7), then gives

$$\mathrm{P}' = \mathrm{P}, \qquad g' = g. \tag{2.4.8}$$

The relative velocity generally changes direction, while its magnitude has the same value before and after scattering. This equality compares the two separated states. Within the interaction region, energy is exchanged between relative kinetic energy and the pair potential, so the instantaneous relative speed generally varies.

The scattering problem therefore determines the change of direction between g′ and g. Once these directions and the conserved total momentum are known, (2.4.6) gives the individual momenta; replacing g by g′ gives the incoming momenta.

The relative speed also enters the collision count. On the straight incident portion of the motion, the particles cover a relative distance $g\Delta t_{\mathrm{kin}}$ during the counting interval. Together with the transverse area of the incident paths, this distance determines the volume containing partners that reach the interaction region during that interval.

Before the force becomes appreciable, particle 2 moves relative to particle 1 along a straight line with velocity g′. The impact parameter b is the perpendicular distance from $\mathrm{R} = 0$ to that line. Let φ be the azimuth of this perpendicular displacement in the plane normal to the incident direction.

The incident lines with impact parameters between b and $b + db$, and azimuths between φ and $\varphi + d\varphi$, occupy the transverse area

$$d\sigma = b\, db\, d\varphi. \tag{2.4.9}$$

From the distribution of incoming pairs to the collision count

The scattering calculation determines the momentum changes in a collision with specified initial momenta and impact parameter. To calculate the collision integral, we also need the number of particles undergoing such collisions. We first count collisions that remove particles from a small momentum element around p_1.

Let $d^3r\, d^3p_1$ be a small phase space element around $(\mathrm{r}, \mathrm{p}_1)$. Its mean particle number at time t is

$$dN = f_1(\mathrm{r}, \mathrm{p}_1, t)\, d^3r\, d^3p_1. \tag{2.4.11}$$

For this loss count, p_1 and p_2 denote the momenta **before** the collision. The relative incident velocity is therefore $\mathrm{g} = (\mathrm{p}_2 - \mathrm{p}_1)/m$, consistently with (2.4.5).

Choose one of the particles counted in (2.4.11). The number of its possible collision partners depends on the pair distribution: knowing the mean number of particles near p_2 alone does not specify how frequently they occur together with the selected particle.

Write $1 = (\mathrm{r}, \mathrm{p}_1)$ and $2 = (\mathrm{r}_2, \mathrm{p}_2)$. Let $f_2^{\mathrm{in}}(1,2,t)$ denote the pair distribution in the separated states before the mutual force becomes appreciable. According to the normalization established in Section 2.3, $f_2^{\mathrm{in}}(1,2,t)\, d1\, d2$ is the mean number of ordered pairs in these elements. Dividing this pair number by the first particle number $f_1(1,t)\, d1$ gives the mean number of partners of the selected particle in $d2$. Thus the mean number of partners with momenta in d^3p_2, **per unit spatial volume** near r_2, is

$$dn_2^{\mathrm{in}} = \frac{f_2^{\mathrm{in}}(1,2,t)}{f_1(1,t)}\, d^3p_2. \tag{2.4.12}$$

The positions of partners that will collide during Δt_{kin} are determined by the incident geometry. In relative coordinates, particle 1 is at $\mathrm{R} = 0$. Surround this point by a sphere of radius $2d$, whose surface lies outside the region of appreciable force. Consider incident paths with impact parameters that lead to scattering, and select the transverse area $d\sigma = b\, db\, d\varphi$ defined in (2.4.9). These paths intersect a small entry patch on the sphere.

Before reaching that patch, particle 2 moves freely relative to particle 1 with speed g. During Δt_{kin}, it travels the relative distance $g\Delta t_{\mathrm{kin}}$. Consequently, the partner positions from which entry occurs during this interval form a column of transverse area $d\sigma$ and length $g\Delta t_{\mathrm{kin}}$. Its volume is

$$dV_{\mathrm{coll}} = g\Delta t_{\mathrm{kin}}\, d\sigma = g\Delta t_{\mathrm{kin}}\, b\, db\, d\varphi. \tag{2.4.13}$$

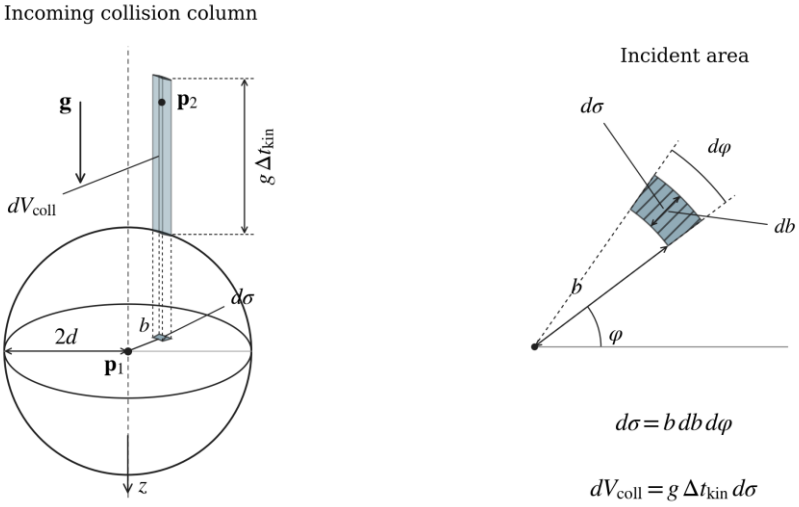


Figure 2.4.1. The shaded column contains the initial partner positions from which entry through the selected sphere patch occurs during Δt_{kin}. The right panel shows its transverse area $d\sigma = b\, db\, d\varphi$. The positive z direction is along g; the labels p_1, p_2 identify the initial particle momenta.

The delay between entry through the sphere and completion of the collision is of order τ_{int}. Counting entries instead of completed collisions therefore changes the count only for collisions near the ends of the counting interval. The relative correction is of order $\tau_{\mathrm{int}}/\Delta t_{\mathrm{kin}}$, which is small under (2.4.3).

To find the number of partners in the column, we now specify their statistics. The approximation called **molecular chaos** treats the states of the two particles before their collision as statistically independent. With the ordered pair normalization of Section 2.3, this gives

$$f_2^{\mathrm{in}}(1,2,t) \simeq \frac{N-1}{N}\, f_1(1,t) f_1(2,t). \tag{2.4.14}$$

Substitution into (2.4.12) gives the conditional partner density $[(N-1)/N]f_1(\mathrm{r}_2,\mathrm{p}_2,t)\,d^3p_2$. The factor $(N-1)/N$ accounts for the $N-1$ particles available as partners of the selected particle. This approximation allows their number density to be calculated from f_1.

For the spatially uniform gas considered here, f_1 is independent of position. For $N \gg 1$, equation (2.4.14) therefore becomes

$$f_2^{\mathrm{in}}(1,2,t) \simeq f_1(\mathrm{r},\mathrm{p}_1,t)\,f_1(\mathrm{r},\mathrm{p}_2,t). \tag{2.4.15}$$

This factorization concerns the statistics before the collision. During the collision, the mutual force couples the momentum changes of the two particles, and their pair distribution evolves according to the two particle dynamics.

The partner density in (2.4.12) is now approximately constant throughout the incident column. Equation (2.4.3) also allows f_1 to be treated as constant during the counting interval. The mean number of collisions of the selected particle with partners in d^3p_2 and incident area $b\,db\,d\varphi$ is consequently

$$dn_2^{\mathrm{in}}\,dV_{\mathrm{coll}} \simeq f_1(\mathrm{r},\mathrm{p}_2,t)\,d^3p_2\,g\Delta t_{\mathrm{kin}}\,b\,db\,d\varphi. \tag{2.4.16}$$

Multiplication by the particle number (2.4.11) gives the loss count for these partner momenta and impact parameters. The gain count concerns collisions with incoming momenta $\mathrm{p}_1',\mathrm{p}_2'$ that produce the specified final momenta $\mathrm{p}_1,\mathrm{p}_2$.

Gain and loss in the momentum distribution

Multiplying the mean number of collisions per particle in (2.4.16) by the particle number in (2.4.11) gives the mean loss count:

$$dN_{\mathrm{loss}} = f_1(\mathrm{r},\mathrm{p}_1,t)\,f_1(\mathrm{r},\mathrm{p}_2,t)\,d^3r\,d^3p_1\,d^3p_2\,g\Delta t_{\mathrm{kin}}\,d\sigma. \tag{2.4.17}$$

Here $\mathrm{p}_1,\mathrm{p}_2$ are the momenta before the collision, and $d\sigma = b\,db\,d\varphi$. The separate collision counts include paths entering the interaction region. Within the short range approximation, these have $0 \le b < d$; more distant paths are represented by free motion.

Dividing (2.4.17) by $\Delta t_{\mathrm{kin}}\,d^3r\,d^3p_1$ and integrating over partner momenta and collision parameters gives the positive loss rate:

$$C_{\mathrm{loss}}[f_1](\mathrm{r},\mathrm{p}_1,t) = \int d^3p_2 \int d\sigma\,g\,f_1(\mathrm{r},\mathrm{p}_1,t)\,f_1(\mathrm{r},\mathrm{p}_2,t). \tag{2.4.18}$$

The gain rate counts collisions with incoming momenta $\mathrm{p}_1',\mathrm{p}_2'$ that produce the specified final momenta $\mathrm{p}_1,\mathrm{p}_2$. Molecular chaos assigns these incoming pairs the product $f_1(\mathrm{r},\mathrm{p}_1',t)f_1(\mathrm{r},\mathrm{p}_2',t)$. To express their count per final momentum element, we change from the incoming to the final collision variables.

The linear relations (2.4.6) have absolute Jacobian $m^3/8$. Since the total momentum P is conserved,

$$\begin{aligned} d^3p_1\,d^3p_2 &= \frac{m^3}{8}\,d^3P\,d^3g, \\ d^3p_1'\,d^3p_2' &= \frac{m^3}{8}\,d^3P\,d^3g'. \end{aligned} \tag{2.4.19}$$

Liouville's theorem preserves the two particle phase volume. Using (2.4.19) and the collision volume (2.4.13), this gives preservation of the complete collision integration measure:

$$g'\,d^3p_1'\,d^3p_2'\,d\sigma = g\,d^3p_1\,d^3p_2\,d\sigma. \tag{2.4.20}$$

The relative speeds satisfy $g' = g$, as established in (2.4.8). Using (2.4.20) with the incoming statistical product gives the mean gain count:

$$dN_{\mathrm{gain}} = f_1(\mathrm{r},\mathrm{p}_1',t)\,f_1(\mathrm{r},\mathrm{p}_2',t)\,d^3r\,d^3p_1\,d^3p_2\,g\Delta t_{\mathrm{kin}}\,d\sigma. \tag{2.4.21}$$

Dividing by $\Delta t_{\mathrm{kin}}\,d^3r\,d^3p_1$ and integrating gives the positive gain rate:

$$C_{\mathrm{gain}}[f_1](\mathrm{r},\mathrm{p}_1,t) = \int d^3p_2 \int d\sigma\,g\,f_1(\mathrm{r},\mathrm{p}_1',t)\,f_1(\mathrm{r},\mathrm{p}_2',t). \tag{2.4.22}$$

Both rates use the statistics before a collision. For loss, those momenta are $\mathrm{p}_1, \mathrm{p}_2$. For gain, they are $\mathrm{p}_1{}', \mathrm{p}_2{}'$: the initial momenta that produce the specified final pair for the collision parameters b, φ.

For paths outside the interaction range, the momenta remain unchanged: $\mathrm{p}_1{}' = \mathrm{p}_1$ and $\mathrm{p}_2{}' = \mathrm{p}_2$. Their gain and loss products are equal. We therefore write the combined impact parameter integral over $0 \le b < \infty$.

For the uniform gas without an external force, the change of f_1 is the gain rate minus the loss rate. Denoting their difference by $C[f_1]$, we obtain

$$\begin{aligned} \frac{\partial f_1(\mathrm{r},\mathrm{p}_1,t)}{\partial t} &= C[f_1](\mathrm{r},\mathrm{p}_1,t) = C_{\mathrm{gain}}[f_1] - C_{\mathrm{loss}}[f_1] \\ &= \int d^3p_2 \int_0^\infty b\ db \int_0^{2\pi} d\,\varphi\ g \\ \times\ [f_1(\mathrm{r},\mathrm{p}_1{}',t)\, f_1(\mathrm{r},\mathrm{p}_2{}',t) &- f_1(\mathrm{r},\mathrm{p}_1,t)\, f_1(\mathrm{r},\mathrm{p}_2,t)]. \end{aligned} \tag{2.4.23}$$

Equation (2.4.23) is the Boltzmann collision integral. Its first product counts collisions that produce the specified momentum p_1; its second product counts collisions starting with that momentum.

For a nonuniform gas, the same calculation applies locally when f_1 varies little over distances of order the mean free path. A region of that size is then approximately uniform for the collision count. The external force must also change the momenta negligibly during τ_{int}, and the counting interval must be short compared with the times of appreciable evolution of f_1 by streaming or external acceleration. Under these conditions, all four distributions in (2.4.23) are evaluated at the same kinetic position r and time t.

Restoring streaming and external acceleration through the operator $\mathcal{L}_1$ gives the Boltzmann kinetic equation:

$$\frac{\partial f_1}{\partial t} + \frac{\mathrm{p}_1}{m} \cdot \nabla_{\mathrm{r}} f_1 + \mathrm{F}^{\mathrm{ext}}(\mathrm{r},t) \cdot \nabla_{\mathrm{p}_1} f_1 = C[f_1](\mathrm{r},\mathrm{p}_1,t). \tag{2.4.24}$$

The collision integral is closed in f_1 because (2.4.15) expresses the statistics before each collision through the two one particle distributions.

The closure problem and the purpose of Bogoliubov's derivation

The collision counting derivation led to the Boltzmann equation (2.4.24) by combining two ingredients: the momentum changes determined by two particle scattering and the statistical population of incoming pairs. Molecular chaos approximated the distribution of approaching particles as the product of the two one particle distributions, as in (2.4.15). This replacement allowed the collision rate to be calculated from f_1.

The exact first BBGKY equation (2.4.1) contains the pair distribution f_2 at separations where the mutual force is appreciable. It therefore requires the pair statistics during the collision. Equation (2.4.15) approximates the distribution of incoming pairs by the product of the two one particle distributions. Here, "incoming" refers to the states of the two particles before the mutual collision whose effect we are calculating. This assumed distribution specifies the population of pairs entering the collision. We calculate how the incoming pair distribution evolves under the mutual force. The resulting f_2 includes the pair correlations generated during an isolated collision, expressed in terms of the current f_1.

The distinction between f_1 and f_2 is essential here. The function f_1 specifies the population of individual particle states, while f_2 specifies how two particle states occur together. Systems with the same f_1 can have different pair statistics and consequently different interaction terms in (2.4.1). Expressing that term through f_1 therefore requires a physical approximation relating the higher distributions to the one particle distribution.

Bogoliubov's approach examines the conditions under which the higher distributions can be calculated from the current f_1. In deriving the Boltzmann collision integral from the BBGKY hierarchy, we shall combine the factorization of the distribution of approaching particles with

interacting pair dynamics to calculate the f_2 entering (2.4.1). Bogoliubov's kinetic hypothesis assumes that the pair, three particle and higher distributions, including their correlations, relax towards forms determined by the current f_1 over a time much shorter than the time for f_1 to change appreciably. We begin by examining the physical meaning of this hypothesis and the separation of relaxation times on which it depends.

The kinetic stage and Bogoliubov's hypothesis

During an isolated binary collision, the momenta of the two particles can change appreciably over the interaction time τ_{int}. To understand how this rapid pair dynamics affects f_1, we return to the exact first BBGKY equation:

$$\mathcal{L}_1 f_1(1,t) = \mathcal{I}_1(1,t) = -\int d2\, \mathrm{F}_{12} \cdot \nabla_{\mathrm{p}_1} f_2(1,2,t). \tag{2.4.1}$$

As defined in Section 2.3, f_2 is a density: the quantity $f_2(1,2,t)\, d1\, d2$ is the mean number of ordered pairs in the two phase space elements $d1$ and $d2$. In (2.4.1), the state of particle 1 is held fixed, while the integration runs over the positions and momenta of particle 2.

Because the pair force is independent of momentum, the momentum derivative can be taken outside the partner integral. Thus the interaction term can also be written as

$$\mathcal{I}_1(1,t) = -\nabla_{\mathrm{p}_1} \cdot [\int d2\, \mathrm{F}_{12} f_2(1,2,t)]. \tag{2.4.25}$$

The expression inside the brackets sums the force contributions from all possible partner states, weighted by the pair density. The momentum divergence then determines the redistribution of the one particle population. The effect of the detailed pair dynamics on f_1 is therefore calculated **after integrating over the partner states**. This integration is the statistical averaging involved in passing from the pair description to the one particle equation.

For the dilute gas considered here, we use the separation of times introduced in (2.4.3): the interaction time τ_{int} is much shorter than the collisional relaxation time τ_{loc}. The temporal resolution Δt_{kin} lies between these times. A collision is completed within this interval, while the collisional change of f_1 remains small. This time separation allows us to calculate an individual collision with the current f_1 held approximately fixed and to follow the evolution of f_1 over longer times.

Bogoliubov's kinetic hypothesis adds a statement about the pair, three particle and higher distributions. It assumes that, after a short initial relaxation, these distributions have approached forms determined by the current f_1. As f_1 evolves, the higher distributions continue to adjust to f_1.

Following Section 2.3, denote the relation that calculates f_s from f_1 by the functional $\mathcal{F}_s$. The functional takes the whole one particle distribution as its input and returns the distribution of the states of s particles:

$$f_s(1,\dots,s,t) \simeq \mathcal{F}_s[\, f_1(t)\,], \qquad s \geq 2. \tag{2.4.26}$$

The meaning of the hypothesis can be stated by comparing two samples of the same gas. Suppose the samples were prepared with different initial pair and higher correlations. At a later time within the kinetic stage, if both samples have the same one particle distribution f_1, relation (2.4.26) assigns both samples the same higher distributions. Within this approximation, the initial pair and higher correlations have lost their independent influence on the subsequent evolution. Any changes of f_1 produced during the initial relaxation remain in the value of f_1 from which the kinetic evolution proceeds.

The functionals $\mathcal{F}_s[f_1]$ still contain correlations generated by interactions. In particular, $\mathcal{F}_2[f_1]$ must describe the correlated pair statistics during a collision. Calculating $\mathcal{F}_2$ and substituting it into (2.4.1) will express the interaction term through f_1. The pair equation and the statistical condition for incoming pairs are needed to carry out that calculation.

The dilute approximation in the first two BBGKY equations

To calculate the interaction term in (2.4.1), we need the pair distribution during a collision. The second BBGKY equation provides its evolution equation. As established in Section 2.3, the operator $\mathcal{L}_2$ contains the mutual force between particles 1 and 2, whereas the integral involving f_3 accounts for forces exerted on them by the other gas particles. We shall use the small density parameter to determine which contributions are required for the binary collision approximation.

The distributions f_s have the normalization $N!/(N-s)!$ introduced in Section 2.3. To display the corresponding density factors explicitly, let V be the system volume, $v = V/N$ the mean volume per particle, and define

$$\tilde{f}_s(1,\dots,s,t) = \frac{V^s(N-s)!}{N!}\, f_s(1,\dots,s,t), \qquad s = 1,2,3. \tag{2.4.27}$$

Thus $f_1 = (N/V)\tilde{f}_1$ and $f_2 = [N(N-1)/V^2]\tilde{f}_2$. Substitution into the first two BBGKY equations gives

$$\begin{aligned} \mathcal{L}_1\tilde{f}_1 &= -\tfrac{N-1}{V}\textstyle\int d2\, \mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2, \\ \mathcal{L}_2\tilde{f}_2 &= -\tfrac{N-2}{V}\textstyle\int d3\, [\mathrm{F}_{13}\cdot\nabla_{\mathrm{p}_1} + \mathrm{F}_{23}\cdot\nabla_{\mathrm{p}_2}]\tilde{f}_3. \end{aligned} \tag{2.4.28}$$

The coefficient in each equation follows by dividing the normalization factor for f_{s+1} by that for f_s, giving $(N-s)/V$. For large N, both coefficients in (2.4.28) approach $N/V = 1/v$.

The integration over $d2 = d^3r_2\, d^3p_2$ covers the gas volume and the full momentum space. At fixed r_1, the force F_{12} becomes negligible when $|\mathrm{r}_2 - \mathrm{r}_1|$ exceeds the interaction range d. Those positions therefore contribute negligibly to this integral, although the pair distribution remains defined there. In the second equation, F_{13} is appreciable when particle 3 is within the force range of particle 1, and F_{23} when it is within that range of particle 2.

The spatial regions in which these force factors are appreciable have volumes of order d^3. Comparing d^3 with the mean volume per particle gives the small parameter

$$\varepsilon = \frac{d^3}{v} \ll 1. \tag{2.4.29}$$

For a uniform gas, $1/v = n$, and ε is the mean number of particles in a volume d^3. Equation (2.4.29) then coincides with the dilute condition (2.4.2). In a nonuniform gas, the corresponding local condition is $n(\mathrm{r},t)d^3 \ll 1$ in the collision region.

Using $1/v = \varepsilon/d^3$, we write the hierarchy in the large N limit as

$$\begin{aligned} \mathcal{L}_1\tilde{f}_1 &= -\tfrac{\varepsilon}{d^3}\textstyle\int d2\, \mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2, \\ \mathcal{L}_2\tilde{f}_2 &= -\tfrac{\varepsilon}{d^3}\textstyle\int d3\, [\mathrm{F}_{13}\cdot\nabla_{\mathrm{p}_1} + \mathrm{F}_{23}\cdot\nabla_{\mathrm{p}_2}]\tilde{f}_3. \end{aligned} \tag{2.4.30}$$

The integral involving $\tilde{f}_3$ in the second equation of (2.4.30) is explicitly multiplied by ε, but the distribution functions also depend on this parameter. To determine which terms of $\tilde{f}_2$ are required for the derivation of the collision integral, we expand $\tilde{f}_2$ and $\tilde{f}_3$ in powers of the small parameter ε. We assume that the expansion has finite coefficients. Superscripts (0) and (1) denote the coefficients of the zeroth and first powers, respectively:

$$\tilde{f}_s = \tilde{f}_s^{(0)} + \varepsilon\, \tilde{f}_s^{(1)} + O(\varepsilon^2), \qquad s = 2,3. \tag{2.4.31}$$

The coefficients are functions of the particle states and time, independent of the expansion parameter. Substitution into both equations of (2.4.30) gives

$$\begin{aligned} \mathcal{L}_1\tilde{f}_1 &= -\tfrac{1}{d^3}\textstyle\int d2\, \mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}[\varepsilon\tilde{f}_2^{(0)} + \varepsilon^2\tilde{f}_2^{(1)}] + O(\varepsilon^3), \\ \mathcal{L}_2\tilde{f}_2^{(0)} + \varepsilon\mathcal{L}_2\tilde{f}_2^{(1)} &= -\tfrac{\varepsilon}{d^3}\textstyle\sum_{i=1}^{2}\int d3\, \mathrm{F}_{i3}\cdot\nabla_{\mathrm{p}_i}\tilde{f}_3^{(0)} + O(\varepsilon^2). \end{aligned} \tag{2.4.32}$$

In (2.4.31), the correction to the pair distribution is $\varepsilon\tilde{f}_2^{(1)}$. The first equation of (2.4.30) multiplies this correction by another factor ε/d^3. Their product produces the term proportional to $\varepsilon^2\tilde{f}_2^{(1)}$ in the first equation of (2.4.32).

Comparing the terms independent of ε in the second equation of (2.4.32) gives $\mathcal{L}_2\tilde{f}_2^{(0)} = 0$. Writing the operator explicitly,

$$[\frac{\partial}{\partial t} + \sum_{i=1}^{2}\left(\frac{\mathrm{p}_i}{m}\cdot\nabla_{\mathrm{r}_i} + \mathrm{F}_i^{\mathrm{ext}}\cdot\nabla_{\mathrm{p}_i}\right) + \mathrm{F}_{12}\cdot\left(\nabla_{\mathrm{p}_1} - \nabla_{\mathrm{p}_2}\right)]\tilde{f}_2^{(0)} = 0. \tag{2.4.33}$$

This is the Liouville equation for an isolated interacting pair subject to the prescribed external forces. Particle 2 exerts the force F_{12} on particle 1, while particle 1 exerts $-\mathrm{F}_{12}$ on particle 2. Their contributions to (2.4.33) are $\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2^{(0)}$ and $-\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_2}\tilde{f}_2^{(0)}$, respectively. Neither contribution carries a factor ε, so both are retained in the equation for the zeroth order coefficient.

Retaining the coefficient $\tilde{f}_2^{(0)}$ in (2.4.31) gives the zeroth order approximation to the pair distribution. This approximation includes the correlations generated during a binary collision. Comparing the terms proportional to ε in the second equation of (2.4.32) shows that the forces exerted by an additional particle contribute to the first correction, $\varepsilon\tilde{f}_2^{(1)}$.

Retaining the term proportional to ε in the first equation of (2.4.32) gives

$$\mathcal{L}_1\tilde{f}_1 = -\frac{\varepsilon}{d^3}\int d2\,\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2^{(0)} + O(\varepsilon^2). \tag{2.4.34}$$

Thus the zeroth order approximation to $\tilde{f}_2$ is sufficient to retain the term proportional to ε in the first equation of (2.4.30). Its first correction affects that equation at order ε^2, as shown in (2.4.32).

Returning to the normalization of Section 2.3, the pair distribution used at this accuracy is

$$f_2(1,2,t) \simeq \frac{N(N-1)}{V^2}\,\tilde{f}_2^{(0)}(1,2,t). \tag{2.4.35}$$

Equation (2.4.33) describes the evolution of the pair distribution at zeroth order in ε. To determine $\tilde{f}_2^{(0)}$ in terms of the one particle distribution f_1, we use the principle of weakening of correlations to specify the distribution of widely separated particles before their mutual collision. As introduced in Section 2.3, this principle expresses factorization at separations much larger than the correlation length ℓ_{corr}. In terms of the scaled distributions, it reads

$$\tilde{f}_2(1,2,t) \to \tilde{f}_1(1,t)\tilde{f}_1(2,t), \qquad |\mathrm{r}_2 - \mathrm{r}_1| \gg \ell_{\mathrm{corr}}. \tag{2.4.36}$$

This factorization specifies the boundary values at large separation. The pair distribution within the force region is determined using the interacting Liouville equation (2.4.33). The following derivation explains how the principle of weakening of correlations is applied to the incoming states and how it is connected to the factorization used in (2.4.15).

How weakening of correlations enters the pair equation

Section 2.1 established the general Liouville result: the distribution density of a Hamiltonian system retains its value along that system's phase space trajectories. For the complete gas, this applies to ρ_N. Retaining the zeroth order coefficient reduced the second BBGKY equation to the Liouville equation (2.4.33) for an interacting pair. We now apply the same general result to this pair equation.

Consider a specified pair state (1,2) at time t. Let $\mathrm{r}_i(t')$ and $\mathrm{p}_i(t')$, with $i = 1,2$, describe the interacting two particle motion that passes through this state at $t' = t$. Write $i(t') = \left(\mathrm{r}_i(t'), \mathrm{p}_i(t')\right)$, so that $1(t) = 1$ and $2(t) = 2$.

For a positive interval τ, constancy of the Liouville density along this motion gives

$$\tilde{f}_2^{(0)}(1,2,t) = \tilde{f}_2^{(0)}(1(t-\tau), 2(t-\tau), t-\tau). \tag{2.4.37}$$

Equation (2.4.37) permits us to use weakening of correlations. It expresses the pair density needed during the collision through the density at earlier states of the same interacting pair.

For the unbound scattering considered here, following the two particle motion backwards reaches separated states before their mutual collision. We take τ sufficiently large that the earlier positions satisfy

$$|\mathrm{r}_2(t-\tau) - \mathrm{r}_1(t-\tau)| \gg d, \ell_{\mathrm{corr}}. \tag{2.4.38}$$

The incoming boundary condition is imposed in the limit $\tau \to \infty$. This limit refers to the isolated two particle motion retained in (2.4.33), for which unbound particles are asymptotically separated before the collision.

At the earlier states in (2.4.38), the principle of weakening of correlations supplies the factorization (2.4.36). Applying it to the right-hand side of (2.4.37) gives

$$\tilde{f}_2^{(0)}(1,2,t) \simeq \tilde{f}_1(1(t-\tau), t-\tau)\, \tilde{f}_1(2(t-\tau), t-\tau). \tag{2.4.39}$$

The present pair density is therefore obtained from a product evaluated at earlier separated states before the collision. These are the incoming states. Their role follows from the constancy of the Liouville density: factorization at these earlier arguments determines the density within the force region through the interacting pair motion.

Equation (2.4.39) also explains how the collision correlations are retained. The earlier state $1(t-\tau)$ depends on both present states 1 and 2, because the momentum evolution of particle 1 involves the force exerted by particle 2. The same holds for $2(t-\tau)$. Consequently, both factors on the right-hand side depend on the present joint pair state through the interacting motion described by (2.4.33). The resulting distribution generally contains correlations during the collision, even though it factorizes at the separated incoming states.

The one particle factors in (2.4.39) still have their explicit earlier positions, momenta and time as arguments. The following calculation will express these factors using the one particle distribution at time t, and then obtain the local pair distribution required in the collision integral.

Calculating the correlated pair distribution

Equation (2.4.39) expresses the pair density during the collision through a product of one particle distributions evaluated at earlier, separated states of the interacting pair. The factorization follows from the principle of weakening of correlations at those incoming states. The interacting pair motion then determines the correlations present during the collision.

The two factors in (2.4.39) still refer to time $t-\tau$. Bogoliubov's kinetic hypothesis (2.4.26) expresses the higher distributions through the one particle distribution at the same time t. The remaining mathematical question is therefore how the product at the earlier incoming states is expressed through f_1 at time t, while retaining the interacting pair dynamics.

The required relation follows from the one particle Liouville equation at zeroth order in ε. In the first equation of (2.4.32), the collision integral is proportional to ε; at zeroth order, the one particle distribution consequently evolves through independent one particle motion. For $\mathrm{F}_i^{\mathrm{ext}} = 0$, this equation is

$$\frac{\partial \tilde{f}_1}{\partial t} + \frac{\mathrm{p}}{m} \cdot \nabla_{\mathrm{r}} \tilde{f}_1 = 0. \tag{2.4.40}$$

During free motion, the momentum p remains constant. Over an interval τ, the position therefore changes from r to $\mathrm{r} + \mathrm{p}\tau/m$. We introduce the one particle evolution operator $S_\tau^{(1)}$ to represent this change of phase space arguments. For any function $A(\mathrm{r}, \mathrm{p})$, its action is defined by

$$S_\tau^{(1)} A(\mathrm{r}, \mathrm{p}) = A\left(\mathrm{r} + \frac{\mathrm{p}}{m}\tau, \mathrm{p}\right). \tag{2.4.41}$$

For $\tau > 0$, a particle at (r, p) at time $t - \tau$ reaches $(\mathrm{r} + \mathrm{p}\tau/m, \mathrm{p})$ at time t. Constancy of the distribution density along this free motion gives

$$\tilde{f}_1(\mathrm{r}, \mathrm{p}, t - \tau) = \tilde{f}_1\left(\mathrm{r} + \frac{\mathrm{p}}{m}\tau, \mathrm{p}, t\right) = S_\tau^{(1)} \tilde{f}_1(\mathrm{r}, \mathrm{p}, t). \tag{2.4.42}$$

Equation (2.4.42) uses the zeroth order evolution (2.4.40). The operator changes the position argument; the explicit time argument of the distribution on its right-hand side is t.

For the pair, the Hamilton equations include the force F_{12} on particle 1 and $-\mathrm{F}_{12}$ on particle 2. The functions $1(t')$ and $2(t')$ defined before (2.4.37) describe the solution passing through the specified state $(1,2)$ at time t. For any function $B(1,2)$, define the two particle evolution operator by

$$S_{-\tau}^{(2)} B(1,2) = B\big(1(t-\tau), 2(t-\tau)\big). \tag{2.4.43}$$

Thus $S_{-\tau}^{(2)}$ evaluates B at the earlier positions and momenta calculated from these two particle Hamilton equations.

Taking the factorization in (2.4.39) as the asymptotic boundary condition for separated incoming particles gives

$$\tilde{f}_2^{(0)}(1,2,t) = \lim_{\tau\to\infty} S_{-\tau}^{(2)} \left(\tilde{f}_1(1, t-\tau)\, \tilde{f}_1(2, t-\tau)\right). \tag{2.4.44}$$

Let $S_\tau^{(1)}(i)$ denote the one particle operator acting on the variables of particle i. Applying (2.4.42) to each factor in (2.4.44), and using the definition (2.4.43), gives

$$\begin{aligned} \tilde{f}_2^{(0)}(1,2,t) &= \lim_{\tau\to\infty} \textstyle\prod_{i=1}^{2} \tilde{f}_1\left(\mathrm{r}_i(t-\tau), \mathrm{p}_i(t-\tau), t-\tau\right) \\ &= \lim_{\tau\to\infty} \textstyle\prod_{i=1}^{2} \tilde{f}_1\left(\mathrm{r}_i(t-\tau) + \frac{\tau}{m}\mathrm{p}_i(t-\tau), \mathrm{p}_i(t-\tau), t\right) \\ &= \lim_{\tau\to\infty} S_{-\tau}^{(2)} S_\tau^{(1)}(1) S_\tau^{(1)}(2) \left(\tilde{f}_1(1,t)\, \tilde{f}_1(2,t)\right). \end{aligned} \tag{2.4.45}$$

The second equality applies (2.4.42) at each earlier particle state. The last equality uses the operator definitions (2.4.41) and (2.4.43).

We denote the limiting operator in the last line of (2.4.45) by σ_2:

$$\sigma_2 = \lim_{\tau\to\infty} S_{-\tau}^{(2)} S_\tau^{(1)}(1) S_\tau^{(1)}(2). \tag{2.4.46}$$

The negative shift in $S_{-\tau}^{(2)}$ selects the separated states before the collision, where weakening of correlations supplies the boundary condition. Equation (2.4.45) then reads

$$\tilde{f}_2^{(0)}(1,2,t) = \sigma_2 \left(\tilde{f}_1(1,t)\, \tilde{f}_1(2,t)\right). \tag{2.4.47}$$

All distribution functions in (2.4.47) refer to time t. The operator σ_2 is calculated from the two particle Hamilton equations, while the product on which it acts is specified by the one particle distribution. Equation (2.4.47) is therefore the zeroth order functional relation of the form (2.4.26), obtained by imposing weakening of correlations at the incoming states.

Using $\tilde{f}_1 = (V/N) f_1$ from (2.4.27), together with (2.4.35), gives

$$\begin{aligned} f_2(1,2,t) &\simeq \frac{N(N-1)}{V^2}\, \sigma_2 \left(\frac{V}{N} f_1(1,t)\, \frac{V}{N} f_1(2,t)\right) \\ &= \frac{N-1}{N}\, \sigma_2\big(f_1(1,t)\, f_1(2,t)\big). \end{aligned} \tag{2.4.48}$$

The factor $(N-1)/N$ tends to unity for large N.

For a spatially uniform gas, $\tilde{f}_1$ depends only on momentum and time. Equation (2.4.41) consequently gives

$$S_\tau^{(1)}(i)\, \tilde{f}_1(\mathrm{r}_i, \mathrm{p}_i, t) = \tilde{f}_1\left(\mathrm{r}_i + \frac{\tau}{m}\mathrm{p}_i, \mathrm{p}_i, t\right) = \tilde{f}_1(\mathrm{p}_i, t). \tag{2.4.49}$$

Thus the one particle operators leave these homogeneous factors unchanged.

For unbound scattering by the short range force, the particle momenta approach constant incoming values as $\tau \to \infty$. Define these momenta by

$$\mathrm{p}_i^{\mathrm{in}} = \lim_{\tau\to\infty} \mathrm{p}_i(t-\tau), \qquad i = 1{,}2. \tag{2.4.50}$$

Using (2.4.43), (2.4.49) and (2.4.50), equation (2.4.47) becomes

$$\begin{aligned} \tilde{f}_2^{(0)}(1{,}2,t) &= \lim_{\tau\to\infty} S_{-\tau}^{(2)} \left(\tilde{f}_1(\mathrm{p}_1,t)\, \tilde{f}_1(\mathrm{p}_2,t) \right) \\ &= \lim_{\tau\to\infty} \textstyle\prod_{i=1}^{2} \tilde{f}_1\,(\mathrm{p}_i(t-\tau),t) \\ &= \tilde{f}_1(\mathrm{p}_1^{\mathrm{in}},t)\, \tilde{f}_1(\mathrm{p}_2^{\mathrm{in}},t). \end{aligned} \tag{2.4.51}$$

Obtaining the Boltzmann collision integral

Equation (2.4.51) expresses the pair coefficient during a collision through the one particle distributions at the incoming momenta. Substitution into (2.4.34) will close the equation for the one particle distribution. The remaining calculation is the integral over the position r_2 and momentum p_2. The second BBGKY equation will allow us to convert this force integral into a difference between the pair distributions at large separation. Their boundary values will give the gain and loss contributions.

We first consider a spatially uniform gas with zero external force. The incoming momenta $\mathrm{p}_1^{\mathrm{in}}, \mathrm{p}_2^{\mathrm{in}}$ retain their definition (2.4.50), as the momenta before the physical forward collision.

For this uniform one particle distribution, $\mathcal{L}_1 \tilde{f}_1 = \partial_t \tilde{f}_1$. Equation (2.4.34) therefore gives $\partial_t \tilde{f}_1 = O(\varepsilon)$, while $\tilde{f}_1 = O(1)$.

An infinitesimal variation $\delta\tilde{f}_1(\mathrm{q},t)$ of the one particle distribution, where q ranges over momentum space, induces a variation $\delta\tilde{f}_2^{(0)}(1{,}2,t)$ of the pair coefficient. The first line below defines the functional derivative by relating these variations. Taking $\delta\tilde{f}_1 = \left(\partial_t \tilde{f}_1\right)\delta t$ gives the second line. Differentiating the product in (2.4.51) then gives the third line. In this partial time derivative, the specified pair state is fixed. The incoming momenta have no explicit time dependence, because they are calculated from that state using the time independent pair potential.

$$\begin{aligned} \delta\tilde{f}_2^{(0)}(1{,}2,t) &= \int d^3q\, \frac{\delta\tilde{f}_2^{(0)}(1{,}2,t)}{\delta\tilde{f}_1(\mathrm{q},t)}\, \delta\tilde{f}_1(\mathrm{q},t), \\ \frac{\partial\tilde{f}_2^{(0)}(1{,}2,t)}{\partial t} &= \int d^3q\, \frac{\delta\tilde{f}_2^{(0)}(1{,}2,t)}{\delta\tilde{f}_1(\mathrm{q},t)} \frac{\partial\tilde{f}_1(\mathrm{q},t)}{\partial t} \\ = \tilde{f}_1(\mathrm{p}_2^{\mathrm{in}},t)\, \frac{\partial\tilde{f}_1(\mathrm{p}_1^{\mathrm{in}},t)}{\partial t} &+ \tilde{f}_1(\mathrm{p}_1^{\mathrm{in}},t)\, \frac{\partial\tilde{f}_1(\mathrm{p}_2^{\mathrm{in}},t)}{\partial t} \\ &= O(\varepsilon). \end{aligned} \tag{2.4.52}$$

Each product in the third line contains one factor of order 1 and one time derivative of order ε. The partial time derivative of the pair coefficient is therefore of order ε.

The collision integral in (2.4.34) already has the prefactor ε/d^3. A correction of order ε to the pair distribution consequently contributes at order ε^2 to the one particle equation. To calculate the collision integral through order ε, we retain the pair equation at zeroth order. At this accuracy, both the time derivative estimated in (2.4.52) and the integral involving $\tilde{f}_3$ in the second equation of (2.4.32) are omitted.

For a uniform gas, the pair coefficient depends on position through $\mathrm{R} = \mathrm{r}_2 - \mathrm{r}_1$. Its gradients with respect to r_1 and r_2 are therefore $-\nabla_{\mathrm{R}}\tilde{f}_2^{(0)}$ and $+\nabla_{\mathrm{R}}\tilde{f}_2^{(0)}$. With $\mathrm{g} = (\mathrm{p}_2 - \mathrm{p}_1)/m$, the streaming contributions combine into $\mathrm{g}\cdot\nabla_{\mathrm{R}}\tilde{f}_2^{(0)}$. The force on particle 1 is $\mathrm{F}_{12} = \nabla_{\mathrm{R}}\Phi(|\mathrm{R}|)$. With zero external force and the time derivative omitted at this accuracy, equation (2.4.33) becomes

$$\left[\mathrm{g}\cdot\nabla_{\mathrm{R}} + \mathrm{F}_{12}\cdot\left(\nabla_{\mathrm{p}_1} - \nabla_{\mathrm{p}_2}\right)\right]\tilde{f}_2^{(0)}(\mathrm{R},\mathrm{p}_1,\mathrm{p}_2,t) = 0. \tag{2.4.53}$$

The time argument remains because the one particle distribution in (2.4.51) evolves on the kinetic time scale.

In (2.4.34), the collision integral contains $\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2^{(0)}$, integrated over r_2 and p_2. Expressing its momentum integral as a spatial derivative will allow the remaining position integral to be evaluated from the pair distribution at large separation. Integrating (2.4.53) over p_2 provides this derivative.

The force F_{12} is independent of p_2. With the decay of the distribution at large momentum assumed in Section 2.3, integration of the derivative with respect to p_2 gives zero. The remaining contributions in (2.4.53) then give the second equality:

$$\begin{gathered}\int d^3p_2\,\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_2}\tilde{f}_2^{(0)}=0,\\ \int d^3p_2\,\mathrm{F}_{12}\cdot\nabla_{\mathrm{p}_1}\tilde{f}_2^{(0)}=-\int d^3p_2\,\mathrm{g}\cdot\nabla_{\mathrm{R}}\tilde{f}_2^{(0)}.\end{gathered}\tag{2.4.54}$$

Substituting the second equality in (2.4.54) into (2.4.34), using $1/v=\varepsilon/d^3$ and $d^3r_2=d^3R$ at fixed r_1, gives

$$\frac{\partial\tilde{f}_1(\mathrm{p}_1,t)}{\partial t}=\frac{1}{v}\int d^3p_2\int d^3R\,\mathrm{g}\cdot\nabla_{\mathrm{R}}\tilde{f}_2^{(0)}+O(\varepsilon^2).\tag{2.4.55}$$

We substitute the operator relation (2.4.47) for $\tilde{f}_2^{(0)}$ in (2.4.55). For the homogeneous one particle factors, (2.4.49) shows that the free one particle operators in (2.4.46) leave each factor unchanged. Hence

$$\begin{aligned}\frac{\partial\tilde{f}_1(\mathrm{p}_1,t)}{\partial t}&=\frac{1}{v}\int d^3p_2\int d^3R\,\mathrm{g}\cdot\nabla_{\mathrm{R}}\,\sigma_2\left(\tilde{f}_1(\mathrm{p}_1,t)\,\tilde{f}_1(\mathrm{p}_2,t)\right)+O(\varepsilon^2)\\&=\frac{1}{v}\int d^3p_2\int d^3R\,\mathrm{g}\cdot\nabla_{\mathrm{R}}\lim_{\tau\to\infty}S_{-\tau}^{(2)}\left(\tilde{f}_1(\mathrm{p}_1,t)\,\tilde{f}_1(\mathrm{p}_2,t)\right)+O(\varepsilon^2).\end{aligned}\tag{2.4.56}$$

In the last line, $S_{-\tau}^{(2)}$ evaluates the product at the momenta $\mathrm{p}_i(t-\tau)$, as in (2.4.51). These momenta depend on the specified relative position R through the two particle Hamilton equations. The derivative ∇_{R} acts on the resulting pair coefficient.

For each fixed pair of momentum arguments $\mathrm{p}_1,\mathrm{p}_2$, the vector g is independent of the integration position. Write $g=|\mathrm{g}|$. We use cylindrical coordinates in the space of relative positions R, choosing the positive axis along g, the velocity of particle 2 relative to particle 1. Let $\hat{\mathrm{z}}$ be the unit vector along this axis. The signed coordinate z is the projection of R onto it; b is the perpendicular distance, and φ is the azimuth. Thus

$$\begin{gathered}\hat{\mathrm{z}}=\frac{\mathrm{g}}{g},\quad z=\mathrm{R}\cdot\hat{\mathrm{z}},\quad b^2=|\mathrm{R}|^2-z^2,\\ d^3R=b\,db\,d\varphi\,dz,\quad \mathrm{g}\cdot\nabla_{\mathrm{R}}=g\,\frac{\partial}{\partial z}.\end{gathered}\tag{2.4.57}$$

Here z is a coordinate of the relative position, measured along an axis chosen separately for each fixed momentum pair.

Using (2.4.57) in (2.4.55), the integration over z gives the upper boundary value minus the lower boundary value. Writing the pair coefficient in the operator form of (2.4.56), we obtain

$$\begin{aligned}\frac{\partial\tilde{f}_1(\mathrm{p}_1,t)}{\partial t}&=\frac{1}{v}\int d^3p_2\int_0^\infty b\;db\int_0^{2\pi}d\,\varphi\,g\int_{-\infty}^{+\infty}d\,z\,\frac{\partial\tilde{f}_2^{(0)}}{\partial z}+O(\varepsilon^2)\\&=\frac{1}{v}\int d^3p_2\int_0^\infty b\;db\int_0^{2\pi}d\,\varphi\,g\lim_{\tau\to\infty}S_{-\tau}^{(2)}\left(\tilde{f}_1(\mathrm{p}_1,t)\,\tilde{f}_1(\mathrm{p}_2,t)\right)\Big|_{z=-\infty}^{z=+\infty}+O(\varepsilon^2).\end{aligned}\tag{2.4.58}$$

In (2.4.58), the limit $\tau\to\infty$ is taken at each fixed pair state, as in (2.4.51). The subsequent limits $z\to-\infty$ and $z\to+\infty$ are taken with $b,\varphi,\mathrm{p}_1,\mathrm{p}_2,t$ fixed.

By definition (2.4.43), $S_{-\tau}^{(2)}$ evaluates the product at earlier states of the interacting pair. Outside the force region, the momenta remain constant. On that free portion of the motion,

$$\begin{gathered}\mathrm{R}(t-\tau)=\mathrm{R}(t)-\frac{\mathrm{p}_2-\mathrm{p}_1}{m}\tau=\mathrm{R}(t)-\mathrm{g}\tau,\\ z(t-\tau)=z(t)-g\tau,\\ |\mathrm{R}(t-\tau)|^2=b^2+(z(t)-g\tau)^2,\qquad\tau>0.\end{gathered}\tag{2.4.59}$$

For $z \to -\infty$, subtracting $g\tau$ makes the negative coordinate more negative. Equation (2.4.59) shows that the separation increases. The earlier motion therefore stays outside the force region. The momenta remain $\mathrm{p}_1, \mathrm{p}_2$, so their incoming values coincide with these specified arguments.

For $z \to +\infty$, evaluating earlier states reduces the positive coordinate and decreases the separation until the pair enters the force region. The earlier positions and momenta within that region are calculated from the interacting Hamilton equations. Continuing to earlier times reaches the separated states before the physical forward collision, with momenta $\mathrm{p}_1^{\mathrm{in}}, \mathrm{p}_2^{\mathrm{in}}$ defined in (2.4.50). The specified momenta $\mathrm{p}_1, \mathrm{p}_2$ at the positive boundary are therefore the momenta after that collision. Equation (2.4.59) applies only to the free portion of this motion.

The two boundary values are consequently

$$\begin{aligned} \lim_{z\to-\infty} \tilde{f}_2^{(0)} &= \tilde{f}_1(\mathrm{p}_1, t)\, \tilde{f}_1(\mathrm{p}_2, t), \\ \lim_{z\to+\infty} \tilde{f}_2^{(0)} &= \tilde{f}_1(\mathrm{p}_1^{\mathrm{in}}, t)\, \tilde{f}_1(\mathrm{p}_2^{\mathrm{in}}, t). \end{aligned} \tag{2.4.60}$$

The second line uses the incoming momenta for a collision ending with the specified pair $\mathrm{p}_1, \mathrm{p}_2$. The superscript in continues to mean before the physical forward collision.

For impact parameters at which the force produces negligible scattering, the momenta remain unchanged to the retained accuracy. The two products in (2.4.60) then coincide and cancel in (2.4.58). Substitution of these boundary values into (2.4.58) gives

$$\begin{aligned} \frac{\partial \tilde{f}_1(\mathrm{p}_1,t)}{\partial t} &= \frac{1}{v} \int d^3 p_2 \int_0^\infty b\ db \int_0^{2\pi} d\,\varphi\, g \\ \times \left(\tilde{f}_1(\mathrm{p}_1^{\mathrm{in}}, t)\, \tilde{f}_1(\mathrm{p}_2^{\mathrm{in}}, t) - \tilde{f}_1(\mathrm{p}_1, t)\, \tilde{f}_1(\mathrm{p}_2, t) \right) &+ O(\varepsilon^2). \end{aligned} \tag{2.4.61}$$

The positive boundary contribution gives the gain of particles with momentum p_1 through collisions ending in that state. The negative boundary contribution gives their loss through collisions starting in that state. Both contributions follow from the pair equation and its incoming boundary condition.

In the gain term, $\mathrm{p}_1^{\mathrm{in}}, \mathrm{p}_2^{\mathrm{in}}$ have the same meaning as the primed momenta in the collision counting formula: their physical forward collision produces the specified momenta $\mathrm{p}_1, \mathrm{p}_2$.

To restore the normalization of f_1, multiply (2.4.61) by N/V and substitute $\tilde{f}_1 = (V/N) f_1$. Since $1/v = N/V$, the coefficient multiplying each product becomes $(N/V)(1/v)(V/N)^2 = 1$. With $b\, db\, d\varphi = d\sigma$, as defined in (2.4.9), this is the collision integral obtained by counting.

The derivation above assumes spatial homogeneity and zero external force. A sufficient condition for using the same collision integral locally in a nonuniform gas is that f_1 and the external potential vary negligibly over distances of order the mean free path, with the external force changing the momenta negligibly during a collision. All four one particle factors are then evaluated at the same kinetic position r, while retaining their respective momentum arguments and time t. With the normalization restored as above, substitution into (2.4.1), retaining streaming and external acceleration in $\mathcal{L}_1$, recovers the Boltzmann kinetic equation (2.4.24).

The scope of the method and extensions beyond binary collisions

Equation (2.4.61) retains the contribution of isolated binary collisions. Bogoliubov's method also specifies how to calculate corrections: the BBGKY hierarchy determines successive coefficients in the expansion in powers of ε. Retaining the first correction to the pair distribution gives, from (2.4.32),

$$\begin{aligned} \mathcal{L}_1 \tilde{f}_1 = &-\frac{\varepsilon}{d^3} \int d2\, \mathrm{F}_{12} \cdot \nabla_{\mathrm{p}_1} \tilde{f}_2^{(0)} \\ &-\frac{\varepsilon^2}{d^3} \int d2\, \mathrm{F}_{12} \cdot \nabla_{\mathrm{p}_1} \tilde{f}_2^{(1)} + O(\varepsilon^3). \end{aligned} \tag{2.4.62}$$

The first integral gives the binary collision contribution derived in (2.4.61). The second gives its correction at order ε^2.

Calculating $\tilde{f}_2^{(1)}$ requires the three particle coefficient $\tilde{f}_3^{(0)}$, which appears in the second equation of (2.4.32). At zeroth order, the third BBGKY equation reduces to the Liouville equation for three interacting particles, with the forces between all three pairs retained. The influence of a fourth particle enters at the next order in ε.

For unbound three particle scattering, the operator construction in (2.4.43)–(2.4.47) extends directly. Define $S_{-\tau}^{(3)}$ as the operator that evaluates a function at the earlier three particle states obtained from their coupled Hamilton equations, with the specified state (1,2,3) at time t. Denote the corresponding limiting operator by σ_3. Weakening of correlations at the separated incoming states gives

$$\begin{aligned} \sigma_3 &= \lim_{\tau\to\infty} S_{-\tau}^{(3)} S_{\tau}^{(1)}(1) S_{\tau}^{(1)}(2) S_{\tau}^{(1)}(3), \\ \tilde{f}_3^{(0)}(1,2,3,t) &= \sigma_3 \left(\tilde{f}_1(1,t)\, \tilde{f}_1(2,t)\, \tilde{f}_1(3,t) \right). \end{aligned} \tag{2.4.63}$$

This coefficient supplies the contribution of particle 3 to the pair equation at order ε. At the same order, the partial time derivative estimated in (2.4.52), omitted in (2.4.53), is also retained. The pair equation with these contributions and its incoming boundary condition determines $\tilde{f}_2^{(1)}$, and hence the second integral in (2.4.62).

The three particle dynamics includes simultaneous interactions and correlated sequences of binary collisions. For example, collisions of particles 1 and 2 with the same particle 3 can correlate their states before a subsequent collision between 1 and 2. The incoming pair statistics are then affected even when the individual collisions are separated in time. Higher orders incorporate four and more particles by continuing the comparison of powers of ε in the hierarchy.

This procedure provides a systematic ordering under the finite-coefficient assumption in (2.4.31). A controlled truncation requires $\varepsilon \ll 1$. In a dense fluid, $\varepsilon = nd^3$ is generally of order unity, so successive powers no longer suppress the higher contributions. Corrections may be comparable to the binary contribution, and retaining only the first few terms loses its justification. Convergence of the formal series is a separate question; a dense-fluid theory requires another justified approximation for the higher distributions.

Bogoliubov's kinetic hypothesis (2.4.26) is broader than this expansion. It postulates that, after a short initial relaxation, the higher distributions are determined by the complete one particle function $f_1(\mathrm{r}, \mathrm{p}, t)$ at the observation time t. Its physical requirement is that the relevant pair, three particle and higher correlations adjust much faster than f_1 changes appreciably. During their adjustment, f_1 changes little; subsequently, the higher distributions continue to follow its evolution.

The hypothesis concerns the loss of independent memory of the initial higher correlations. Their influence during the initial relaxation can change f_1, and those changes remain in the distribution from which the kinetic evolution proceeds. Once the hypothesis applies, separate initial data for the higher distributions are no longer required.

Interaction correlations remain present in the functionals $\mathcal{F}_s[f_1]$. The dilute pair coefficient in (2.4.47) already illustrates this. In a dense fluid, substantial correlations between neighbouring particles are likewise compatible with a functional description through f_1, provided they adjust rapidly to it. The strength of a correlation and its relaxation time are separate physical properties.

Spatial weakening of correlations concerns a different property: sufficiently distant particles become statistically independent, as in (2.4.36). This property may remain valid in a dense fluid with a finite correlation length. Its extension to collision separations, however, requires the influence of surrounding particles. The second equation of (2.4.30) represents that influence through f_3. The isolated operator $S_{-\tau}^{(2)}$ omits those forces, so transporting a distant factorized

product with that operator gives only the binary approximation. Spatial weakening alone therefore supplies neither the complete dense-fluid functional nor the required separation of relaxation times.

The interaction energy provides a physical reason to examine whether f_1 is sufficient. Let $E_{\mathrm{int}}(t)$ be the mean energy of the pair interactions. Since f_2 counts ordered pairs, each physical pair is counted twice, giving

$$E_{\mathrm{int}}(t) = \frac{1}{2}\int d1\, d2\, \Phi(|\mathrm{r}_1 - \mathrm{r}_2|)\, f_2(1,2,t). \tag{2.4.64}$$

States with the same f_1 have the same mean kinetic energy, but different pair distributions can give different interaction energies. A closure through f_1 alone presupposes that the pair correlations relevant to the evolution, including their energy contribution, have become determined by f_1.

If pair correlations evolve as slowly as f_1, the reduced description can retain f_2 alongside f_1. The generalized kinetic hypothesis then expresses f_s, with $s \geq 3$, through both current functions. The one particle and pair equations evolve f_1 and f_2, with f_3 supplied by this generalized closure.

Collision invariants and the transition to the H-theorem

For the dilute gas, the collision integral (2.4.23) describes how elastic binary collisions change the momentum distribution. Each collision preserves particle number, total momentum and total kinetic energy. We now derive the corresponding conservation conditions, introduced in Section 2.2, directly from the gain and loss terms.

We assume that the momentum integrals below converge. To identify the quantities conserved by collisions, we multiply the collision integral by a function $\psi(\mathbf{p}_1)$ and integrate over momentum:

$$I_\psi(\mathbf{r}, t) = \int d^3p_1\, \psi(\mathbf{p}_1)\, C[f_1](\mathbf{r}, \mathbf{p}_1, t). \tag{2.4.65}$$

All distribution factors in the calculation are evaluated at the same position $\mathbf{r}$ and time t. The abbreviations

$$f_i = f_1(\mathbf{r}, \mathbf{p}_i, t), \qquad f_i' = f_1(\mathbf{r}, \mathbf{p}_i', t), \qquad \psi_i = \psi(\mathbf{p}_i), \qquad \psi_i' = \psi(\mathbf{p}_i')$$

refer to $i = 1,2$; here the subscript on f_i labels a momentum argument of the one-particle distribution. As in the collision integral, $\mathbf{p}_1', \mathbf{p}_2'$ are the incoming momenta that produce $\mathbf{p}_1, \mathbf{p}_2$. The relative speed is $g = |\mathbf{p}_2 - \mathbf{p}_1|/m$, and $d\sigma = b\, db\, d\varphi$. Substitution of (2.4.23) into (2.4.65) gives

$$I_\psi = \int d^3p_1\, d^3p_2 \int b\, db\, d\varphi\, g\, \psi_1\, (f_1' f_2' - f_1 f_2). \tag{2.4.66}$$

Exchanging the labels of the two identical particles leaves the collision measure and both distribution products unchanged, while ψ_1 becomes ψ_2. Averaging the original integral and the integral with exchanged labels therefore gives

$$I_\psi = \frac{1}{2}\int d^3p_1\, d^3p_2 \int b\, db\, d\varphi\, g\, (\psi_1 + \psi_2)(f_1' f_2' - f_1 f_2). \tag{2.4.67}$$

The next change of variables interchanges the initial and final collision states. In (2.4.67), however, the primed momenta are functions of $\mathbf{p}_1, \mathbf{p}_2, b, \varphi$. To make the change explicit, we first write the same integral with all four momenta as integration variables and impose the scattering relations with Dirac delta functions.

For specified $\mathbf{p}_1, \mathbf{p}_2, b, \varphi$, the two-particle scattering problem determines the incoming momenta $\mathbf{p}_i^{\mathrm{in}}(\mathbf{p}_1, \mathbf{p}_2; b, \varphi)$. With these arguments understood on the right-hand side, the required weight is

$$W(\mathbf{p}_1, \mathbf{p}_2; \mathbf{p}_1', \mathbf{p}_2') = \int b\, db\, d\varphi\, g\, \delta^{(3)}(\mathbf{p}_1' - \mathbf{p}_1^{\mathrm{in}})\, \delta^{(3)}(\mathbf{p}_2' - \mathbf{p}_2^{\mathrm{in}}).$$

Integration over $\mathbf{p}_1'$ and $\mathbf{p}_2'$ sets $\mathbf{p}_i' = \mathbf{p}_i^{\mathrm{in}}$ in the remaining factors. The four momentum variables are therefore constrained by the same scattering relations as in (2.4.67), which becomes

$$I_\psi = \frac{1}{2}\int d^3p_1\, d^3p_2\, d^3p_1'\, d^3p_2'\, W\, (\psi_1 + \psi_2)(f_1' f_2' - f_1 f_2).$$

Here and below, W has the arguments displayed in its definition. Reversibility of the elastic collision and the invariance of the complete collision measure in (2.4.20) give

$$W(\mathbf{p}_1, \mathbf{p}_2; \mathbf{p}_1', \mathbf{p}_2') = W(\mathbf{p}_1', \mathbf{p}_2'; \mathbf{p}_1, \mathbf{p}_2).$$

We can now interchange the four integration variables in pairs,

$$\mathbf{p}_1 \leftrightarrow \mathbf{p}_1', \qquad \mathbf{p}_2 \leftrightarrow \mathbf{p}_2'.$$

This permutation has absolute Jacobian one. The symmetry of W restores its original arguments, while the other factors transform as

$$\psi_1 + \psi_2 \mapsto \psi_1' + \psi_2', \qquad f_1' f_2' - f_1 f_2 \mapsto f_1 f_2 - f_1' f_2'.$$

$$I_\psi = -\frac{1}{2} \int d^3p_1\, d^3p_2\, d^3p_1'\, d^3p_2'\, W\, (\psi_1' + \psi_2')(f_1' f_2' - f_1 f_2).$$

Averaging the two expressions for I_ψ gives

$$I_\psi = \frac{1}{4} \int d^3p_1\, d^3p_2\, d^3p_1'\, d^3p_2'\, W\, (\psi_1 + \psi_2 - \psi_1' - \psi_2')(f_1' f_2' - f_1 f_2).$$

Finally, substitution of the definition of W and integration over $\mathbf{p}_1', \mathbf{p}_2'$ using the delta functions return the original collision measure. We obtain the Boltzmann lemma,

$$I_\psi = \tfrac{1}{4} \int d^3p_1\, d^3p_2 \int b\, db\, d\varphi\, g\, (\psi_1 + \psi_2 - \psi_1' - \psi_2')(f_1' f_2' - f_1 f_2). \tag{2.4.68}$$

The first factor in parentheses is the difference between the sum of ψ for the final pair and its sum for the initial pair. A function whose sum is conserved in every allowed collision is called a collision invariant. It satisfies

$$\psi(\mathbf{p}_1) + \psi(\mathbf{p}_2) = \psi(\mathbf{p}_1') + \psi(\mathbf{p}_2'). \tag{2.4.69}$$

For such a function, this factor in (2.4.68) vanishes in every collision, and hence $I_\psi = 0$.

Particle number is conserved because each binary collision has two particles before and two particles after scattering. Conservation of total momentum and kinetic energy gives the other four basic collision invariants. Together, the five functions are

$$1, \qquad p_x, \qquad p_y, \qquad p_z, \qquad \frac{p^2}{2m}. \tag{2.4.70}$$

Choosing these functions successively in (2.4.65) gives

$$\begin{aligned} \int d^3p_1\, C[f_1](\mathbf{r}, \mathbf{p}_1, t) &= 0, \\ \int d^3p_1\, \mathbf{p}_1\, C[f_1](\mathbf{r}, \mathbf{p}_1, t) &= 0, \\ \int d^3p_1\, \tfrac{p_1^2}{2m}\, C[f_1](\mathbf{r}, \mathbf{p}_1, t) &= 0. \end{aligned} \tag{2.4.71}$$

Thus collisions make no contribution to the local rates of change of particle number, momentum or kinetic energy. Streaming can transport these quantities between different positions, and the external force can change momentum and energy.

For example, integrating the Boltzmann equation (2.4.24) over momentum and using the particle-number identity in (2.4.71) removes the collision integral. Using the definitions of number density n and mean velocity $\mathbf{u}$ from Section 2.2, the streaming integral becomes $\nabla_{\mathbf{r}} \cdot (n\mathbf{u})$. Since $\mathbf{F}^{\text{ext}}$ is independent of momentum, its contribution is a momentum boundary integral, which vanishes when f_1 decays sufficiently rapidly at large momentum. The result is the continuity equation,

$$\frac{\partial n}{\partial t} + \nabla_{\mathbf{r}} \cdot (n\mathbf{u}) = 0. \tag{2.4.72}$$

Many different momentum distributions have the same particle number, momentum and kinetic energy. Their conservation therefore leaves open the question of how collisions drive relaxation among these distributions. Section 2.5 introduces the H-function and uses the identity (2.4.68) to calculate its change due to collisions. The resulting sign determines the direction of collisional relaxation, while the equality condition identifies the local Maxwell distribution.

2.5 The Boltzmann H-theorem

Section 2.4 showed that elastic collisions conserve particle number, momentum and kinetic energy. These conservation laws constrain the redistribution of particles among momenta, but they do not determine the direction of that redistribution. We now derive a functional of f_1 whose time derivative has a definite sign under the Boltzmann equation. We then determine when the derivative vanishes and relate the result to equilibrium and entropy.

The H-function and the assumptions

The identity (2.4.68) contains the combination $\psi(\mathrm{p}_1) + \psi(\mathrm{p}_2) - \psi(\mathrm{p}_1') - \psi(\mathrm{p}_2')$. Choosing ψ to be a logarithm turns this sum into a logarithm of the ratio of the pair products $f_1(\mathrm{r}, \mathrm{p}_1, t) f_1(\mathrm{r}, \mathrm{p}_2, t)$ and $f_1(\mathrm{r}, \mathrm{p}_1', t) f_1(\mathrm{r}, \mathrm{p}_2', t)$ that occur in the collision integral. This is the reason for the following definition.

Let $f_{\mathrm{ref}} > 0$ be a fixed constant with the same units as f_1, and let $\mathcal{V}$ be the fixed spatial region occupied by the gas. Define the Boltzmann H-function by

$$H(t) = \int_{\mathcal{V}} d^3 r \int d^3 p \, f_1(\mathrm{r}, \mathrm{p}, t) \ln \frac{f_1(\mathrm{r},\mathrm{p},t)}{f_{\mathrm{ref}}}. \tag{2.5.1}$$

The reference constant makes the logarithm dimensionless. Since $\int d^3 r \, d^3 p \, f_1 = N$, changing f_{ref} adds only a time-independent constant proportional to N. It therefore has no effect on dH/dt. No averaging cell or additional distribution is introduced in (2.5.1).

We assume that f_1 is positive and sufficiently regular, that H and the required collision integrals and moments are finite, and that its momentum tails make the integrations by parts below valid. The external force $\mathrm{F}^{\mathrm{ext}}(\mathrm{r}, t)$ remains independent of momentum, as in Sections 2.2 and 2.4. We use periodic spatial boundaries or stationary walls with specular reflection, so that the spatial boundary contribution to dH/dt vanishes. Specular reflection reverses the normal component of momentum and preserves its tangential components. The sign proof can also be extended to distributions with zeros by a suitable limiting procedure; the equality argument below concerns smooth positive distributions.

Time derivative of H

Differentiating (2.5.1) gives

$$\frac{dH}{dt} = \int_{\mathcal{V}} d^3 r \int d^3 p \, \left(1 + \ln \frac{f_1}{f_{\mathrm{ref}}}\right) \frac{\partial f_1}{\partial t}. \tag{2.5.2}$$

Insert the Boltzmann equation (2.4.24). For the spatial streaming term, use $\nabla_{\mathrm{r}}[f_1 \ln(f_1/f_{\mathrm{ref}})] = \big(1 + \ln(f_1/f_{\mathrm{ref}})\big) \nabla_{\mathrm{r}} f_1$. If $d\mathrm{S}$ denotes the outward directed surface element of $\partial\mathcal{V}$, the resulting contribution is

$$\begin{aligned} &- \int_{\mathcal{V}} d^3 r \int d^3 p \, \frac{\mathrm{p}}{m} \cdot \nabla_{\mathrm{r}} [f_1 \ln \frac{f_1}{f_{\mathrm{ref}}}] \\ &= - \oint_{\partial\mathcal{V}} d\,\mathrm{S} \cdot \int d^3 p \, \frac{\mathrm{p}}{m} f_1 \ln \frac{f_1}{f_{\mathrm{ref}}} = 0. \end{aligned} \tag{2.5.3}$$

For periodic boundaries, the contributions from opposite faces cancel. At a specular wall, the incident and reflected distributions have equal values. Their normal velocities have opposite signs, so their contributions to the surface integral cancel in pairs.

The force term is a divergence in momentum space because $\mathrm{F}^{\mathrm{ext}}$ is independent of p. Its contribution is

$$\begin{aligned} &- \int_{\mathcal{V}} d^3 r \int d^3 p \, \mathrm{F}^{\mathrm{ext}} \cdot \nabla_{\mathrm{p}} [f_1 \ln \frac{f_1}{f_{\mathrm{ref}}}] \\ &= - \int_{\mathcal{V}} d^3 r \int d^3 p \, \nabla_{\mathrm{p}} \cdot [\mathrm{F}^{\mathrm{ext}} f_1 \ln \frac{f_1}{f_{\mathrm{ref}}}] = 0. \end{aligned} \tag{2.5.4}$$

Here the boundary integral at large momentum vanishes by the assumed decay. The collision term is therefore the only remaining contribution. Its part weighted by 1 vanishes because $\int d^3p\, C[f_1] = 0$, as established in (2.4.71). Thus

$$\frac{dH}{dt} = \int_{\mathcal{V}} d^3r \int d^3p_1 \ln\frac{f_1(\mathrm{r},\mathrm{p}_1,t)}{f_{\mathrm{ref}}}\, C[f_1](\mathrm{r},\mathrm{p}_1,t). \tag{2.5.5}$$

This reduction does not require spatial homogeneity. Streaming can redistribute the integrand of H in space, but it gives no net change of H under the stated boundary conditions.

The sign of the collisional contribution

At each fixed r and t, apply (2.4.68) with $\psi(\mathrm{p}) = \ln(f_1(\mathrm{r},\mathrm{p},t)/f_{\mathrm{ref}})$. Its possible dependence on r and t does not affect the exchanges of momentum variables used to derive that identity. The primed momenta retain their meaning in (2.4.23): they are the incoming momenta that produce the specified pair $\mathrm{p}_1, \mathrm{p}_2$. The collision integration uses $g = |\mathrm{p}_2 - \mathrm{p}_1|/m$ and $d\sigma = b\, db\, d\varphi$, defined in (2.4.5) and (2.4.9). The four logarithms combine as

$$\psi(\mathrm{p}_1) + \psi(\mathrm{p}_2) - \psi(\mathrm{p}_1{}') - \psi(\mathrm{p}_2{}') = \ln\frac{f_1(\mathrm{r},\mathrm{p}_1,t) f_1(\mathrm{r},\mathrm{p}_2,t)}{f_1(\mathrm{r},\mathrm{p}_1{}',t) f_1(\mathrm{r},\mathrm{p}_2{}',t)}. \tag{2.5.6}$$

Combining the logarithms divides each pair product by f_{ref}^2; the identical reference factors cancel in their ratio. Substituting (2.5.6) into the symmetrized identity and then into (2.5.5) gives

$$\begin{aligned}\frac{dH}{dt} = & -\frac{1}{4}\int_{\mathcal{V}} d^3r \int d^3p_1 \int d^3p_2 \int d\sigma\, g \\ & \times [f_1(\mathrm{r},\mathrm{p}_1,t) f_1(\mathrm{r},\mathrm{p}_2,t) - f_1(\mathrm{r},\mathrm{p}_1{}',t) f_1(\mathrm{r},\mathrm{p}_2{}',t)] \\ & \times \ln\frac{f_1(\mathrm{r},\mathrm{p}_1,t) f_1(\mathrm{r},\mathrm{p}_2,t)}{f_1(\mathrm{r},\mathrm{p}_1{}',t) f_1(\mathrm{r},\mathrm{p}_2{}',t)}.\end{aligned} \tag{2.5.7}$$

For any positive numbers x and y, monotonicity of the logarithm implies that $x - y$ and $\ln x - \ln y$ have the same sign. Consequently,

$$(x - y)\ln\frac{x}{y} \geq 0. \tag{2.5.8}$$

Equality in (2.5.8) holds if and only if $x = y$. Apply it with $x = f_1(\mathrm{r},\mathrm{p}_1,t) f_1(\mathrm{r},\mathrm{p}_2,t)$ and $y = f_1(\mathrm{r},\mathrm{p}_1{}',t) f_1(\mathrm{r},\mathrm{p}_2{}',t)$. The relative speed g and the area element $d\sigma = b\, db\, d\varphi$ are nonnegative. Every contribution to the integral in (2.5.7) is therefore nonnegative before multiplication by $-1/4$, and

$$\boxed{\frac{dH}{dt} \leq 0.} \tag{2.5.9}$$

Equation (2.5.9) is the Boltzmann H-theorem under the assumptions stated above. The collision integral decreases H whenever the two pair products differ on a set of collisions with nonzero integration weight.

Equality and the local Maxwell distribution

Because the integrand in (2.5.7) has a fixed sign, $dH/dt = 0$ requires, at almost every position and for almost every collision with nonzero weight,

$$f_1(\mathrm{r},\mathrm{p}_1,t) f_1(\mathrm{r},\mathrm{p}_2,t) = f_1(\mathrm{r},\mathrm{p}_1{}',t) f_1(\mathrm{r},\mathrm{p}_2{}',t). \tag{2.5.10}$$

For a smooth positive distribution, this condition extends by continuity to the allowed collisions. Taking its logarithm gives

$$\begin{aligned}\psi(\mathrm{p}_1) + \psi(\mathrm{p}_2) &= \psi(\mathrm{p}_1{}') + \psi(\mathrm{p}_2{}'), \\ \psi(\mathrm{p}) &= \ln\frac{f_1(\mathrm{r},\mathrm{p},t)}{f_{\mathrm{ref}}}.\end{aligned} \tag{2.5.11}$$

Thus ψ is a collision invariant in the precise sense of (2.4.69). Equation (2.4.70) lists the five invariants $1, p_x, p_y, p_z, p^2/(2m)$. To obtain the equality distribution, we must also justify that a smooth invariant has no further independent momentum dependence.

We work at fixed r, t and assume that the allowed elastic scattering connects all directions of the relative velocity at each nonzero g. This is the usual three-dimensional scattering case; a collision law that preserves additional quantities would need a separate equality analysis. At fixed total pair momentum P and relative speed g, equations (2.4.6)-(2.4.8) allow the relative velocity to change direction while preserving the pair energy. Let $\delta\mathrm{p}$ be an infinitesimal change of the first momentum on this surface. The second changes by $-\delta\mathrm{p}$. Conservation of energy and differentiation of the invariant condition give

$$\begin{aligned}(\mathrm{p}_1 - \mathrm{p}_2)\cdot\delta\mathrm{p} = 0,\\ [\nabla_{\mathrm{p}_1}\psi(\mathrm{p}_1) - \nabla_{\mathrm{p}_2}\psi(\mathrm{p}_2)]\cdot\delta\mathrm{p} = 0.\end{aligned} \tag{2.5.12}$$

The first line says that $\delta\mathrm{p}$ can be any tangent direction perpendicular to $\mathrm{p}_1 - \mathrm{p}_2$. The second says that the difference of the two gradients is perpendicular to every such direction. That gradient difference must therefore be parallel to $\mathrm{p}_1 - \mathrm{p}_2$.

Let $K(\mathrm{p})$ be the Hessian matrix of ψ, with entries $K_{\alpha\beta} = \partial^2\psi/\,\partial p_\alpha\,\partial p_\beta$, where $\alpha, \beta = x, y, z$. Choose $\mathrm{p}_2 = \mathrm{p}_1 + \delta p\,\mathrm{e}$, where e is any unit vector and δp is a small momentum increment. Divide the gradient difference by δp and take $\delta p \to 0$. It follows that $K(\mathrm{p}_1)\mathrm{e}$ is parallel to e for every direction. Choosing the three coordinate directions makes K diagonal; choosing sums of two coordinate directions makes its diagonal entries equal. Denote their common value by the scalar function $\lambda(\mathrm{p})$, and let $\delta_{\alpha\beta}$ be the Kronecker delta. Then

$$K_{\alpha\beta}(\mathrm{p}) = \lambda(\mathrm{p})\delta_{\alpha\beta}. \tag{2.5.13}$$

The vanishing mixed second derivatives in (2.5.13) mean that $\partial\psi/\,\partial p_\alpha$ depends only on p_α. Each diagonal second derivative therefore depends only on its own coordinate. Since the three diagonal derivatives are equal for independently variable p_x, p_y, p_z, their common value λ must be constant in momentum. Integrating twice gives the general invariant. Denote its scalar coefficients by $a_0(\mathrm{r}, t)$ and $a_2(\mathrm{r}, t)$ and its vector coefficient by $\mathrm{a}_1(\mathrm{r}, t)$. Then

$$\ln\frac{f_1}{f_{\mathrm{ref}}} = a_0 + \mathrm{a}_1\cdot\mathrm{p} + a_2\frac{p^2}{2m}. \tag{2.5.14}$$

Normalizability over all momenta requires $a_2 < 0$. Introduce a positive parameter T and a vector u by

$$a_2 = -\frac{1}{k_B T}, \qquad \mathrm{a}_1 = \frac{\mathrm{u}}{k_B T}. \tag{2.5.15}$$

Completing the square in (2.5.14) then yields

$$f_1 = f_{\mathrm{ref}}\exp\left(a_0 + \frac{mu^2}{2k_B T}\right)\exp[-\frac{(\mathrm{p}-m\mathrm{u})^2}{2mk_B T}]. \tag{2.5.16}$$

The Gaussian is centered at $m\mathrm{u}$, so its mean particle velocity is u. Its normalization uses

$$\int d^3p\,\exp[-\frac{(\mathrm{p}-m\mathrm{u})^2}{2mk_B T}] = (2\pi m k_B T)^{3/2}. \tag{2.5.17}$$

Fixing the remaining prefactor by $n = \int d^3p\, f_1$ gives

$$f_{\mathrm{LE}}(\mathrm{r}, \mathrm{p}, t) = \frac{n}{(2\pi m k_B T)^{3/2}}\exp[-\frac{(\mathrm{p}-m\mathrm{u})^2}{2mk_B T}]. \tag{2.5.18}$$

All three fields in (2.5.18) depend on r, t. Each Cartesian Gaussian variance is $mk_B T$, so

$$\int d^3p\,\frac{(\mathrm{p}-m\mathrm{u})^2}{2m}\,f_{\mathrm{LE}} = \frac{3}{2}nk_B T. \tag{2.5.19}$$

Hence the parameters n, u, T are exactly the density, flow velocity and kinetic temperature defined in Section 2.2. Equation (2.5.18) is the same local Maxwell distribution f_{LE} used there.

Conversely, the logarithm of (2.5.18) has the form (2.5.14). In the sum of two such logarithms, the constant term cancels between incoming and outgoing states, the linear term cancels by momentum conservation, and the quadratic term cancels by energy conservation. Thus every allowed collision satisfies (2.5.10), and

$$C[f_{\mathrm{LE}}] = 0. \tag{2.5.20}$$

The equality condition is local. An arbitrary choice of fields n, u, T in (2.5.18) does not automatically solve the full Boltzmann equation. If the distribution is exactly local Maxwellian, that equation also requires

$$\mathcal{L}_1 f_{\mathrm{LE}} = \frac{\partial f_{\mathrm{LE}}}{\partial t} + \frac{\mathrm{p}}{m} \cdot \nabla_{\mathrm{r}} f_{\mathrm{LE}} + \mathrm{F}^{\mathrm{ext}} \cdot \nabla_{\mathrm{p}} f_{\mathrm{LE}} = 0. \tag{2.5.21}$$

Spatial gradients or external forces can make $\mathcal{L}_1 f_{\mathrm{LE}}$ nonzero even when $C[f_{\mathrm{LE}}] = 0$. In a hydrodynamic approximation, small departures from the local Maxwell form provide the collision term needed to balance the slow evolution of the fields.

Equilibrium minimum and the meaning of monotonic decrease

For a concrete global equilibrium statement, specialize to a spatially homogeneous gas with no external force and periodic boundaries. Let V be the volume of $\mathcal{V}$. In addition to the fixed particle number N, define the total gas momentum $\mathrm{P}_{\mathrm{tot}}$ and total kinetic energy E_{kin} by

$$\begin{aligned} \mathrm{P}_{\mathrm{tot}} &= \int_{\mathcal{V}} d^3 r \int d^3 p \, \mathrm{p} f_1, \\ E_{\mathrm{kin}} &= \int_{\mathcal{V}} d^3 r \int d^3 p \, \frac{p^2}{2m} f_1. \end{aligned} \tag{2.5.22}$$

These quantities are time independent by (2.4.71); there is no external force or boundary momentum or energy transfer. The symbol $\mathrm{P}_{\mathrm{tot}}$ refers to the whole gas, whereas P in the collision kinematics refers to one pair.

Define the uniform density n_{eq}, mean velocity u_{eq} and temperature T_{eq} from these conserved quantities:

$$\begin{aligned} n_{\mathrm{eq}} &= \frac{N}{V}, \qquad \mathrm{u}_{\mathrm{eq}} = \frac{\mathrm{P}_{\mathrm{tot}}}{mN}, \\ \frac{3}{2} N k_B T_{\mathrm{eq}} &= E_{\mathrm{kin}} - \frac{1}{2} m N u_{\mathrm{eq}}^2. \end{aligned} \tag{2.5.23}$$

Assume positive thermal energy, so $T_{\mathrm{eq}} > 0$. The uniform Maxwell distribution with the same three conserved moments is

$$f_{\mathrm{eq}}(\mathrm{p}) = \frac{n_{\mathrm{eq}}}{(2\pi m k_B T_{\mathrm{eq}})^{3/2}} \exp\left[-\frac{(\mathrm{p} - m\mathrm{u}_{\mathrm{eq}})^2}{2 m k_B T_{\mathrm{eq}}}\right]. \tag{2.5.24}$$

It is stationary: its collision term vanishes, it has no spatial gradient or explicit time dependence, and the external force is zero. Write $H[f_1]$ for the functional (2.5.1) evaluated on f_1, and define $H_{\mathrm{eq}} = H[f_{\mathrm{eq}}]$. The logarithm of $f_{\mathrm{eq}}/f_{\mathrm{ref}}$ grows only quadratically with momentum, so the Gaussian tail gives a finite H_{eq}.

The function $\ln(f_{\mathrm{eq}}/f_{\mathrm{ref}})$ is a linear combination of 1, the three momentum components, and $p^2/(2m)$ with constant coefficients. Since f_1 and f_{eq} have matching moments,

$$\int_{\mathcal{V}} d^3 r \int d^3 p \, (f_1 - f_{\mathrm{eq}}) \ln \frac{f_{\mathrm{eq}}}{f_{\mathrm{ref}}} = 0. \tag{2.5.25}$$

Split $\ln(f_1/f_{\mathrm{ref}}) = \ln(f_1/f_{\mathrm{eq}}) + \ln(f_{\mathrm{eq}}/f_{\mathrm{ref}})$ in $H[f_1]$ and subtract $H[f_{\mathrm{eq}}]$. Equation (2.5.25) removes the second contribution, leaving

$$H[f_1] - H_{\mathrm{eq}} = \int_{\mathcal{V}} d^3 r \int d^3 p \, f_1 \ln \frac{f_1}{f_{\mathrm{eq}}}. \tag{2.5.26}$$

For positive x, y, put $z = x/y$. The function $z\ln z - z + 1$ has derivative $\ln z$ and its minimum is zero at $z = 1$. Therefore

$$x \ln \frac{x}{y} - x + y \geq 0. \tag{2.5.27}$$

Equality in (2.5.27) holds if and only if $x = y$. Use $x = f_1$, $y = f_{\mathrm{eq}}$ and integrate. The terms $-f_1 + f_{\mathrm{eq}}$ integrate to zero because both distributions count N particles. Equations (2.5.26) and (2.5.27) give

$$H[f_1] \geq H_{\mathrm{eq}}. \tag{2.5.28}$$

Equality in (2.5.28) requires $f_1 = f_{\mathrm{eq}}$ almost everywhere. Thus the equilibrium Maxwell distribution minimizes H at fixed $N, \mathrm{P}_{\mathrm{tot}}, E_{\mathrm{kin}}$ in this setting. For a solution existing for all $t \geq 0$, the nonincreasing function $H(t)$ has a finite lower bound. It consequently has a finite limit, which we denote by H_∞:

$$\lim_{t\to\infty} H(t) = H_\infty \geq H_{\mathrm{eq}}. \tag{2.5.29}$$

This statement alone does not establish $H_\infty = H_{\mathrm{eq}}$ or convergence of the whole distribution to f_{eq}. Such convergence requires further information about the solution and its long-time dynamics. The H-theorem also supplies no relaxation rate. The figure illustrates the additional case in which relaxation to equilibrium does occur.

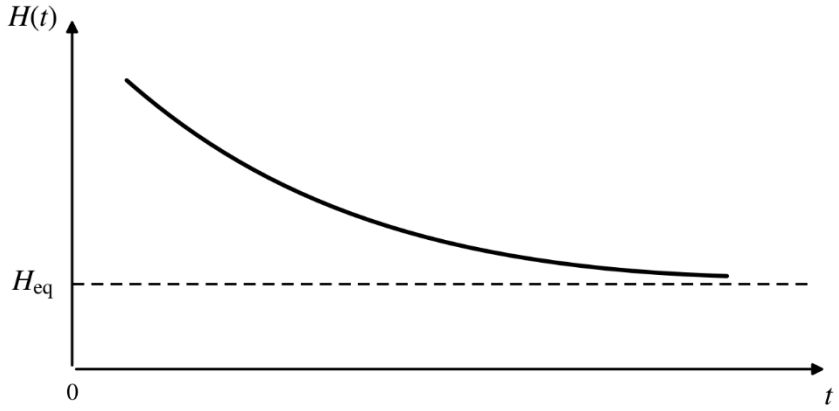


Figure 2.5.1. Schematic $H(t)$ for relaxation to uniform Maxwell equilibrium. The dashed line marks H_{eq}; the curve does not represent a specified relaxation law.

Relation to entropy

At fixed N, let S_0 be a time-independent additive constant specifying the entropy convention. Define the kinetic entropy functional by

$$S_{\mathrm{kin}}[f_1] = -k_B H[f_1] + S_0. \tag{2.5.30}$$

The sign result (2.5.9) immediately gives

$$\frac{dS_{\mathrm{kin}}}{dt} = -k_B \frac{dH}{dt} \geq 0. \tag{2.5.31}$$

To determine the thermodynamic meaning of this functional, evaluate it on the local Maxwell distribution already obtained. The logarithm entering $H[f_{\mathrm{LE}}]$ is

$$\ln \frac{f_{\mathrm{LE}}}{f_{\mathrm{ref}}} = \ln \frac{n}{f_{\mathrm{ref}}(2\pi m k_B T)^{3/2}} - \frac{(\mathrm{p}-m\mathrm{u})^2}{2mk_B T}. \tag{2.5.32}$$

In the definition of $H[f_{\mathrm{LE}}]$, each term in (2.5.32) is multiplied by f_{LE} and integrated over momentum. The first term is independent of momentum, so its contribution is n times that term. The second contributes $-3n/2$ by (2.5.19). Hence

$$H[f_{\mathrm{LE}}] = \int_{\mathcal{V}} d^3 r\, n[\ln \frac{n}{f_{\mathrm{ref}}(2\pi m k_B T)^{3/2}} - \frac{3}{2}]. \tag{2.5.33}$$

For example, choosing the additive convention $S_0 = Nk_B$ yields

$$S_{\mathrm{kin}}[f_{\mathrm{LE}}] = k_B \int_{\mathcal{V}} d^3 r\, n[\ln \frac{f_{\mathrm{ref}}(2\pi m k_B T)^{3/2}}{n} + \frac{5}{2}]. \tag{2.5.34}$$

This has the state dependence of the classical monatomic ideal-gas entropy; the remaining additive constant per particle is fixed by f_{ref}. At local equilibrium, the expression in square brackets gives the entropy per particle, in units of k_B, of an element with local density n and temperature T. Integrating over the gas gives its thermodynamic entropy within the dilute ideal-gas approximation. The flow velocity does not appear because the kinetic energy relative to that flow determines the temperature.

Away from local equilibrium, (2.5.30) defines an entropy functional of the retained one particle distribution. It does not include the independent many particle correlation information contained in $f_2, f_3, \ldots$. In particular, it cannot by itself supply the nonideal entropy corrections of a dense interacting gas. The local equilibrium calculation above establishes the thermodynamic interpretation in the regime where the local Maxwell form is applicable.

Microscopic reversibility and the scope of the theorem

Section 2.1 established that Hamiltonian dynamics preserves phase space volume and transports ρ_N without changing its value along a trajectory. Let $\rho_{N,\mathrm{ref}} > 0$ be a fixed constant with the same units as ρ_N. For a sufficiently regular full distribution with finite integrals and vanishing boundary terms, the Liouville equation gives

$$\frac{d}{dt}\int d\Gamma\, \rho_N \ln\frac{\rho_N}{\rho_{N,\mathrm{ref}}} = -\int d\Gamma\, \nabla_\Gamma \cdot \left[\dot{\Gamma}\rho_N \ln\frac{\rho_N}{\rho_{N,\mathrm{ref}}}\right] = 0. \tag{2.5.35}$$

The divergence form follows from $\partial_t \rho_N = -\dot{\Gamma}\cdot\nabla_\Gamma \rho_N$ and $\nabla_\Gamma \cdot \dot{\Gamma} = 0$. Thus the corresponding fine-grained integral is conserved. The decreasing one particle functional H belongs to the closed Boltzmann description. Its sign law requires the collision approximation and the factorization of the incoming pair distribution in (2.4.15); it does not follow from exact marginalisation alone.

For a time-reversal invariant microscopic system, reverse all particle momenta at some later time. The subsequent exact trajectories retrace the original motion. Pairs that were leaving a collision then become pairs approaching the reversed collision. The correlations generated in the original collision are consequently present in the incoming pairs of the reversed evolution. Those pairs generally fail the independence condition used to derive the Boltzmann collision integral. A one particle equation imposing that condition therefore need not describe this reversed preparation.

The kinetic resolution $\tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}$ makes the internal force history of a binary collision unresolved while retaining the slower evolution of f_1. The incoming correlation condition supplies the statistical time direction of the closure. Choosing a temporal resolution alone does not imply that condition or the inequality (2.5.9).

The equality analysis identifies the local Maxwell form toward which collisional relaxation can drive the momentum distribution. The time τ_{loc} defined in (2.4.3) characterizes that relaxation, but its value is not calculated by the H-theorem. When local relaxation is fast compared with the evolution of $n, \boldsymbol{u}, T$, these fields can support the subsequent hydrodynamic description.

2.6 Kinetic description of plasma and the Vlasov equation

Section 2.3 showed that the interaction term in the equation for f_1 contains two contributions: a force calculated from the one-particle distribution and a correction that requires the pair correlation g_2. Sections 2.4 and 2.5 retained the correlations generated during isolated binary encounters and obtained the Boltzmann description. We now develop the other approximation identified in Section 2.3, in which the force produced by many charged particles is the leading effect.

For a Coulomb interaction, a particle experiences forces from charges far beyond its nearest neighbours. If the interaction with one neighbour is weak, the combined electric force of many particles can still change the distribution appreciably. A kinetic equation for this regime must therefore retain the electric field generated by the particle density. The field changes the distribution, while the changing distribution changes the field. Our first task is to derive a closed equation that includes this mutual dependence.

The resulting equation also allows us to study two concrete physical problems. A stationary charge inside a plasma attracts or repels electrons and therefore changes the potential that it would

produce in vacuum. We shall calculate the resulting charge redistribution and the distance over which it reduces the electric field. A small electron-density disturbance produces an electric field even without an additional charge. We shall then determine whether that disturbance oscillates and whether its field can decrease when collisions are negligible.

The plasma model and its uniform reference state

We consider plasma containing electrons and positive ions, with zero net charge in its unperturbed state. To describe the electron response with one kinetic equation, we consider N classical, nonrelativistic electrons of mass m and charge $-e$, where $e > 0$ is the magnitude of the elementary charge. The positive ions are represented by a prescribed uniform background of charge density en_0. Here n_0 is the electron number density in the neutral, unperturbed state. Keeping the background fixed isolates the electron response; the motion of the ions is outside this model.

We restrict the calculation to electrostatic fields. In SI units, with ϵ_0 denoting the vacuum permittivity, the electron pair interaction energy and the force on electron 1 due to electron 2 are

$$\begin{aligned} \Phi(|\mathbf{r}_1 - \mathbf{r}_2|) &= \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}, \\ \mathbf{F}_{12} &= -\nabla_{\mathbf{r}_1}\Phi = \frac{e^2}{4\pi\epsilon_0}\frac{\mathbf{r}_1-\mathbf{r}_2}{|\mathbf{r}_1-\mathbf{r}_2|^3}. \end{aligned} \tag{2.6.1}$$

The force points away from electron 2, as required for repulsion between two negative charges. The symbol Φ retains its meaning from the preceding sections: it is a pair interaction energy. The electric potential introduced below will be denoted by the lower-case symbol ϕ.

The statistical variable remains the distribution f_1 defined in Section 2.2. The quantity $f_1(\mathbf{r}, \mathbf{p}, t)\, d^3r\, d^3p$ is the mean electron number in the corresponding one-particle phase-space element. Its normalization and density moment are

$$\int d^3r\, d^3p\, f_1(\mathbf{r}, \mathbf{p}, t) = N, \qquad n(\mathbf{r}, t) = \int d^3p\, f_1(\mathbf{r}, \mathbf{p}, t). \tag{2.6.2}$$

Thus f_1/N, rather than f_1, would be the probability density for one randomly selected electron. We initially consider a large neutral system. The calculations of screening and of a density wave will concern its bulk, where boundary effects can be neglected.

Both disturbances will be measured relative to a plasma prepared with uniform density n_0, zero mean flow, and temperature $T_0 > 0$. The corresponding Maxwell distribution is the uniform specialization of f_{LE} in Section 2.2 and of f_{eq} in Section 2.5:

$$f_{\mathrm{eq}}(\mathbf{p}) = \frac{n_0}{(2\pi m k_B T_0)^{3/2}} \exp\left(-\frac{p^2}{2mk_BT_0}\right), \qquad \int d^3p\, f_{\mathrm{eq}} = n_0. \tag{2.6.3}$$

The unperturbed electron charge density is $-en_0$ and cancels the positive background. With no imposed field, the bulk electric field is therefore zero. The Maxwell form specifies the prepared reference state about which we shall calculate the electron response.

The self-consistent electric force from the hierarchy

The first BBGKY equation identifies exactly what must be approximated. With $1 = (\mathbf{r}_1, \mathbf{p}_1)$ and $d2 = d^3r_2\, d^3p_2$, it is

$$\mathcal{L}_1 f_1(1, t) = -\int d2\, \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} f_2(1,2,t). \tag{2.6.4}$$

As in Section 2.3, $\mathcal{L}_1$ contains the time derivative, spatial streaming, and acceleration by the prescribed external force. For the present model, the prescribed force includes the force of the fixed positive background. The electron-electron force is the contribution on the right of (2.6.4).

Section 2.3 separated the independently distributed part of the pair population from its correlation correction:

$$f_2(1,2,t) = \frac{N-1}{N} f_1(1,t) f_1(2,t) + g_2(1,2,t). \tag{2.6.5}$$

The factor $(N-1)/N$ follows from the normalization of f_2 to the number $N(N-1)$ of ordered distinct pairs. Define the mean electron force $\mathbf{F}_{\mathrm{mf}}$ by averaging the pair force with the one-particle distribution of electron 2:

$$\mathbf{F}_{\mathrm{mf}}(1,t) = \frac{N-1}{N}\int d2\,\mathbf{F}_{12} f_1(2,t). \tag{2.6.6}$$

To see how this force enters the kinetic equation, insert the first term of (2.6.5) into (2.6.4). The momentum derivative acts only on $f_1(1,t)$, because $f_1(2,t)$ depends on the variables of electron 2. Its contribution is consequently

$$\begin{aligned} -\frac{N-1}{N}\int d2\,\mathbf{F}_{12} f_1(2,t)\cdot\nabla_{\mathbf{p}_1} f_1(1,t) \\ = -\mathbf{F}_{\mathrm{mf}}(1,t)\cdot\nabla_{\mathbf{p}_1} f_1(1,t). \end{aligned} \tag{2.6.7}$$

Moving (2.6.7) to the left gives

$$\left(\mathcal{L}_1 + \mathbf{F}_{\mathrm{mf}}\cdot\nabla_{\mathbf{p}_1}\right) f_1(1,t) = -\int d2\,\mathbf{F}_{12}\cdot\nabla_{\mathbf{p}_1} g_2(1,2,t). \tag{2.6.8}$$

Equation (2.6.8) is still exact. The mean force is already determined by f_1, whereas the right-hand side requires the additional pair information g_2. This identifies the closure step: the Vlasov approximation keeps the mean force and neglects the contribution on the right to the accuracy being considered.

We need physical conditions under which this step is useful. Let $a = n_0^{-1/3}$ be the characteristic electron separation. Weak coupling means that the Coulomb interaction energy at this separation is small compared with the thermal energy:

$$a = n_0^{-1/3}, \qquad \frac{e^2}{4\pi\epsilon_0 a} \ll k_B T_0. \tag{2.6.9}$$

We also consider smooth density variations on a length L much greater than a, so that a region of size L^3 contains many electrons. The density average in (2.6.6) then describes a collective force. The initial pair distribution is assumed to have a correlation force contribution small enough to omit from (2.6.8) on the timescale being considered.

Denote by τ_{coll} the time on which Coulomb encounters appreciably change the distribution through the correlation contribution in (2.6.8). We study evolution over times short compared with τ_{coll}. This retains the change produced by the collective electric field while neglecting accumulated collisional changes. The binary-encounter resolution used for the dilute gas in Sections 2.1-2.4 served a different calculation: there the force during a short encounter was replaced by its net scattering effect. Here the electric force remains explicitly resolved in the evolution equation.

The connection between the mean force and the density is particularly simple because (2.6.1) is independent of momentum. Integrating over $\mathbf{p}_2$ in (2.6.6) gives

$$\mathbf{F}_{\mathrm{mf}}(\mathbf{r},t) = \frac{N-1}{N}\frac{e^2}{4\pi\epsilon_0}\int d^3r'\, n(\mathbf{r}',t)\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}. \tag{2.6.10}$$

For $N \gg 1$, the normalization factor can be replaced by one. Denote the total electric field of the electrons and background by $\mathbf{E}$. The total force on an electron is then $-e\mathbf{E}$. The background and electron charges are combined before taking the infinite-system limit. Their net charge density, denoted by ρ_{el}, determines the field through Gauss's law:

$$\rho_{\mathrm{el}}(\mathbf{r},t) = e[n_0 - n(\mathbf{r},t)], \qquad \nabla_{\mathbf{r}}\cdot\mathbf{E} = \frac{\rho_{\mathrm{el}}}{\epsilon_0}. \tag{2.6.11}$$

The second relation is Gauss's law. In the electrostatic approximation, the potential ϕ is defined by $\mathbf{E} = -\nabla_{\mathbf{r}}\phi$. Gauss's law therefore becomes Poisson's equation,

$$\nabla_{\mathbf{r}}^2\phi = \frac{e}{\epsilon_0}(n - n_0), \qquad \mathbf{E} = -\nabla_{\mathbf{r}}\phi. \tag{2.6.12}$$

Neglecting the correlation contribution in (2.6.8) now gives the Vlasov equation,

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}} f_1 - e\mathbf{E}\cdot\nabla_{\mathbf{p}} f_1 = 0. \tag{2.6.13}$$

The equation is closed together with (2.6.2) and (2.6.12). At a given time, the momentum integral of f_1 gives the electron density. The difference between this density and n_0 determines the charge density and hence the electric field, once field boundary conditions are supplied. That field appears in (2.6.13) and determines how f_1 changes. This dependence of the force on the same distribution that it evolves is the self-consistency of the field. The uniform Maxwell distribution (2.6.3) is a stationary solution: its spatial and time derivatives vanish, and its charge density gives $\mathbf{E} = 0$.

To see how the equation transports the statistical population of one-particle states, write it in conservation form. Since $\mathbf{p}/m$ is independent of $\mathbf{r}$ and $\mathbf{E}$ is independent of $\mathbf{p}$, (2.6.13) is equivalent to

$$\frac{\partial f_1}{\partial t} + \nabla_{\mathbf{r}} \cdot \left(\frac{\mathbf{p}}{m} f_1\right) + \nabla_{\mathbf{p}} \cdot (-e\mathbf{E} f_1) = 0. \tag{2.6.14}$$

This is a continuity equation for the mean electron population in one-particle phase space. Spatial streaming changes the population of a phase-space element through its coordinate-space boundary. The electric force redistributes that population through its momentum-space boundary.

Integrating (2.6.14) over momentum makes the momentum boundary term vanish when f_1 decays sufficiently rapidly. With the flow velocity $\mathbf{u}$ defined in Section 2.2, the result is

$$n\mathbf{u} = \int d^3p \, \frac{\mathbf{p}}{m} f_1, \qquad \frac{\partial n}{\partial t} + \nabla_{\mathbf{r}} \cdot (n\mathbf{u}) = 0. \tag{2.6.15}$$

A solution of the Vlasov-Poisson system requires an initial distribution and field boundary conditions compatible with its charge density. For a localized perturbation of the infinite uniform plasma, the perturbing potential tends to zero at infinity. For a neutral periodic system, we take the mean electric field to vanish and fix the irrelevant additive constant in ϕ. These are the settings used below for the localized screening problem and the density-disturbance calculation, respectively.

Small disturbances of the uniform plasma

The closed system is nonlinear: the field determined by f_1 multiplies a momentum derivative of f_1. To calculate the response of the uniform plasma to a weak charge or a weak density disturbance, we retain only the first change from the reference state (2.6.3). This is the purpose of linearization.

Denote the distribution change by δf_1 and its density moment by δn:

$$f_1 = f_{\text{eq}} + \delta f_1, \qquad n = n_0 + \delta n, \qquad \delta n = \int d^3p \, \delta f_1. \tag{2.6.16}$$

The unperturbed field vanishes, so $\mathbf{E}$ and ϕ are themselves perturbing quantities. The first-order response is the part proportional to the disturbance amplitude. Products of two perturbing quantities belong to the next order. Substitution into (2.6.13), using the spatial uniformity of f_{eq}, gives

$$\frac{\partial \delta f_1}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} \delta f_1 - e\mathbf{E} \cdot \nabla_{\mathbf{p}} f_{\text{eq}} - e\mathbf{E} \cdot \nabla_{\mathbf{p}} \delta f_1 = 0. \tag{2.6.17}$$

Only the last term contains a product of two perturbations. Omitting it gives the linear kinetic equation; Poisson's equation gives the accompanying field equation:

$$\begin{aligned} &\frac{\partial \delta f_1}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} \delta f_1 = e\mathbf{E} \cdot \nabla_{\mathbf{p}} f_{\text{eq}}, \\ &\nabla_{\mathbf{r}}^2 \phi = \frac{e}{\epsilon_0} \delta n, \qquad \mathbf{E} = -\nabla_{\mathbf{r}} \phi. \end{aligned} \tag{2.6.18}$$

The first equation determines the change of the distribution caused by the field. The second determines the field caused by the density moment of that change. In the screening problem there will also be a prescribed external charge in the second equation. In the density-disturbance problem the field will be produced entirely by δn. The approximation that made the force a mean field and the approximation that made its response linear are separate steps.

The electron response to a stationary charge

In vacuum, the potential of a positive charge decreases as the inverse distance from that charge. Inside a plasma, that potential changes the electron distribution: electrons are attracted towards the charge, and their additional negative charge contributes to the same electric potential. The stationary potential must therefore be calculated together with the induced electron density. This calculation determines how effectively the plasma reduces the field of an embedded charge.

We represent the embedded object by a fixed positive test charge Q at the origin. Let $\delta^{(3)}(\mathbf{r})$ denote the three-dimensional Dirac delta with integral one; the source charge density is then $Q\delta^{(3)}(\mathbf{r})$. The electron plasma extends to infinity, with $n \to n_0$ and $\phi \to 0$ far from the charge. The positive background remains fixed. Poisson's equation becomes

$$\nabla^2\phi = \frac{e}{\epsilon_0}\delta n - \frac{Q}{\epsilon_0}\delta^{(3)}(\mathbf{r}). \tag{2.6.19}$$

We study the stationary Maxwell response at the reference temperature T_0. This specifies the stationary momentum dependence: the density may depend on position, while the normalized Maxwell momentum distribution is unchanged. Thus

$$f_1(\mathbf{r},\mathbf{p}) = \frac{n(\mathbf{r})}{n_0} f_{\mathrm{eq}}(\mathbf{p}), \qquad \nabla_{\mathbf{p}} f_{\mathrm{eq}} = -\frac{\mathbf{p}}{mk_BT_0} f_{\mathrm{eq}}. \tag{2.6.20}$$

The stationary Vlasov equation expresses the balance between the spatial density gradient and acceleration by the electrostatic force. Substituting (2.6.20) into (2.6.13), with $\mathbf{E} = -\nabla\phi$, gives

$$\frac{f_{\mathrm{eq}}}{n_0}\frac{\mathbf{p}}{m} \cdot [\nabla n - \frac{en}{k_BT_0}\nabla\phi] = 0. \tag{2.6.21}$$

The bracket must vanish because the equation holds for every momentum direction. Dividing the resulting relation by n gives $\nabla \ln n = (e/k_BT_0)\nabla\phi$. Integration and the far-field conditions fix the integration constant:

$$n(\mathbf{r}) = n_0 \exp\left(\frac{e\phi(\mathbf{r})}{k_BT_0}\right). \tag{2.6.22}$$

For the weak response being considered, $|e\phi| \ll k_BT_0$. Expanding (2.6.22) to first order and using (2.6.20) gives

$$\delta n = \frac{n_0 e}{k_BT_0}\phi, \qquad \delta f_1 = \frac{e\phi}{k_BT_0} f_{\mathrm{eq}}. \tag{2.6.23}$$

The signs have a direct meaning. A positive potential increases the electron density, so the induced charge density $-e\delta n$ is negative and opposes the positive source. A negative source would reverse these signs in the linear equations.

Inserting (2.6.23) into (2.6.19) produces a coefficient with the dimensions of an inverse length squared. We define the electron Debye length λ_D by this coefficient:

$$\lambda_D^2 = \frac{\epsilon_0 k_B T_0}{n_0 e^2}, \qquad (\nabla^2 - \lambda_D^{-2})\phi = -\frac{Q}{\epsilon_0}\delta^{(3)}(\mathbf{r}). \tag{2.6.24}$$

This length has arisen from the competition between the electric response and thermal motion, through the density-potential relation (2.6.23). Its role in screening follows from solving the potential equation.

The source and the reference plasma are spherically symmetric. For radial distance $r = |\mathbf{r}| > 0$, (2.6.24) therefore reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) - \frac{\phi}{\lambda_D^2} = 0. \tag{2.6.25}$$

The substitution $y(r) = r\phi(r)$ removes the radial first-derivative term. The resulting equation and its solution, with constants A and B, are

$$y'' - \lambda_D^{-2} y = 0, \qquad y(r) = Ae^{-r/\lambda_D} + Be^{r/\lambda_D}. \tag{2.6.26}$$

The boundary condition $\phi \to 0$ at infinity requires $B = 0$. The remaining constant is fixed by the source charge. Integrating (2.6.24) over a sphere and then shrinking its radius to zero gives

$$\lim_{r\to 0} 4\pi r^2 \frac{d\phi}{dr} = -\frac{Q}{\epsilon_0}, \qquad A = \frac{Q}{4\pi\epsilon_0}. \tag{2.6.27}$$

Here the volume integral of the term proportional to ϕ tends to zero, whereas the delta source contributes Q. The potential is consequently

$$\phi(r) = \frac{Q}{4\pi\epsilon_0 r} e^{-r/\lambda_D}. \tag{2.6.28}$$

At distances small compared with λ_D, the exponential factor is close to one and the potential approaches the Coulomb form. At distances large compared with λ_D, the additional exponential factor strongly suppresses it. This is electrostatic screening. The screening length is the electron Debye length for the fixed-background model; allowing the ions to respond would require including their density change as well.

The potential alone does not show where the compensating charge is located. Denote the induced charge density by $\rho_{\text{ind}} = -e\delta n$. Equations (2.6.23) and (2.6.28) give

$$\rho_{\text{ind}}(r) = -\frac{\epsilon_0}{\lambda_D^2}\phi(r) = -\frac{Q}{4\pi\lambda_D^2 r} e^{-r/\lambda_D}. \tag{2.6.29}$$

To determine how much charge has accumulated within a given distance, define $Q_{\text{ind}}(r)$ as the induced charge inside the sphere of radius r. Writing the radial integration variable as s, integration of (2.6.29) over that sphere yields

$$\begin{aligned} Q_{\text{ind}}(r) &= 4\pi \int_0^r s^2\, \rho_{\text{ind}}(s)\, ds \\ &= -Q[1 - \left(1 + \frac{r}{\lambda_D}\right) e^{-r/\lambda_D}]. \end{aligned} \tag{2.6.30}$$

In this linear solution, $Q_{\text{ind}}(r) \to -Q$ as $r \to \infty$: the integrated electron response compensates the source. The total enclosed charge, denoted by $Q_{\text{enc}}(r)$, includes the source and the induced charge. Gauss's law relates it directly to the radial field component E_r:

$$\begin{aligned} Q_{\text{enc}}(r) = Q + Q_{\text{ind}}(r) = Q\left(1 + \frac{r}{\lambda_D}\right) e^{-r/\lambda_D}, \\ E_r(r) = \frac{Q_{\text{enc}}(r)}{4\pi\epsilon_0 r^2}. \end{aligned} \tag{2.6.31}$$

Thus Q_{enc}/Q is also the ratio of the screened electric field to the vacuum field $Q/(4\pi\epsilon_0 r^2)$. The decrease of the field can now be attributed quantitatively to the induced charge contained inside the sphere.

A thin spherical shell between r and $r + dr$ contains induced charge $dQ_{\text{ind}} = 4\pi r^2 \rho_{\text{ind}}(r)\, dr$. Although the density magnitude in (2.6.29) increases towards the origin, the shell volume decreases there. The magnitude of the shell charge per unit radius is $-dQ_{\text{ind}}/dr$. Dividing by Q/λ_D gives its dimensionless form:

$$-\frac{\lambda_D}{Q}\frac{dQ_{\text{ind}}}{dr} = \frac{r}{\lambda_D} e^{-r/\lambda_D}. \tag{2.6.32}$$

This quantity has its maximum at $r = \lambda_D$. Figure 2.6.1 shows both the shell contribution and the accumulated charge. At one Debye length, only about 26% of the compensating charge lies inside the sphere; at three Debye lengths the fraction is about 80%. The response is spread over several Debye lengths, and the field decreases continuously with distance.

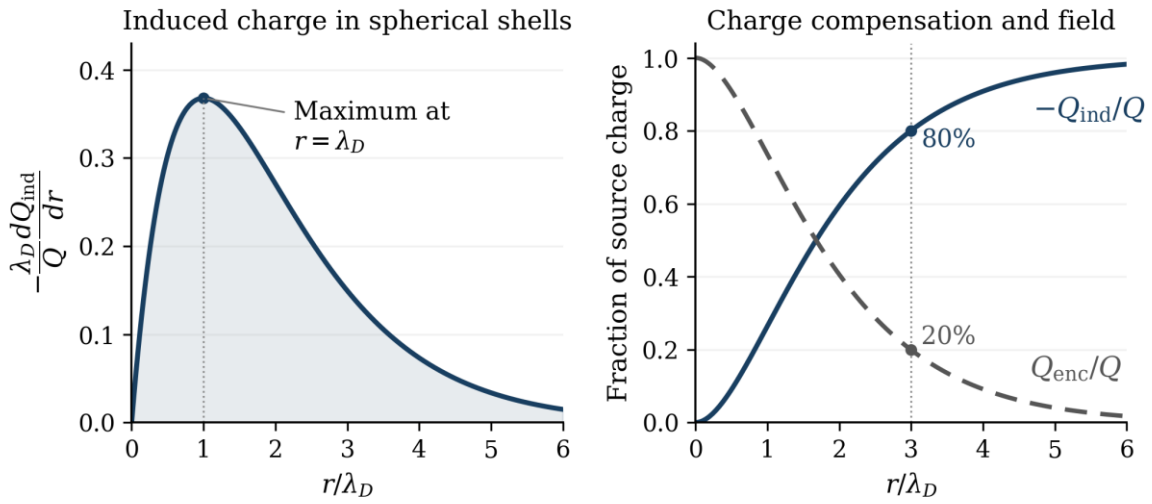


Figure 2.6.1. Screening as charge compensation in the linear point-source solution. Left: the normalized magnitude of the induced charge per radial interval, (2.6.32), is largest at one Debye length. Right: the accumulated compensating fraction $-Q_{\mathrm{ind}}/Q$ and the remaining charge fraction Q_{enc}/Q from (2.6.30) and (2.6.31). The latter is also the electric field relative to its vacuum value. At $r = 3\lambda_D$, about 80% of the source charge is compensated and about 20% of its vacuum field remains.

The local linearity condition remains essential. The ideal point-source potential (2.6.28) diverges at the origin and eventually violates $|e\phi| \ll k_B T_0$. The source normalization above is the mathematical normalization of the linear potential equation; the linear density (2.6.29) describes the electron response only outside the region where this condition fails. We have calculated the stationary response with the specified Maxwell momentum dependence. Its preparation or its approach after a charge is suddenly introduced would require a separate time-dependent calculation.

The derived length also allows us to check the collective approximation quantitatively. Let N_D be the mean electron number in a sphere of radius λ_D. Then

$$N_D = \frac{4\pi}{3} n_0 \lambda_D^3 = \frac{4\pi}{3}\left(\frac{\lambda_D}{a}\right)^3, \qquad \frac{e^2}{4\pi\epsilon_0 a k_B T_0} = \frac{1}{4\pi}\left(\frac{a}{\lambda_D}\right)^2. \tag{2.6.33}$$

When $a \ll \lambda_D$, the response extends over a region containing many electrons, $N_D \gg 1$, while the typical pair interaction is weak. These are the conditions used to treat the induced density as a continuous source of the mean electric field.

For example, an electron plasma with

$$n_0 = 10^{16}\,\mathrm{m}^{-3}, \qquad T_0 = 10^5\,\mathrm{K} \tag{2.6.34}$$

has the length and particle-number scales

$$\lambda_D \simeq 2.18 \times 10^{-4}\,\mathrm{m}, \qquad a \simeq 4.64 \times 10^{-6}\,\mathrm{m}, \qquad N_D \simeq 4.35 \times 10^5. \tag{2.6.35}$$

Here a is much smaller than the screening length, and a Debye sphere contains many electrons. For a source $Q = e$, the distance $e^2/(4\pi\epsilon_0 k_B T_0)$ is about $1.67 \times 10^{-10}\,\mathrm{m}$. Since this is much smaller than λ_D, the potential energy $|e\phi|$ is small compared with $k_B T_0$ throughout the distances that contribute most of the screening response.

The evolution of an electron density disturbance

Screening concerned a stationary response to a prescribed charge. We now study a plasma whose electron density is initially slightly nonuniform, with no added charge maintaining the disturbance. A region with an excess of electrons has net negative charge relative to the fixed background. Its electric field changes the electron flow, and that flow changes the density through (2.6.15). The problem is to determine the resulting density and field as functions of time.

The uniform reference state has no preferred spatial direction. We study a sinusoidal density variation along the coordinate x and denote its positive wave number by k. The distance between

successive maxima is the wavelength $2\pi/k$. Because the linear equations have spatially uniform coefficients, different spatial Fourier components evolve independently. Studying this sinusoidal component therefore gives a building block for a general small density disturbance.

Complex spatial amplitudes simplify the derivatives: differentiating e^{ikx} gives ike^{ikx}. The physical quantities are their real parts. Define the distribution, density, potential, and field amplitudes by

$$\begin{gathered}\delta f_1(x,\mathbf{p},t) = \mathrm{Re}[\delta f_{1,k}(\mathbf{p},t)e^{ikx}],\\ \delta n(x,t) = \mathrm{Re}[\delta n_k(t)e^{ikx}],\\ \phi(x,t) = \mathrm{Re}[\phi_k(t)e^{ikx}], \qquad E_x(x,t) = \mathrm{Re}[E_k(t)e^{ikx}].\end{gathered} \tag{2.6.36}$$

The potential depends only on x, so the electric field is directed along x as well. Such a field is called longitudinal: it is parallel to the direction of the spatial density variation. A simple initial disturbance changes the density while leaving the Maxwell momentum dependence and the mean flow unchanged. For a real initial density amplitude $\delta n_k(0)$, it is

$$\delta f_{1,k}(\mathbf{p},0) = \frac{\delta n_k(0)}{n_0} f_{\mathrm{eq}}(\mathbf{p}), \qquad |\delta n_k(0)| \ll n_0. \tag{2.6.37}$$

This gives $\delta n(x,0) = \delta n_k(0)\cos(kx)$ and zero initial mean flow. The initial electric field is fixed by the charge density through Poisson's equation. The calculation below keeps the initial distribution explicit, so it can also describe other small preparations.

Substituting (2.6.36) into (2.6.18) leaves equations for time and momentum only:

$$\begin{gathered}\frac{\partial \delta f_{1,k}}{\partial t} + ik\frac{p_x}{m}\delta f_{1,k} = eE_k(t)\frac{\partial f_{\mathrm{eq}}}{\partial p_x},\\ -k^2\phi_k(t) = \frac{e}{\epsilon_0}\delta n_k(t), \qquad \delta n_k = \int d^3p\, \delta f_{1,k},\\ E_k(t) = -ik\phi_k(t).\end{gathered} \tag{2.6.38}$$

Before solving these equations, we can identify the electric restoring effect directly from the density and momentum moments. Let δu_x denote the first-order flow velocity along x, and let $\delta P_{xx}^{\mathrm{kin}}$ denote the first-order change of the pressure-tensor component defined in Section 2.2. At zero reference flow, their definitions are

$$n_0\delta u_x = \int d^3p\, \frac{p_x}{m}\delta f_1, \qquad \delta P_{xx}^{\mathrm{kin}} = \int d^3p\, \frac{p_x^2}{m}\delta f_1. \tag{2.6.39}$$

The correction from the squared mean flow to the pressure is second order, so it does not enter these definitions. Integrating the linear kinetic equation first with weight one and then with weight p_x gives

$$\begin{gathered}\frac{\partial \delta n}{\partial t} + n_0\frac{\partial \delta u_x}{\partial x} = 0,\\ mn_0\frac{\partial \delta u_x}{\partial t} + \frac{\partial \delta P_{xx}^{\mathrm{kin}}}{\partial x} = -en_0E_x.\end{gathered} \tag{2.6.40}$$

The force moment uses $\int p_x\, \partial_{p_x} f_{\mathrm{eq}}\, d^3p = -n_0$, obtained by integration by parts. Differentiating the first line of (2.6.40) in time, substituting the second, and using $\partial_x E_x = -e\delta n/\epsilon_0$ gives

$$\frac{\partial^2 \delta n}{\partial t^2} + \frac{n_0e^2}{m\epsilon_0}\delta n = \frac{1}{m}\frac{\partial^2 \delta P_{xx}^{\mathrm{kin}}}{\partial x^2}. \tag{2.6.41}$$

The positive coefficient of δn has the sign of a restoring force. Define the positive electron plasma frequency ω_p by this coefficient. If the pressure-gradient contribution is omitted, the density equation becomes

$$\omega_p^2 = \frac{n_0e^2}{m\epsilon_0}, \qquad \frac{\partial^2 \delta n}{\partial t^2} + \omega_p^2\delta n = 0. \tag{2.6.42}$$

The density therefore undergoes harmonic oscillation with frequency ω_p in this approximation. An excess of electrons gives a negative second time derivative of that excess, and a deficit gives the opposite sign.

For comparison with thermal motion, use the thermal-speed notation of Section 2.1 with a definite convention: here v_{th} is the root-mean-square velocity along one Cartesian direction of the Maxwell state. Its value and its relation to the screening length are

$$v_{\mathrm{th}}^2 = \frac{1}{n_0}\int d^3p\, \frac{p_x^2}{m^2} f_{\mathrm{eq}} = \frac{k_B T_0}{m}, \qquad \lambda_D = \frac{v_{\mathrm{th}}}{\omega_p}. \tag{2.6.43}$$

For a smooth thermal disturbance, the pressure change is of order $k_B T_0 \delta n$. Its contribution to (2.6.41), for a Fourier component of wave number k, is therefore of relative order $\left(k v_{\mathrm{th}}/\omega_p\right)^2 = (k\lambda_D)^2$. At long wavelengths, $k\lambda_D \ll 1$, the electric restoring term dominates and the frequency is close to ω_p.

The moment equations explain why oscillations occur, but do not determine the pressure response: $\delta P_{xx}^{\mathrm{kin}}$ depends on the evolving momentum distribution. They also do not determine whether the field amplitude decays. Both questions require solving the kinetic equation (2.6.38), which retains the different responses of different electron momenta.

The frequency response and the resonant integral

We want the response to the initial disturbance, rather than a solution with an arbitrarily assigned time dependence. A one-sided time transform converts (2.6.38) into algebraic equations and retains the initial distribution as an explicit source term. Introduce a complex frequency ω and define

$$\widehat{\delta f}_{1,k}(\mathbf{p},\omega) = \int_0^\infty d\,t\, e^{i\omega t}\delta f_{1,k}(\mathbf{p},t). \tag{2.6.44}$$

The hats on $\hat{\phi}_k$ and $\hat{E}_k$ denote the same transform of their respective time amplitudes. Initially $\mathrm{Im}\omega$ is positive and sufficiently large for convergence: the factor $e^{-\mathrm{Im}\omega\, t}$ suppresses the integrand at large time. Integration by parts then gives

$$\int_0^\infty d\,t\, e^{i\omega t}\frac{\partial \delta f_{1,k}}{\partial t} = -\delta f_{1,k}(\mathbf{p},0) - i\omega\widehat{\delta f}_{1,k}. \tag{2.6.45}$$

Applying this identity to the first equation in (2.6.38), and using $\hat{E}_k = -ik\hat{\phi}_k$, yields

$$\widehat{\delta f}_{1,k} = \frac{i\,\delta f_{1,k}(\mathbf{p},0) + ek\hat{\phi}_k\, \partial f_{\mathrm{eq}}/\partial p_x}{\omega - kp_x/m}. \tag{2.6.46}$$

The first numerator term comes from the specified initial state. The second is the distribution change produced by the electric potential. The denominator contains the response frequency ω and the streaming frequency kp_x/m of electrons with momentum component p_x.

To insert (2.6.46) into Poisson's equation, the transverse momenta can be integrated out. Define the one-dimensional marginal $\overline{f}_{\mathrm{eq}}$ by this integration; a prime on it will denote differentiation with respect to p_x:

$$\begin{gathered}\overline{f}_{\mathrm{eq}}(p_x) = \int dp_y\, dp_z\, f_{\mathrm{eq}}(\mathbf{p}) = \frac{n_0}{(2\pi m k_B T_0)^{1/2}} e^{-p_x^2/(2mk_BT_0)}, \\ \int_{-\infty}^{\infty} d\,p_x\, \overline{f}_{\mathrm{eq}}(p_x) = n_0.\end{gathered} \tag{2.6.47}$$

The transformed Poisson equation contains a term proportional to $\hat{\phi}_k$ from the electron response. Bringing that term to the left defines the dimensionless dispersion function $\mathcal{D}(k,\omega)$:

$$\mathcal{D}(k,\omega) = 1 + \frac{e^2}{\epsilon_0 k}\int_{-\infty}^{\infty} \frac{\overline{f}\prime_{\mathrm{eq}}(p_x)}{\omega - kp_x/m}\, dp_x. \tag{2.6.48}$$

With this definition, the potential is determined by

$$\mathcal{D}(k,\omega)\hat{\phi}_k(\omega) = -\frac{ie}{\epsilon_0 k^2}\int d^3p\, \frac{\delta f_{1,k}(\mathbf{p},0)}{\omega - kp_x/m}. \tag{2.6.49}$$

Equation (2.6.49) separates the dependence on the initial disturbance, on the right, from the response of the plasma, in $\mathcal{D}$. The time-dependent potential is recovered by the inverse transform. If $\sigma > 0$ is chosen above the singularities of the transformed response, this inversion is

$$\phi_k(t) = \frac{1}{2\pi}\int_{-\infty+i\sigma}^{\infty+i\sigma} d\,\omega\, e^{-i\omega t}\hat{\phi}_k(\omega). \tag{2.6.50}$$

This integral initially follows a horizontal line in the upper half of the complex ω plane. For $t > 0$, the factor $e^{-i\omega t}$ decreases as the integration line is moved down. Where continuation of the transformed response permits such a displacement, each crossed simple pole contributes a residue multiplied by $e^{-i\omega t}$ evaluated at that pole. Zeros of $\mathcal{D}$ produce these poles unless the numerator in (2.6.49) also vanishes there. The frequencies of these collective field contributions therefore satisfy the dispersion equation

$$\mathcal{D}(k,\omega) = 0. \tag{2.6.51}$$

The initial distribution determines how strongly each contribution is excited. We are seeking the frequency and decay rate of a collective field contribution; the full momentum distribution can also retain other time dependence from its initial preparation.

The integral in (2.6.48) requires care when ω approaches the real axis. For a real initial disturbance, the physical oscillation combines contributions with opposite real frequencies. We calculate the one with positive real frequency, denoted by $\omega_r > 0$. At frequency ω_r, the denominator vanishes at the resonant momentum

$$p_{\mathrm{res}} = \frac{m\omega_r}{k}. \tag{2.6.52}$$

At this momentum the electron velocity along x equals ω_r/k, the velocity of the spatial phase of the oscillation. The singularity cannot be handled by simply omitting its value: how the integral approaches it affects the imaginary part of the response and hence the decay rate.

The initial-value construction specifies that approach. The transform was defined for positive imaginary frequency. Writing $\omega = \omega_r + i\eta$, where $\eta > 0$ has units of frequency, puts the momentum pole at $p_{\mathrm{res}} + im\eta/k$, above the real momentum axis.

Let PV denote the principal value of the momentum integral: equal small intervals are removed on either side of p_{res}, and their width is then taken to zero. Taking $\eta \to 0^+$ while keeping the integration path below the pole gives

$$\begin{aligned}\lim_{\eta\to 0^+}\int_{-\infty}^{\infty}\frac{\overline{f}'_{\mathrm{eq}}(p_x)}{\omega_r - kp_x/m + i\eta}\,dp_x &= \mathrm{PV}\int_{-\infty}^{\infty}\frac{\overline{f}'_{\mathrm{eq}}(p_x)}{\omega_r - kp_x/m}\,dp_x \\ &\quad -\frac{i\pi m}{k}\overline{f}'_{\mathrm{eq}}(p_{\mathrm{res}}).\end{aligned} \tag{2.6.53}$$

The first term on the right is the principal-value integral. The remaining term is the contribution of the small semicircle below the pole in Figure 2.6.2. Along that semicircle from left to right, the integral of $1/(p_x - p_{\mathrm{res}})$ is $i\pi$. Since the denominator in (2.6.53) is $-(k/m)(p_x - p_{\mathrm{res}})$ in the limit, the semicircle contributes $-i\pi(m/k)\overline{f}'_{\mathrm{eq}}(p_{\mathrm{res}})$. This fixes the sign explicitly.

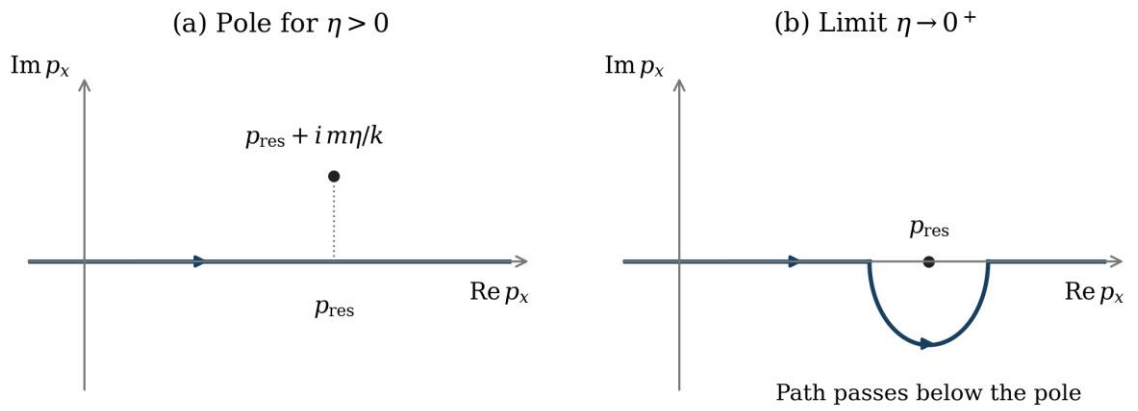


Figure 2.6.2. The resonant pole and the causal momentum contour in (2.6.53). The arrows indicate integration from left to right. In the limit the contour passes below the pole, giving the principal value and the negative imaginary term.

We shall seek a decaying contribution, for which the frequency lies in the lower half-plane. Its dispersion function must be the continuation of the function already defined by the initial-value transform. As the pole moves down, the momentum path must remain below it. Replacing that path by a new, undeformed real-axis integral after the crossing would change the function. This prescription is called causal because it belongs to the response generated by the specified state at $t = 0$ for later times; it does not introduce a finite collision rate.

Denote the real and imaginary parts of the limiting dispersion function by $\mathcal{D}_R$ and $\mathcal{D}_I$. Equation (2.6.53) gives

$$\begin{aligned} \mathcal{D}_R(k,\omega_r) &= 1 + \frac{e^2}{\epsilon_0 k}\,\mathrm{PV}\int_{-\infty}^{\infty} \frac{\overline{f}'_{\mathrm{eq}}(p_x)}{\omega_r - kp_x/m}\,dp_x, \\ \mathcal{D}_I(k,\omega_r) &= -\frac{\pi m e^2}{\epsilon_0 k^2}\,\overline{f}'_{\mathrm{eq}}(p_{\mathrm{res}}). \end{aligned} \tag{2.6.54}$$

The imaginary part depends on the slope of the momentum distribution at resonance. For the Maxwell marginal, $\overline{f}'_{\mathrm{eq}} = -p_x \overline{f}_{\mathrm{eq}}/(mk_BT_0)$, which is negative at $p_{\mathrm{res}} > 0$. Consequently $\mathcal{D}_I > 0$. We shall use this sign when determining whether the field contribution grows or decays.

The oscillation frequency and its decay rate

The moment argument in (2.6.41) suggests a frequency close to ω_p when $k\lambda_D \ll 1$. We now calculate the thermal correction and the decay of that collective field contribution. In this regime, ω_r is much larger than kv_{th}: for momenta of order mv_{th}, the streaming frequency kp_x/m is small compared with the oscillation frequency. The resonant momentum, by contrast, satisfies $p_{\mathrm{res}}/(mv_{\mathrm{th}}) \simeq 1/(k\lambda_D) \gg 1$ and lies in the Maxwell tail.

These two momentum ranges enter differently. The electrons with typical thermal momenta determine the leading real part of the frequency through the principal-value integral. The distribution's slope at the resonant momentum determines the imaginary part through (2.6.54). For the first calculation, expand the denominator in powers of the streaming frequency:

$$\frac{1}{\omega_r - kp_x/m} \sim \frac{1}{\omega_r}\left[1 + \frac{kp_x}{m\omega_r} + \frac{k^2p_x^2}{m^2\omega_r^2} + \frac{k^3p_x^3}{m^3\omega_r^3} + \cdots\right]. \tag{2.6.55}$$

This is an asymptotic expansion of the principal-value integral for $\omega_r/(kv_{\mathrm{th}}) \gg 1$. It is not a convergent expansion at the resonant momentum. The resonant contribution is already retained separately in $\mathcal{D}_I$.

To evaluate the real part, we need four moments of the derivative of the Maxwell marginal. Its decay at large $|p_x|$ permits integration by parts, and its symmetry makes the odd moments of $\overline{f}_{\mathrm{eq}}$ vanish. The required results are

$$\begin{gathered}\int_{-\infty}^{\infty} \overline{f}\,'_{\mathrm{eq}}\, dp_x = 0, \quad \int_{-\infty}^{\infty} p_x\, \overline{f}\,'_{\mathrm{eq}}\, dp_x = -n_0, \\ \int_{-\infty}^{\infty} p_x^2\, \overline{f}\,'_{\mathrm{eq}}\, dp_x = 0, \quad \int_{-\infty}^{\infty} p_x^3\, \overline{f}\,'_{\mathrm{eq}}\, dp_x = -3n_0 m k_B T_0.\end{gathered} \tag{2.6.56}$$

For example, the last integral is $-3\int p_x^2 \overline{f}_{\mathrm{eq}}\, dp_x = -3n_0 m k_B T_0$. Inserting these moments into (2.6.55) and then into (2.6.54) gives

$$\mathcal{D}_R(k,\omega_r) \simeq 1 - \frac{\omega_p^2}{\omega_r^2} - \frac{3\omega_p^2 k^2 v_{\mathrm{th}}^2}{\omega_r^4}. \tag{2.6.57}$$

Setting this expression to zero and keeping the first correction in $(k\lambda_D)^2$ yields

$$\omega_r^2 \simeq \omega_p^2 + 3k^2 v_{\mathrm{th}}^2 = \omega_p^2[1 + 3(k\lambda_D)^2]. \tag{2.6.58}$$

The nonzero frequency as $k \to 0$ comes from the electric restoring term already found in (2.6.41). Thermal motion raises the frequency at finite k. The coefficient 3 follows from the momentum moment in (2.6.56); it is therefore determined by the kinetic calculation, rather than by an assumed relation between pressure and density.

To calculate a weak decay, define a positive decay rate γ by writing the complex frequency as

$$\omega = \omega_r - i\gamma, \qquad e^{-i\omega t} = e^{-i\omega_r t} e^{-\gamma t}. \tag{2.6.59}$$

Assume $\gamma \ll \omega_r$. Expanding the continued dispersion function about the real frequency, and retaining its leading small imaginary contribution, gives

$$\begin{gathered}0 \simeq \mathcal{D}_R(k,\omega_r) + i\left[\mathcal{D}_I(k,\omega_r) - \gamma \frac{\partial \mathcal{D}_R}{\partial \omega_r}\right], \\ \gamma \simeq \frac{\mathcal{D}_I(k,\omega_r)}{\partial \mathcal{D}_R(k,\omega_r)/\partial \omega_r}.\end{gathered} \tag{2.6.60}$$

The real part vanishes by the frequency condition. A term involving $\gamma\ \partial \mathcal{D}_I / \partial \omega_r$ is of higher order in the small resonant contribution. At leading order, (2.6.57) gives $\partial \mathcal{D}_R / \partial \omega_r \simeq 2\omega_p^2/\omega_r^3 > 0$. Together with $\mathcal{D}_I > 0$ for the Maxwell distribution, this proves that γ is positive: the collective field contribution decays.

Evaluating the derivative of the Maxwell marginal at $p_{\mathrm{res}} = m\omega_r/k$ in (2.6.54) gives

$$\mathcal{D}_I(k,\omega_r) = \sqrt{\frac{\pi}{2}}\, \frac{\omega_p^2 \omega_r}{k^3 v_{\mathrm{th}}^3} \exp\left(-\frac{\omega_r^2}{2k^2 v_{\mathrm{th}}^2}\right). \tag{2.6.61}$$

The resulting decay rate is

$$\gamma \simeq \sqrt{\frac{\pi}{8}}\, \frac{\omega_r^4}{k^3 v_{\mathrm{th}}^3} \exp\left(-\frac{\omega_r^2}{2k^2 v_{\mathrm{th}}^2}\right). \tag{2.6.62}$$

The thermal correction in (2.6.58) is small relative to ω_p^2, but it contributes a finite constant to this exponent. Using $\lambda_D = v_{\mathrm{th}}/\omega_p$, we find

$$\frac{\omega_r^2}{2k^2 v_{\mathrm{th}}^2} = \frac{1}{2(k\lambda_D)^2} + \frac{3}{2} + O((k\lambda_D)^2). \tag{2.6.63}$$

We therefore retain this constant while replacing the prefactor by its leading value. The long-wavelength decay rate is

$$\frac{\gamma}{\omega_p} \simeq \sqrt{\frac{\pi}{8}}\, (k\lambda_D)^{-3} \exp\left[-\frac{1}{2(k\lambda_D)^2} - \frac{3}{2}\right]. \tag{2.6.64}$$

The relative corrections to this formula are of order $(k\lambda_D)^2$. At small $k\lambda_D$, resonance requires electrons with velocity ω_r/k far above v_{th}. Their Maxwell population is exponentially small, which accounts for the small decay rate. The frequency changes only quadratically with $k\lambda_D$, whereas the

decay rate changes rapidly through the exponential. Figure 2.6.3 displays both dependencies within the long-wavelength regime.

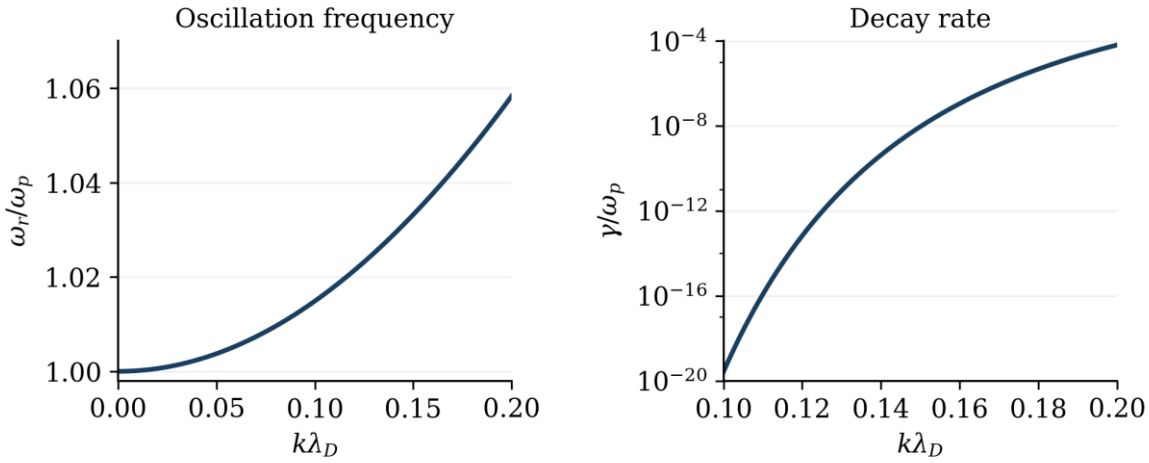


Figure 2.6.3. The long-wavelength estimates (2.6.58) and (2.6.64), plotted for $k\lambda_D \leq 0.20$. The decay-rate panel uses a logarithmic vertical scale. Both curves are evaluated using the stated asymptotic formulas.

For the density and temperature in (2.6.34), the characteristic speed and frequency are

$$v_{\mathrm{th}} \simeq 1.23 \times 10^{6}\ \mathrm{m\,s^{-1}}, \qquad \omega_p \simeq 5.64 \times 10^{9}\ \mathrm{s^{-1}}. \tag{2.6.65}$$

As a numerical illustration, a component with $k\lambda_D = 0.20$ has the following wavelength, oscillation frequency, and leading asymptotic decay rate:

$$\begin{gathered} \frac{2\pi}{k} \simeq 6.86 \times 10^{-3}\ \mathrm{m}, \\ \omega_r \simeq 5.97 \times 10^{9}\ \mathrm{s^{-1}}, \qquad \gamma \simeq 3.7 \times 10^{5}\ \mathrm{s^{-1}}. \end{gathered} \tag{2.6.66}$$

The corresponding oscillation period $2\pi/\omega_r$ is about 1.05 ns, while the amplitude decay time γ^{-1} is about 2.7 μs. These values illustrate the separation between rapid oscillation and slow collisionless decay; the decay rate is an asymptotic estimate. The condition $\omega_p \tau_{\mathrm{coll}} \gg 1$ permits collisions to be neglected during an oscillation. To observe the much slower decay predicted here without an appreciable collisional change, the stronger time condition $\tau_{\mathrm{coll}} \gg \gamma^{-1}$ is needed.

Collisionless damping and the H-theorem

The decay obtained above is called Landau damping. It is a decay of the collective electric-field contribution, obtained from the Vlasov equation without a collision integral. Section 2.5 related irreversible relaxation in the Boltzmann equation to a decrease of the H-function. We must therefore determine what decreases in the present calculation and whether the same change of H occurs.

The distinction follows from the difference between the full momentum distribution and its density moment. Solving the first equation in (2.6.38) with an integrating factor, and denoting the integration time by t', gives

$$\begin{gathered} \delta f_{1,k}(\mathbf{p}, t) = \delta f_{1,k}(\mathbf{p}, 0) e^{-ikp_x t/m} \\ + e \frac{\partial f_{\mathrm{eq}}}{\partial p_x} \int_0^t E_k\,(t') e^{-ikp_x (t-t')/m}\, dt'. \end{gathered} \tag{2.6.67}$$

The first term is the streaming of the initial distribution. The second is the change caused by the electric field between the preparation at 0 and the observation at t. At each fixed momentum, the streaming factor has unit magnitude; its phase, however, varies with p_x. Consequently its integral over momentum can become small even though the momentum-resolved term has not decreased in magnitude.

For the initial Maxwell density disturbance (2.6.37), this cancellation can be calculated directly. The density moment of the first term in (2.6.67) is a Gaussian Fourier integral:

$$\int d^3p\, \delta f_{1,k}(\mathbf{p},0)e^{-ikp_x t/m} = \delta n_k(0)\exp[-\tfrac{(kv_{\mathrm{th}}t)^2}{2}]. \tag{2.6.68}$$

This is the density contribution from free streaming of the initial disturbance. The self-consistent field supplies the second term in (2.6.67), so this Gaussian is not the density evolution of the plasma. The full response includes the plasma oscillation and the decay obtained from the dispersion function. The integral nevertheless shows explicitly how a density moment can decrease through cancellation of different momentum phases.

Two momenta separated by Δp_x acquire a phase difference $k\Delta p_x t/m$. A phase difference of 2π therefore corresponds, for $t > 0$, to the momentum interval

$$\Delta p_x = \frac{2\pi m}{kt}. \tag{2.6.69}$$

The momentum dependence becomes finer as time increases. The development of these different phases and their cancellation in moments is called phase mixing. Thus a small collective field at late times does not imply that the full distribution has become the original Maxwell distribution. Information about the disturbance remains in its momentum dependence.

We can compare this statement directly with the H-theorem by returning to the full Vlasov equation, whose leading field response was calculated above. We use a finite neutral periodic region $\mathcal{V}$ and assume a positive, regular distribution with sufficient momentum decay and finite integrals. The H-function and the constant reference phase-space density $f_{\mathrm{ref}} > 0$ retain their definitions from Section 2.5:

$$H(t) = \int_{\mathcal{V}} d^3r \int d^3p\, f_1 \ln\left(\frac{f_1}{f_{\mathrm{ref}}}\right). \tag{2.6.70}$$

The two transport coefficients in (2.6.14) have zero total phase-space divergence:

$$\nabla_{\mathbf{r}} \cdot \frac{\mathbf{p}}{m} + \nabla_{\mathbf{p}} \cdot (-e\mathbf{E}) = 0. \tag{2.6.71}$$

The first term vanishes because $\mathbf{p}/m$ does not depend on position; the second because the electrostatic force does not depend on momentum. Define $h = f_1 \ln(f_1/f_{\mathrm{ref}})$. Multiplying (2.6.13) by $1 + \ln(f_1/f_{\mathrm{ref}})$ and using (2.6.71) gives

$$\frac{\partial h}{\partial t} + \nabla_{\mathbf{r}} \cdot \left(\frac{\mathbf{p}}{m} h\right) + \nabla_{\mathbf{p}} \cdot (-e\mathbf{E}h) = 0. \tag{2.6.72}$$

The spatial surface terms cancel between opposite faces of the periodic region, and the momentum surface term vanishes at infinity. Integrating (2.6.72) therefore yields

$$\frac{dH}{dt} = 0. \tag{2.6.73}$$

The Boltzmann collision integral in Section 2.5 changed H because it changed the distribution through binary scattering. Vlasov transport conserves this H while developing fine momentum dependence. There is no conflict with a decreasing field contribution: the field depends on a momentum integral of f_1, whereas H depends on the full distribution before that integral is taken.

Energy conservation provides a second check. For the density-disturbance problem, there is no imposed test charge or external time-dependent field, and the fixed background carries no current. Retain E_{kin} for the total particle kinetic energy, as in Section 2.5. Define the electrostatic field energy W_E and the electric current density $\mathbf{j}$ by

$$E_{\mathrm{kin}} = \int_{\mathcal{V}} d^3r \int d^3p\, \frac{p^2}{2m} f_1, \qquad W_E = \frac{\epsilon_0}{2}\int_{\mathcal{V}} d^3r\, |\mathbf{E}|^2,$$
$$\mathbf{j} = -e\int d^3p\, \frac{\mathbf{p}}{m} f_1 = -en\mathbf{u}. \tag{2.6.74}$$

Multiplying (2.6.13) by $p^2/(2m)$, integrating, and using the same boundary conditions gives

$$\frac{dE_{\mathrm{kin}}}{dt} = -e\int_{\mathcal{V}} d^3r\, \mathbf{E} \cdot \int d^3p\, \frac{\mathbf{p}}{m} f_1 = \int_{\mathcal{V}} d^3r\, \mathbf{j} \cdot \mathbf{E}. \tag{2.6.75}$$

The sign follows by integrating the momentum derivative by parts: the gradient of $p^2/(2m)$ is $\mathbf{p}/m$. The field does work on the electron distribution at the rate $\mathbf{j} \cdot \mathbf{E}$.

Since the background is fixed, the number continuity equation (2.6.15) also gives charge continuity. Differentiating Gauss's law in time then yields

$$\frac{\partial \rho_{\mathrm{el}}}{\partial t} + \nabla \cdot \mathbf{j} = 0, \qquad \nabla \cdot \left(\epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \mathbf{j} \right) = 0. \tag{2.6.76}$$

Multiply the second relation by ϕ and integrate over $\mathcal{V}$. The periodic surface terms cancel, and $\nabla\phi = -\mathbf{E}$, so the remaining volume integral is $\int_{\mathcal{V}} \mathbf{E} \cdot (\epsilon_0 \, \partial_t \mathbf{E} + \mathbf{j}) \, d^3r = 0$. It follows that

$$\frac{dW_E}{dt} = -\int_{\mathcal{V}} d^3 \, r \, \mathbf{j} \cdot \mathbf{E}. \tag{2.6.77}$$

Equations (2.6.75) and (2.6.77) therefore give

$$\frac{d}{dt}(E_{\mathrm{kin}} + W_E) = 0. \tag{2.6.78}$$

A reduction of field energy is accompanied by an increase of electron kinetic energy. This exact balance is compatible with conservation of H: neither statement requires the full distribution to become Maxwellian. The damping calculation describes the collective field and density response, while the distribution retains the momentum structure generated by its evolution.

The two applications show why retaining the collective electric field matters. The stationary density response produces screening, and the time-dependent density response produces plasma oscillations with collisionless damping. These effects are present before the correlation contribution in (2.6.8) appreciably changes the distribution. On times comparable with τ_{coll}, that contribution must be restored. In a weakly coupled plasma, the accumulated effect of many small-angle Coulomb deflections then leads to a collisional kinetic correction. Its derivation requires the pair-correlation dynamics that the present mean-field closure has neglected.

2.7 The Pauli master equation

Quantum states and the purpose of the kinetic description

The preceding subsections described relaxation starting from classical particle dynamics. We now seek a kinetic description starting from quantum mechanics. Its statistical variables will be the populations of the quantum states of the complete N particle system.

Let $\hat{H}$ be a time-independent Hamiltonian whose orthonormal eigenstates ψ_n form a complete basis, with corresponding energies E_n:

$$\hat{H}\psi_n = E_n\psi_n. \tag{2.7.1}$$

The label n collects all quantum numbers needed to specify a basis state of the entire system.

The statistical preparation used in the derivation is an ensemble in which the state ψ_n is prepared with probability $w_n(t)$ at the initial time t. These probabilities are the weights of a **statistical mixture**. They specify how frequently the different initial states occur among the ensemble members.

This mixture can be represented by a density operator $\hat{\rho}(t)$, constructed as a weighted sum of the projectors $|\psi_n\rangle\langle\psi_n|$ onto the prepared states:

$$\hat{\rho}(t) = \textstyle\sum_n w_n(t) |\psi_n\rangle\langle\psi_n|, \qquad w_n(t) \geq 0, \qquad \textstyle\sum_n w_n(t) = 1. \tag{2.7.2}$$

The normalization concerns alternative states of the whole system. The one-particle distribution f_1 used earlier instead counts particles in phase space and is normalized to N.

A statistical mixture and a coherent superposition have different meanings. In the mixture, the different preparations occur with probabilities $w_n(t)$. In a coherent superposition, the basis states occur within a single wavefunction with complex amplitudes and definite relative phases. The

probabilities of basis-state measurement outcomes alone do not specify those phases. Equation (2.7.2) explicitly selects the initial mixture used here.

Under $\widehat{H}$ alone, each prepared basis state acquires only a phase, so its projector and the mixture populations remain unchanged. A weak additional interaction $\delta\widehat{H}(s)$ couples different basis states and allows these populations to change. The interaction may be time independent or explicitly dependent on time.

Each ensemble member has its own wavefunction $\Psi(s)$. For a member initially prepared in ψ_n, its subsequent evolution obeys the Schrödinger equation, with $\hbar$ denoting the reduced Planck constant:

$$i\hbar\frac{\partial\Psi(s)}{\partial s} = [\widehat{H} + \delta\widehat{H}(s)]\Psi(s), \qquad \Psi(t) = \psi_n. \tag{2.7.3}$$

The ensemble subsequently consists of the evolved wavefunctions of all its initially prepared members. The initial weights remain attached to those members, while the probabilities of finding the **fixed basis states** ψ_n can change. At a later time s, these basis-state populations are $w_n(s) = \langle\psi_n|\hat{\rho}(s)|\psi_n\rangle$.

The interaction generally also generates matrix elements $\langle\psi_n|\hat{\rho}(s)|\psi_m\rangle$ with $n \neq m$. These contain information about quantum coherence between different basis states. Thus the form (2.7.2) specifies the initial preparation; its preservation under the full quantum evolution is not assumed.

Our objective is to establish the statistical and temporal conditions under which the populations $w_n(s)$ obey a closed balance equation with transition rates. We shall first calculate their finite change from the specified initial mixture, then examine the approximation that leads to the Pauli equation.

The population change over a finite time interval

The initial ensemble is the statistical mixture defined in (2.7.2). For an interval of duration $\tau > 0$, we seek the change $w_n(t+\tau) - w_n(t)$ produced by the quantum evolution of its members. This finite population increment will be the starting point for the kinetic approximation.

For the transition calculation, the perturbation is switched on at time t and acts until $t + \tau$. The conditional probability $P(n; n'; t, \tau)$ describes a system initially prepared in ψ_n being found in $\psi_{n'}$ at the end of this interval.

Because the initial ensemble is a mixture, contributions from its different initial states are added as probabilities. The population of state n receives probability from systems initially in other states and loses probability through transitions out of n. The probability of remaining in n is one minus the total probability of leaving it. Consequently,

$$w_n(t+\tau) - w_n(t) = \sum_{n'\neq n}[w_{n'}(t)P(n'; n; t, \tau) - w_n(t)P(n; n'; t, \tau)]. \tag{2.7.4}$$

The first term is the gain of probability from initial states n'; the second is the loss from the initial state n. This relation uses the mixture at the beginning of the interval. During the interval, each member may evolve into a superposition, and that quantum evolution is included in the conditional probabilities P.

To calculate these probabilities, consider one member initially prepared in ψ_n. Its wavefunction, governed by (2.7.3), is expanded as

$$\Psi(s) = \sum_k a_k(s)e^{-iE_k(s-t)/\hbar}\psi_k, \qquad a_n(t) = 1, \qquad a_k(t) = 0 \quad (k \neq n). \tag{2.7.5}$$

The exponential factors describe evolution under $\widehat{H}$ alone. The additional interaction changes the amplitudes $a_k(s)$. Its matrix element between ψ_k and $\psi_{n'}$ is denoted by $\langle\psi_{n'}|\delta\widehat{H}(s)|\psi_k\rangle$. Substitution into the Schrödinger equation, followed by projection onto $\psi_{n'}$, gives

$$i\hbar\frac{da_{n'}}{ds} = \sum_k \langle\psi_{n'}|\delta\widehat{H}(s)|\psi_k\rangle e^{i(E_{n'}-E_k)(s-t)/\hbar}a_k(s). \tag{2.7.6}$$

This equation is exact. At zeroth order in the interaction, $a_n(s) = 1$ and all other amplitudes vanish. Substituting these values on its right-hand side and integrating gives the amplitudes to first order. For $n' \neq n$,

$$a_{n'}(t+\tau) \simeq -\frac{i}{\hbar}\int_t^{t+\tau} d\,s\,\langle\psi_{n'}|\delta\widehat{H}(s)|\psi_n\rangle e^{i(E_{n'}-E_n)(s-t)/\hbar}. \tag{2.7.7}$$

The lower bound is the time at which the initial amplitudes are specified. The conditional transition probability is $P(n;n';t,\tau) = |a_{n'}(t+\tau)|^2$. Its first nonzero contribution is therefore quadratic in the interaction. The approximation is used over intervals for which the perturbative corrections to the amplitudes, and the total probability of leaving the initial state, remain small compared with one.

We now specialize to an interaction that is constant during the interval, $\delta\widehat{H}(s) = \delta\widehat{H}$. Performing the integral in (2.7.7) gives

$$P(n;n';\tau) \simeq 4|\langle\psi_{n'}|\delta\widehat{H}|\psi_n\rangle|^2 \frac{\sin^2[(E_{n'}-E_n)\tau/(2\hbar)]}{(E_{n'}-E_n)^2}, \qquad n' \neq n, \quad E_{n'} \neq E_n. \tag{2.7.8}$$

For a constant interaction, the probability depends on the duration τ, rather than the switch-on time. When two distinct states have the same unperturbed energy, $E_{n'} = E_n$, the exponential in (2.7.7) equals one and the time integral gives τ. In that case,

$$P(n;n';\tau) \simeq \frac{\tau^2}{\hbar^2}|\langle\psi_{n'}|\delta\widehat{H}|\psi_n\rangle|^2, \qquad n' \neq n, \quad E_{n'} = E_n. \tag{2.7.9}$$

Hermiticity makes the matrix elements for the two directions complex conjugates. The energy-dependent factor in (2.7.8) is also unchanged when n and n' are exchanged. Thus, at the order retained,

$$\langle\psi_n|\delta\widehat{H}|\psi_{n'}\rangle = \langle\psi_{n'}|\delta\widehat{H}|\psi_n\rangle^*, \qquad P(n;n';\tau) = P(n';n;\tau). \tag{2.7.10}$$

The gain and loss contributions in (2.7.4) therefore contain the same transition probability. Their dependence on the energy difference and the interval duration can be written using

$$I(x,\tau) = \begin{cases} \dfrac{2\hbar}{\pi\tau}\dfrac{\sin^2(x\tau/2\hbar)}{x^2}, & x \neq 0, \\ \dfrac{\tau}{2\pi\hbar}, & x = 0, \end{cases} \tag{2.7.11}$$

where x denotes an energy difference. Substitution of the calculated transition probabilities into (2.7.4) then yields

$$\frac{w_n(t+\tau)-w_n(t)}{\tau} \simeq \frac{2\pi}{\hbar}\sum_{n'\neq n}|\langle\psi_{n'}|\delta\widehat{H}|\psi_n\rangle|^2\, I(E_{n'}-E_n,\tau)[w_{n'}(t)-w_n(t)]. \tag{2.7.12}$$

Using probability conservation in (2.7.4) includes the loss from each initial state consistently at the same second order as the calculated transition probabilities.

Equation (2.7.12) gives the finite population increment for the specified initial mixture. Its dependence on the calculation interval is explicit in $I(E_{n'}-E_n,\tau)$. The next question is whether there is a range of durations for which the statistical sum on the right becomes independent of τ at the retained accuracy. Establishing that range will justify the passage from this finite increment to a differential kinetic equation.

The kinetic time resolution and the Pauli equation

Equation (2.7.12) gives the population change over the time interval from t to $t+\tau$. Its dependence on the duration τ is contained in $I(E_{n'}-E_n,\tau)$. The function defined in (2.7.11) has the delta-function limit

$$\lim_{\tau\to\infty} I(x,\tau) = \delta(x). \tag{2.7.13}$$

This limit is used under an integral over energy. For a macroscopic system with densely spaced energy levels, the sum over final states n' in (2.7.12) is approximated by an integral over the final energy. This integral includes the density of final states—the number of states per unit energy—

together with the squared interaction matrix elements and the population difference $w_{n'}(t) - w_n(t)$.

To state when the delta-function approximation applies, let δE denote the typical spacing between adjacent final energy levels. Let ΔE denote the smallest energy scale over which any of the other factors in the energy integral changes appreciably. The energy width of $I(x,\tau)$ is of order $\hbar/\tau$, and the required inequalities are

$$\delta E \ll \frac{\hbar}{\tau} \ll \Delta E. \tag{2.7.14}$$

The first inequality means that many final levels lie within this width, permitting replacement of the sum by an energy integral. The second means that the other factors vary little across the width, permitting replacement of I by the delta function inside that integral.

The duration τ is also restricted by perturbation theory. The transition amplitudes calculated in (2.7.7) must remain small, and the total probability of leaving an initial state must be small compared with one. For the constant interaction considered here, sufficient restrictions are

$$\frac{\tau}{\hbar}|\langle\psi_{n'}|\delta\hat{H}|\psi_n\rangle| \ll 1, \qquad \sum_{n'\neq n} P\,(n;n';\tau) \ll 1. \tag{2.7.15}$$

We assume that the interaction is weak enough for the same finite duration τ to satisfy both (2.7.14) and (2.7.15). Thus the limit in (2.7.13) provides an approximation to the energy integral within the time range where the perturbative transition probabilities remain valid.

Using (2.7.8) and (2.7.11), and replacing I by its delta-function limit, gives

$$P(n;n';\tau) \simeq \tau\,\frac{2\pi}{\hbar}|\langle\psi_{n'}|\delta\hat{H}|\psi_n\rangle|^2\delta(E_{n'} - E_n). \tag{2.7.16}$$

As with (2.7.13), this expression is used under the integral over final energies. After that integration, the transition probability is proportional to the duration τ. Its coefficient defines the transition probability per unit time, or **transition rate**. Denoting the rate from n to n' by $\tilde{w}(n;n')$, we obtain

$$\tilde{w}(n;n') = \frac{2\pi}{\hbar}|\langle\psi_{n'}|\delta\hat{H}|\psi_n\rangle|^2\delta(E_{n'} - E_n), \qquad n' \neq n. \tag{2.7.17}$$

The delta function restricts the transitions to states with $E_{n'} = E_n$, expressing conservation of the unperturbed energy at this accuracy. Hermiticity gives equal squared matrix elements for the two directions of a transition. Since the delta function is also unchanged when n and n' are exchanged,

$$\tilde{w}(n;n') = \tilde{w}(n';n).$$

Substituting $P(n;n';\tau) \simeq \tau\tilde{w}(n;n')$ into the population balance (2.7.4) makes the population increment proportional to τ at the retained accuracy.

We now describe the populations at a coarser resolution in time, using durations τ satisfying (2.7.14)–(2.7.15). Variations on times shorter than this resolution are unresolved. In this kinetic description, the finite population change per unit time is represented by the derivative of a smoothly varying population:

$$\frac{dw_n(t)}{dt} \simeq \frac{w_n(t+\tau) - w_n(t)}{\tau}. \tag{2.7.18}$$

Using the transition rates in the balance (2.7.4) then gives the **Pauli master equation**:

$$\frac{dw_n(t)}{dt} = \sum_{n'\neq n}[\tilde{w}(n';n)w_{n'}(t) - \tilde{w}(n;n')w_n(t)]. \tag{2.7.19}$$

The first term describes probability gained through transitions into state n; the second describes probability lost through transitions out of it. On summing over n, each transition contributes once as a gain and once as a loss. Consequently, $\sum_n d\,w_n/dt = 0$, and the normalization in (2.7.2) is preserved.

Relaxation and microcanonical equilibrium

We now consider an isolated system, for which $\delta\widehat{H}$ describes interactions within the system. According to (2.7.17), transitions conserve the unperturbed energy. An ensemble initially confined to a narrow energy interval therefore remains within that interval.

Let E denote the prescribed energy. The function $\Delta(E - E_n)$ equals one when state n belongs to the specified narrow interval about E, and zero otherwise. We denote the number of states in this interval by $\Gamma(E)$, and their populations by $w_n(E,t)$. The populations outside the interval remain zero. In the relaxation calculation below, all sums are restricted to states inside it.

Using the symmetry $\widetilde{w}(n;n') = \widetilde{w}(n';n)$, the Pauli equation becomes

$$\frac{dw_n(E,t)}{dt} = \sum_{n'\neq n} \widetilde{w}\,(n;n')[w_{n'}(E,t) - w_n(E,t)]. \tag{2.7.20}$$

We want to establish whether these populations approach stationary values. Equation (2.7.20) is a linear system with coefficients independent of time. Exponential functions are useful for solving such a system because differentiation reproduces the same function multiplied by a constant. Since the coefficient matrix is real and symmetric, its independent exponential solutions form a complete set and have real exponents.

Let t_0 denote the time at which the initial populations are specified. Label the independent exponential solutions by j, denote their coefficients in population n by $c_n^{(j)}$, and their exponential parameters by λ_j, with units of inverse time. The general solution within the selected energy interval can then be written as

$$w_n(E,t) = \sum_j c_n^{(j)}\, e^{-\lambda_j (t-t_0)}.$$

The coefficients are determined by the transition rates and the initial populations. At $t = t_0$, they satisfy

$$w_n(E,t_0) = \sum_j c_n^{(j)}.$$

Each exponential term satisfies the linear equation separately. For one fixed j, write $c_n = c_n^{(j)}$ and $\lambda = \lambda_j$. Substitution into (2.7.20), followed by cancellation of the common exponential factor, gives

$$-\lambda c_n = \sum_{n'\neq n} \widetilde{w}\,(n;n')(c_{n'} - c_n). \tag{2.7.21}$$

Multiplying by c_n and summing over n, we obtain

$$-\lambda \sum_n c_n^2 = \sum_n \sum_{n'\neq n} \widetilde{w}\,(n;n') c_n (c_{n'} - c_n).$$

Exchanging the summation labels n and n' leaves the rate unchanged and replaces $c_n(c_{n'} - c_n)$ by $c_{n'}(c_n - c_{n'})$. Averaging these two forms of the double sum and using

$$c_n(c_{n'} - c_n) + c_{n'}(c_n - c_{n'}) = -(c_{n'} - c_n)^2$$

yields

$$\lambda \sum_n c_n^2 = \frac{1}{2} \sum_n \sum_{n'\neq n} \widetilde{w}\,(n;n')(c_{n'} - c_n)^2. \tag{2.7.22}$$

Every term on the right is nonnegative. For a nonzero exponential solution, $\sum_n c_n^2 > 0$, so $\lambda \geq 0$. Thus contributions with $\lambda > 0$ decay as time increases, while those with $\lambda = 0$ are stationary.

Denote the stationary populations by $w_n^{\mathrm{eq}}(E)$. They satisfy (2.7.20) with a zero left-hand side, corresponding to $\lambda = 0$ in (2.7.21). Setting $c_n = w_n^{\mathrm{eq}}(E)$ in (2.7.22) therefore makes its right-hand side zero. Each squared difference multiplied by a positive transition rate must vanish:

$$w_n^{\mathrm{eq}}(E) = w_{n'}^{\mathrm{eq}}(E) \qquad \text{whenever } \widetilde{w}(n;n') > 0. \tag{2.7.23}$$

Suppose that any two states within the prescribed energy interval can be connected by a sequence of transitions with nonzero rates. Applying (2.7.23) at each step makes their stationary probabilities equal. Normalization fixes this common probability to $1/\Gamma(E)$, while the probabilities outside the interval are zero. Written over the full set of quantum states, the result is

$$w_n^{\mathrm{eq}}(E) = \frac{\Delta(E-E_n)}{\Gamma(E)}, \qquad \Gamma(E) = \sum_n \Delta\,(E - E_n). \tag{2.7.24}$$

The sum defining $\Gamma(E)$ runs over all quantum states and counts those selected by $\Delta(E - E_n)$. Equation (2.7.24) is the microcanonical distribution.

The condition concerning allowed transitions is essential. If no transitions connect two groups of states, the total probability of each group is conserved. The stationary probabilities are then equal within each connected group, while the probability assigned to each group depends on the initial ensemble.

When the states within the prescribed energy interval are all connected by allowed transitions, the stationary solution is unique after normalization. All other exponential contributions have $\lambda > 0$ and decay. The Pauli equation therefore predicts

$$w_n(E,t) \to \frac{\Delta(E-E_n)}{\Gamma(E)} \qquad \text{as } t - t_0 \to \infty. \tag{2.7.25}$$

For a discrete spectrum of relaxation rates with a smallest positive value $\lambda_{\min}$, the longest relaxation time is $1/\lambda_{\min}$. In a limit where the relaxation spectrum becomes continuous, the approach to equilibrium need not follow a single exponential law.

The Pauli master equation can also be reduced to the spatially homogeneous Boltzmann equation for a dilute gas. For pair interactions, summing the many particle population balance over the states of all particles except one gives an equation for the one particle distribution. In the classical limit, approximating the distribution of particles before a collision by the product of their one particle distributions yields the Boltzmann gain and loss terms discussed in §2.4.

2.8 Hydrodynamic regime and transport in a dilute gas

The hydrodynamic regime and the second coarse scale

Section 2.5 identified the local Maxwell distribution f_{LE} in (2.5.18), whose parameters are the local density $n(\mathbf{r},t)$, mean velocity $\mathbf{u}(\mathbf{r},t)$ and temperature $T(\mathbf{r},t)$. We now consider the evolution of a spatially nonuniform gas after collisional relaxation has brought its momentum distribution close to this form. Our aim is to obtain equations for these three fields and to calculate the momentum and heat fluxes that determine their evolution.

Elastic collisions redistribute particles among momentum states. At each position, the collision integral contributes zero to the changes of particle density, momentum density and kinetic energy density, as expressed by (2.4.71). Collisional relaxation therefore preserves the local moments defining $n(\mathbf{r},t)$, $\mathbf{u}(\mathbf{r},t)$ and $T(\mathbf{r},t)$. These fields evolve through spatial transport and external acceleration. In the hydrodynamic regime, their appreciable evolution occurs over the time τ_H, which is much longer than the local collisional relaxation time τ_{loc}.

This separation allows a temporal resolution Δt_{hyd} satisfying

$$\tau_{\mathrm{loc}} \ll \Delta t_{\mathrm{hyd}} \ll \tau_H. \tag{2.8.1}$$

The lower bound makes the observation interval long compared with local collisional relaxation. The upper bound keeps changes of the hydrodynamic fields small during that interval, so their subsequent evolution remains resolved.

Collisions continue during this evolution. Using the mean interval between collisions τ_{mfp}, the mean number of collisions experienced by one particle during Δt_{hyd} is of order

$$\frac{\Delta t_{\mathrm{hyd}}}{\tau_{\mathrm{mfp}}} \sim \frac{\Delta t_{\mathrm{hyd}}}{\tau_{\mathrm{loc}}} \gg 1, \tag{2.8.2}$$

where we have used $\tau_{\mathrm{loc}} \sim \tau_{\mathrm{mfp}}$, as in (2.4.3). Repeated collisions maintain the distribution close to the local Maxwell form while its parameters evolve slowly. At the Maxwell distribution, the gain and loss contributions balance; the vanishing collision integral expresses this balance.

This temporal resolution constitutes the **second coarse scale**. At the kinetic resolution, $\tau_{\mathrm{int}} \ll \Delta t_{\mathrm{kin}} \ll \tau_{\mathrm{loc}}$, an individual collision is represented by its completed momentum changes, while relaxation of the momentum distribution remains resolved. At the hydrodynamic resolution (2.8.1), that local relaxation is also unresolved, and the retained evolution is primarily the evolution of $n, \mathbf{u}, T$.

The spatial resolution must be consistent with this description. Let L be the characteristic length over which the hydrodynamic fields vary appreciably. Choose a spatial cell containing many particles, and denote its linear size by Δx_{hyd}. With λ_{mfp} denoting the mean free path, we require

$$\lambda_{\mathrm{mfp}} \ll \Delta x_{\mathrm{hyd}} \ll L. \tag{2.8.3}$$

The cell is larger than the distance associated with molecular free flight, while its size is small enough for $n, \mathbf{u}, T$ to be approximately uniform within it. These conditions allow local density, velocity and temperature to be assigned to each cell and their spatial variations to be followed across the gas.

In the local Maxwell approximation,

$$f_1(\mathbf{r}, \mathbf{p}, t) \simeq f_{\mathrm{LE}}(\mathbf{r}, \mathbf{p}, t). \tag{2.8.4}$$

Equation (2.8.4) is appropriate after local collisional relaxation, when $\lambda_{\mathrm{mfp}}/L \ll 1$ and $\tau_{\mathrm{loc}}/\tau_H \ll 1$. The momentum dependence on the right is specified by the three fields through (2.5.18).

In the local rest frame, the Maxwell distribution is isotropic: its pressure tensor is isotropic and its heat flux vanishes. To describe viscous stresses and heat conduction, we must calculate the small departures from this distribution. We shall obtain these departures from the Boltzmann equation and evaluate their contributions to the pressure tensor and heat flux.

The hydrodynamic approximation uses the two small ratios λ_{mfp}/L and $\tau_{\mathrm{loc}}/\tau_H$. They measure spatial variation over a mean free path and temporal variation during local relaxation, respectively. The separate condition $\varepsilon = nd^3 \ll 1$, introduced in §2.4, justifies the dilute gas treatment of collisions.

Conservation equations obtained from the Boltzmann equation

The Boltzmann equation determines the evolution of the one-particle distribution $f_1(\mathbf{r}, \mathbf{p}, t)$. Hydrodynamics seeks a description in terms of the number density n, mean velocity $\mathbf{u}$, and temperature T. Our aim is to derive equations for these five fields and establish how the pressure, viscosity, and transport of internal energy enter them.

The mean velocity describes the collective motion of the gas, but individual particles also move relative to that mean. This relative motion is essential for fluid mechanics. Particles carry momentum and energy between neighbouring regions even in the local rest frame, where the mean velocity vanishes. To obtain the fluid equations, we must therefore distinguish transport by the mean flow from transport by molecular motion relative to it.

As in Section 2.2, we write the relative velocity as

$$\mathbf{c} = \frac{\mathbf{p}}{m} - \mathbf{u}.$$

We shall use angular brackets for averages over the local momentum distribution:

$$\langle A\rangle = \frac{1}{n}\int A f_1\, d^3p, \qquad n = \int f_1\, d^3p.$$

By the definition of the mean velocity, $\langle \mathbf{c}\rangle = 0$.

Consider first momentum transport in the local rest frame. A particle carries momentum mc_α, and its velocity in the direction β is c_β. The momentum flux therefore involves the average product $\langle c_\alpha c_\beta\rangle$. When $\alpha = \beta$, this is a mean-square relative velocity and determines a normal pressure. When the indices differ, the product describes transport of one component of momentum in another spatial direction. Together, these averages determine the pressure tensor, including the contributions that will produce viscous stresses.

Internal-energy transport requires a different average. The relative kinetic energy carried by a particle is $mc^2/2$, so its transport involves $\langle c^2 c_\beta\rangle$. Although the mean relative velocity is zero, the particles moving in opposite directions need not carry equal amounts of energy. The internal-energy flux can therefore be nonzero.

The derivation below will show where these two moments enter the equations for $\mathbf{u}$ and T. Conservation laws determine the structure of those equations. To obtain a closed hydrodynamic description, we must subsequently evaluate the moments in terms of $n, \mathbf{u}, T$ and their spatial variations. This is the step at which viscosity and thermal conductivity become explicit.

We use Cartesian indices, with summation over repeated indices. The external force $\mathbf{F}^{\mathrm{ext}}(\mathbf{r}, t)$ acts on each particle and is independent of momentum. The distribution is assumed to decay sufficiently rapidly for momentum boundary terms to vanish. The Boltzmann equation reads

$$\frac{\partial f_1}{\partial t} + \frac{p_\beta}{m}\frac{\partial f_1}{\partial r_\beta} + F_\beta^{\mathrm{ext}}\frac{\partial f_1}{\partial p_\beta} = C[f_1]. \tag{2.8.5}$$

We begin with the local densities whose evolution is to be determined. Integrating f_1 over momentum gives the particle number density. Integrating $p_\alpha f_1$ gives the momentum density mnu_α, while integrating $[p^2/(2m)]f_1$ gives the total kinetic-energy density. Thus an equation for each density is obtained by multiplying the Boltzmann equation by the corresponding single-particle quantity and integrating over momentum.

This explains the choice of the multiplying functions, or weights, 1, p_α, and $p^2/(2m)$. They select particle number, momentum, and kinetic energy, respectively. These quantities are conserved in elastic collisions, so their collision contributions vanish:

$$\int A(\mathbf{p})\, C[f_1]\, d^3p = 0, \qquad A = 1,\ p_\alpha,\ \frac{p^2}{2m},$$

as established in (2.4.71). Collisions redistribute momentum and energy among particles, but do not create a local source of these conserved quantities.

Integrating (2.8.5) with weight 1 gives the continuity equation,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_\beta}(nu_\beta) = 0. \tag{2.8.6}$$

Its particle flux, nu_β, is already expressed through the hydrodynamic fields.

For momentum, the transported quantity is p_α. Multiplying the streaming term in (2.8.5) by p_α produces the flux

$$\int \frac{p_\alpha p_\beta}{m} f_1\, d^3p.$$

It contains both transport of the mean momentum by the fluid and transport due to relative molecular motion. To separate them, we use

$$c_\alpha = \frac{p_\alpha}{m} - u_\alpha, \qquad \int c_\alpha f_1\, d^3p = 0. \tag{2.8.7}$$

The momentum flux measured in the local rest frame is the kinetic pressure tensor,

$$P_{\alpha\beta}^{\mathrm{kin}} = m\int c_\alpha c_\beta f_1\, d^3p = mn\langle c_\alpha c_\beta\rangle. \tag{2.8.8}$$

Here α labels the momentum component being transported, and β labels the direction of transport. Substituting $p_\alpha = m(u_\alpha + c_\alpha)$ into the total flux and using (2.8.7) eliminates the terms linear in $\mathbf{c}$:

$$\int \frac{p_\alpha p_\beta}{m} f_1\, d^3p = mnu_\alpha u_\beta + P_{\alpha\beta}^{\mathrm{kin}}. \tag{2.8.9}$$

The first term is the momentum density mnu_α carried with the mean velocity u_β. The second transfers momentum relative to that flow.

At this stage, the pressure tensor is left general. Its isotropic part describes ordinary pressure. Its anisotropic part describes directional differences in momentum transport. Near local equilibrium, velocity gradients produce such anisotropy, and the resulting momentum transfer gives viscous forces. Viscosity is therefore already implicit in the distribution appearing in (2.8.8); determining it requires calculating how that distribution responds to velocity gradients.

We now integrate (2.8.5) with weight p_α. The collision term vanishes by momentum conservation. For the external-force term, integration by parts gives

$$\int p_\alpha F_\beta^{\mathrm{ext}} \frac{\partial f_1}{\partial p_\beta}\, d^3p = -F_\beta^{\mathrm{ext}} \int f_1 \frac{\partial p_\alpha}{\partial p_\beta}\, d^3p = -nF_\alpha^{\mathrm{ext}}. \tag{2.8.10}$$

Moving this contribution to the right and using (2.8.9), we obtain

$$\frac{\partial}{\partial t}(mnu_\alpha) + \frac{\partial}{\partial r_\beta}(mnu_\alpha u_\beta + P_{\alpha\beta}^{\mathrm{kin}}) = nF_\alpha^{\mathrm{ext}}. \tag{2.8.11}$$

Equation (2.8.11) describes changes in momentum density. To obtain the acceleration of the fluid, we expand the derivatives of mnu_α and $mnu_\alpha u_\beta$. The terms containing derivatives of the density combine into

$$mu_\alpha\left[\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_\beta}(nu_\beta)\right],$$

which vanishes by continuity. The remaining terms give

$$mn\left(\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta}\right)u_\alpha = nF_\alpha^{\mathrm{ext}} - \frac{\partial P_{\alpha\beta}^{\mathrm{kin}}}{\partial r_\beta}. \tag{2.8.12}$$

The derivative in parentheses follows the mean flow. The term $\partial_t u_\alpha$ describes the velocity change at a fixed position, while $u_\beta\, \partial_{r_\beta} u_\alpha$ accounts for the change encountered as a fluid element moves through a spatially varying velocity field.

The equation now has the form of Newton's second law per unit volume. The mass density mn multiplies the fluid acceleration. On the right are the external force density and the force due to momentum exchange with the surrounding gas. Both pressure forces and viscous forces enter through the spatial variation of $P_{\alpha\beta}^{\mathrm{kin}}$.

We next turn to temperature. The moment with weight $p^2/(2m)$ follows the total kinetic energy. This includes the energy of the mean flow as well as the energy of motion relative to it:

$$\int \frac{p^2}{2m} f_1\, d^3p = \frac{1}{2}mnu^2 + \varepsilon_{\mathrm{kin}}.$$

The first contribution is determined by the mean velocity, whose equation we have already obtained. The second is the internal kinetic energy and determines the temperature. We shall derive its equation directly by measuring particle energy relative to the mean flow.

With $c^2 = c_\alpha c_\alpha$, the internal-energy density and its flux in the local rest frame are

$$\varepsilon_{\mathrm{kin}} = \int \frac{mc^2}{2} f_1\, d^3p = \frac{3}{2}nk_BT, \qquad q_\beta^{\mathrm{kin}} = \int \frac{mc^2}{2} c_\beta f_1\, d^3p. \tag{2.8.13}$$

The equality $\varepsilon_{\mathrm{kin}} = (3/2)nk_BT$ defines the kinetic temperature through the mean energy of particle motion relative to the flow. The pressure tensor retains information about the distribution of this

motion among different directions, while $\mathbf{q}^{\mathrm{kin}}$ describes the transport of internal energy relative to the mean flow.

The vector $\mathbf{q}^{\mathrm{kin}}$ is the internal-energy flux relative to the mean flow, conventionally called the heat flux. It is proportional to the third velocity moment introduced above:

$$q_\beta^{\mathrm{kin}} = \frac{mn}{2}\langle c^2 c_\beta \rangle.$$

The fluid motion also carries internal energy, giving the convective flux $u_\beta \varepsilon_{\mathrm{kin}}$. These two contributions must be kept separate when deriving the temperature equation.

To follow internal energy directly, we multiply (2.8.5) by $mc^2/2$. This introduces no new collision invariant: the relative kinetic energy is a combination of the three conserved quantities,

$$\frac{mc^2}{2} = \frac{p^2}{2m} - u_\alpha p_\alpha + \frac{mu^2}{2}.$$

At fixed position and time, $\mathbf{u}$ is independent of the momentum integration variable. Hence

$$\int \tfrac{mc^2}{2} C[f_1]\, d^3p = \int (\tfrac{p^2}{2m} - u_\alpha p_\alpha + \tfrac{mu^2}{2}) C[f_1]\, d^3p = 0. \tag{2.8.14}$$

For the external-force contribution, we use $\partial(mc^2/2)/\,\partial p_\beta = c_\beta$. Integration by parts then gives

$$\int \tfrac{mc^2}{2} F_\beta^{\mathrm{ext}} \tfrac{\partial f_1}{\partial p_\beta}\, d^3p = -F_\beta^{\mathrm{ext}} \int c_\beta f_1\, d^3p = 0. \tag{2.8.15}$$

At a given position, a momentum-independent force accelerates all particles equally. Its direct work changes the energy of the mean motion, while the internal energy measures motion relative to that mean.

The remaining calculation requires care because the relative velocity depends on $\mathbf{r}, t$ through $\mathbf{u}(\mathbf{r}, t)$. Consequently, $mc^2/2$ also changes when the local mean velocity changes. At fixed momentum,

$$\tfrac{\partial}{\partial t}(\tfrac{mc^2}{2}) = -mc_\alpha \tfrac{\partial u_\alpha}{\partial t}, \qquad \tfrac{\partial}{\partial r_\beta}(\tfrac{mc^2}{2}) = -mc_\alpha \tfrac{\partial u_\alpha}{\partial r_\beta}. \tag{2.8.16}$$

These derivatives must be included when moving time and spatial derivatives outside the momentum integrals.

For the time derivative, the additional term contains the vanishing first moment of $\mathbf{c}$, so

$$\int \frac{mc^2}{2} \frac{\partial f_1}{\partial t}\, d^3p = \frac{\partial \varepsilon_{\mathrm{kin}}}{\partial t}.$$

For spatial transport, the additional term also contains the particle velocity p_β/m. Its integral therefore involves the second moment,

$$m \int c_\alpha \frac{p_\beta}{m} f_1\, d^3p = P_{\alpha\beta}^{\mathrm{kin}}.$$

Using the product rule and separating $p_\beta/m = u_\beta + c_\beta$, we obtain

$$\int \tfrac{mc^2}{2} \tfrac{p_\beta}{m} \tfrac{\partial f_1}{\partial r_\beta}\, d^3p = \tfrac{\partial}{\partial r_\beta}(u_\beta \varepsilon_{\mathrm{kin}} + q_\beta^{\mathrm{kin}}) + P_{\alpha\beta}^{\mathrm{kin}} \tfrac{\partial u_\alpha}{\partial r_\beta}. \tag{2.8.17}$$

The pressure tensor thus enters the energy equation as well as the momentum equation. It transfers momentum between neighbouring regions; when their mean velocities differ, this transfer also exchanges energy between mean motion and internal motion.

Combining the moment integrals gives

$$\tfrac{\partial \varepsilon_{\mathrm{kin}}}{\partial t} + \tfrac{\partial}{\partial r_\beta}(u_\beta \varepsilon_{\mathrm{kin}}) = -\tfrac{\partial q_\beta^{\mathrm{kin}}}{\partial r_\beta} - P_{\alpha\beta}^{\mathrm{kin}} \tfrac{\partial u_\alpha}{\partial r_\beta}. \tag{2.8.18}$$

The left side follows internal energy transported by the mean flow. The first term on the right changes that energy through transport relative to the flow. The second describes mechanical work.

Substituting $\varepsilon_{\mathrm{kin}} = (3/2)nk_BT$ and using continuity gives

$$\frac{3}{2}nk_B\left(\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta}\right)T = -\frac{\partial q_\beta^{\mathrm{kin}}}{\partial r_\beta} - P_{\alpha\beta}^{\mathrm{kin}} \frac{\partial u_\alpha}{\partial r_\beta}. \tag{2.8.19}$$

If the pressure tensor is isotropic, denote its equal diagonal components by p. The mechanical term is then $-p\nabla \cdot \mathbf{u}$. Compression therefore raises the temperature, while expansion lowers it. The anisotropic contribution will describe viscous heating once the pressure tensor has been related to velocity gradients.

We have obtained five evolution equations: continuity for n, three momentum equations for $\mathbf{u}$, and one temperature equation. These equations identify how molecular motion enters fluid mechanics. The second velocity moment determines the pressure tensor,

$$P_{\alpha\beta}^{\mathrm{kin}} = mn\langle c_\alpha c_\beta \rangle,$$

while the third moment determines the internal-energy flux,

$$q_\beta^{\mathrm{kin}} = \frac{mn}{2}\langle c^2 c_\beta \rangle.$$

Both are averages over the one-particle momentum distribution f_1, with $\mathbf{c} = (\mathbf{p} - m\mathbf{u})/m$. In particular, $\langle c_\alpha c_\beta \rangle$ involves two components of the same particle's momentum relative to the local mean.

The equations do not yet determine the evolution of $n, \mathbf{u}, T$ by themselves. These five fields specify the local particle density, mean momentum, and mean relative kinetic energy. They do not specify, for example, whether the mean-square relative momenta are equal in different directions, or whether different relative momentum components have a nonzero average product. Nor do they specify how much internal energy is transported in each direction. Consequently, they do not determine the pressure tensor and internal-energy flux without further information about f_1.

Hydrodynamic closure consists in supplying constitutive relations that express the pressure tensor $P_{\alpha\beta}^{\mathrm{kin}}$ and internal-energy flux q_β^{kin} in terms of $n, \mathbf{u}, T$ and their spatial derivatives. Substituting these relations into the momentum and temperature equations gives a system containing only the five unknown fields n, u_x, u_y, u_z, T. The pressure tensor and internal-energy flux are then calculated from those fields, rather than remaining additional unknown quantities.

Their definitions as momentum integrals of f_1 do not by themselves provide this closure: those integrals still require knowledge of the full distribution. Closure supplies the relations needed to evolve the hydrodynamic fields without solving separately for f_1.

This closure must be distinguished from the closure encountered in the BBGKY hierarchy. There, the equation for the one-particle distribution involved the two-particle distribution, whose equation involved the three-particle distribution, and so on. Closing that hierarchy required an approximation for the statistical dependence between different particles. The derivation of the Boltzmann equation supplied such a kinetic closure.

Here, we already have a closed kinetic equation for f_1. The additional problem arises because we seek a description using only a few moments of that distribution. A closed equation for the full function f_1 does not automatically provide closed equations for a selected set of its moments.

Evaluating the pressure tensor and internal-energy flux requires the momentum dependence of f_1, which conservation laws alone do not determine. We shall first evaluate them using the local Maxwell distribution. Including viscosity and thermal conduction requires determining from the Boltzmann equation how spatial gradients modify that distribution. The resulting dependence of the pressure tensor on velocity gradients determines the viscosity coefficients; the dependence of the internal-energy flux on temperature gradients determines the thermal conductivity.

Although the conserved moments of the collision integral vanish, the collision integral remains in the kinetic equation used to determine f_1. Its dependence on particle momenta and collision rates therefore enters the calculation of these transport coefficients.

The next subsection develops the simplest hydrodynamic closure by evaluating the fluxes in the local Maxwell approximation. This gives the inviscid Euler equations and establishes the starting point for subsequently including viscous stresses and thermal conduction.

Local equilibrium, the Euler equations and thermodynamic equilibrium

Local equilibrium specifies the momentum distribution at each position, while allowing the number density n, mean velocity $\mathbf{u}$, and temperature T to vary in space and time. We first evaluate the kinetic pressure tensor and internal-energy flux using the local Maxwell approximation (2.8.4). These expressions supply the hydrodynamic closure and give the Euler equations. We then examine what further conditions distinguish thermodynamic equilibrium from a gas that is only locally equilibrated.

In the local rest frame, the Maxwell distribution (2.5.18) is isotropic. Consequently, the off-diagonal integrals of $c_\alpha c_\beta$ vanish, and the three diagonal integrals are equal. Their sum is fixed by the internal-energy density: $m\int d^3p\, c^2 f_{\mathrm{LE}} = 3nk_BT$, from (2.8.13). Each diagonal component of the pressure tensor is therefore nk_BT.

The heat flux vanishes because its integrand, $mc^2 c_\beta f_{\mathrm{LE}}/2$, changes sign under $c_\beta \to -c_\beta$, while the Maxwell distribution remains unchanged. Denoting the scalar pressure by p, and using the Kronecker delta $\delta_{\alpha\beta}$, which equals one for $\alpha = \beta$ and zero otherwise, we obtain

$$P^{\mathrm{kin}}_{\alpha\beta} = p\,\delta_{\alpha\beta}, \qquad p = nk_BT, \qquad \mathbf{q}^{\mathrm{kin}} = 0. \tag{2.8.20}$$

These equalities hold for moments evaluated with f_{LE}. The short initial collisional relaxation brings the momentum distribution close to this form. During the subsequent hydrodynamic evolution, spatial transport continues: particles move between regions with different densities, mean velocities and temperatures. As explained in Section 2.5, the resulting derivatives of f_{LE} generally make $\mathcal{L}_1 f_{\mathrm{LE}} \neq 0$, even though $C[f_{\mathrm{LE}}] = 0$. The transport terms therefore continually generate departures from the local Maxwell form, while collisions tend to reduce those departures.

The hydrodynamic conditions ensure that the fields change little over a mean free path and during a local relaxation time. The distribution consequently remains close to f_{LE}. Using (2.8.20) neglects the anisotropic part of the kinetic pressure tensor and the nonzero kinetic heat flux produced by these departures. We shall calculate them when treating viscosity and heat conduction.

We retain the continuity equation (2.8.6), replace $P^{\mathrm{kin}}_{\alpha\beta}$ by $p\delta_{\alpha\beta}$ in the momentum balance (2.8.12), and set $\mathbf{q}^{\mathrm{kin}} = 0$ in the temperature balance (2.8.19). Using $p = nk_BT$, the resulting closed system is

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r_\beta}(nu_\beta) = 0, \tag{2.8.21}$$

$$mn\left(\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta}\right)u_\alpha = nF^{\mathrm{ext}}_\alpha - \frac{\partial p}{\partial r_\alpha}, \tag{2.8.22}$$

$$\left(\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta}\right)T = -\frac{2}{3}T\,\frac{\partial u_\beta}{\partial r_\beta}. \tag{2.8.23}$$

Together with $p = nk_BT$, these are the **Euler equations for a monatomic ideal gas**.

Equation (2.8.22) expresses Newton's second law for the mean flow. The pressure force per unit volume is $-\nabla_{\mathbf{r}} p$: a spatial pressure difference produces an imbalance between the forces exerted on opposite faces of a small gas volume.

With the heat flux set to zero, temperature changes in a gas volume moving with the mean flow are caused by pressure work. The derivative on the left of (2.8.23) is the rate of change of its temperature. Compression has $\partial_{r_\beta} u_\beta < 0$, so the right side is positive and the temperature rises. Expansion gives the opposite sign and lowers the temperature.

This equation also distinguishes convection from thermal equilibration. Convection transports gas with its local temperature. When the volume neither contracts nor expands, its temperature

remains unchanged in this approximation, even if neighbouring volumes have different temperatures. Heat transfer between those volumes requires the nonzero heat flux omitted in (2.8.20). Local Maxwell relaxation establishes the momentum distribution at each local temperature; it does not make temperatures at different positions equal.

The pressure gradient determines the fluid acceleration in (2.8.22). To understand how this force evolves, we must determine how the pressure changes when a fluid element is compressed or expanded.

In the Euler approximation, a moving fluid element exchanges no heat with its surroundings. Compression increases its density, but also raises its temperature through mechanical work. Both changes increase the pressure. Consequently, its pressure rises more rapidly with density than it would if its temperature were held constant.

Continuity gives the fractional rate of change of density as $-\nabla_{\mathbf{r}} \cdot \mathbf{u}$, while (2.8.23) gives the fractional rate of change of temperature as $-(2/3)\nabla_{\mathbf{r}} \cdot \mathbf{u}$, both following the mean flow. Since $p = nk_B T$, these contributions add:

$$\begin{aligned} (\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta})p &= -\frac{5}{3} p \frac{\partial u_\beta}{\partial r_\beta}, \\ (\frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta})(\frac{p}{n^{5/3}}) &= 0. \end{aligned} \tag{2.8.24}$$

Equation (2.8.24) therefore expresses the **adiabatic pressure–density response** of a monatomic ideal gas. It determines how the pressure of a fluid element changes as that element moves, contracts or expands. This pressure response also enters the description of compressive disturbances, such as sound waves.

The constant value of $p/n^{5/3}$ belongs to a particular moving fluid element; different elements may have different values. Equivalently, $T^{3/2}/n$, and hence the local equilibrium entropy per particle in (2.5.34), remains constant following each element. The Euler equations transport these entropy values with the flow, while omitting the heat conduction that would redistribute energy between regions at different temperatures.

Local equilibrium has allowed us to describe a gas whose density, mean velocity and temperature can still evolve. We now seek its thermodynamic equilibrium state at rest. For this state, the local Maxwell distribution must itself satisfy the stationary Boltzmann equation. We shall use this requirement to determine the spatial dependence of the density and temperature.

We consider a gas in a fixed container, subject to a time-independent external potential $U_{\text{ext}}(\mathbf{r})$, with $\mathbf{F}^{\text{ext}} = -\nabla_{\mathbf{r}} U_{\text{ext}}$. We seek equilibrium with zero mean velocity relative to the container. This specifies the meaning of "at rest": the mean flow vanishes, while the particles retain their thermal motion.

For a stationary state with $\mathbf{u} = 0$, the acceleration in (2.8.22) vanishes. Pressure forces must then balance the external force:

$$\nabla_{\mathbf{r}} p = n\mathbf{F}^{\text{ext}} = -n\nabla_{\mathbf{r}} U_{\text{ext}}. \tag{2.8.25}$$

This is a hydrostatic balance which establishes mechanical equilibrium: the pressure force balances the external force. The Euler equations do not, however, require thermal equilibrium between different positions. When $\mathbf{u} = 0$, the temperature equation (2.8.23) reduces to $0 = 0$ and imposes no condition on the temperature profile.

For example, without an external force, a gas at rest with constant pressure and spatially varying n, T satisfies the Euler equations whenever nT is constant. Such a state is mechanically balanced, but its temperature gradient would drive heat conduction if that transport process were included. It is therefore not a state of thermodynamic equilibrium.

To determine the thermodynamic equilibrium distribution, we require the local Maxwell distribution to satisfy the full stationary Boltzmann equation. Since its collision integral vanishes by (2.5.20), the transport terms must also vanish, giving

$$\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}f_{\mathrm{LE}}-\nabla_{\mathbf{r}}U_{\mathrm{ext}}\cdot\nabla_{\mathbf{p}}f_{\mathrm{LE}}=0. \tag{2.8.26}$$

We substitute (2.5.18), allowing its density and temperature to depend on position. Differentiating its prefactor and exponential, then cancelling the common Maxwell factor, gives

$$\frac{\mathbf{p}}{m}\cdot\left[\frac{\nabla_{\mathbf{r}}n}{n}-\frac{3}{2}\frac{\nabla_{\mathbf{r}}T}{T}+\frac{\mathbf{p}^{2}}{2mk_{B}T^{2}}\nabla_{\mathbf{r}}T+\frac{\nabla_{\mathbf{r}}U_{\mathrm{ext}}}{k_{B}T}\right]=0. \tag{2.8.27}$$

The left-hand side of (2.8.27) must vanish for every momentum $\mathbf{p}$. At a fixed position, the density, temperature and their gradients are fixed coefficients, so we can examine how this expression depends on the momentum components.

Most terms contain one power of momentum, supplied by the factor $\mathbf{p}/m$ outside the brackets. The temperature-gradient term containing $\mathbf{p}^{2}$, however, contributes

$$\frac{\mathbf{p}^{2}}{2m^{2}k_{B}T^{2}}(\mathbf{p}\cdot\nabla_{\mathbf{r}}T).$$

This contribution contains three powers of momentum: two from $\mathbf{p}^{2}$ and one from the scalar product. It is therefore a cubic term in the **left-hand side of the stationary kinetic equation**, whereas the remaining terms are linear.

Terms with these different momentum dependences cannot cancel for every momentum magnitude and direction. The cubic contribution must vanish separately, which requires

$$\nabla_{\mathbf{r}}T=0.$$

Thus the stationary Boltzmann equation supplies the condition missing from hydrostatic balance: the thermodynamic equilibrium temperature is spatially uniform.

Denote its constant value by T_{eq}. The remaining linear terms in (2.8.27) give

$$T=T_{\mathrm{eq}},\qquad\nabla_{\mathbf{r}}\ln n=-\frac{\nabla_{\mathbf{r}}U_{\mathrm{ext}}}{k_{B}T_{\mathrm{eq}}}. \tag{2.8.28}$$

Let $n_{\mathrm{eq}}(\mathbf{r})$ denote the equilibrium density, and choose a reference position $\mathbf{r}_{0}$. Integrating the second relation yields

$$n_{\mathrm{eq}}(\mathbf{r})=n_{\mathrm{eq}}(\mathbf{r}_{0})\exp\left[-\frac{U_{\mathrm{ext}}(\mathbf{r})-U_{\mathrm{ext}}(\mathbf{r}_{0})}{k_{B}T_{\mathrm{eq}}}\right]. \tag{2.8.29}$$

The reference density is fixed by the total particle number. Substitution into the Maxwell distribution gives

$$f_{\mathrm{eq}}(\mathbf{r},\mathbf{p})=\frac{n_{\mathrm{eq}}(\mathbf{r}_{0})}{(2\pi mk_{B}T_{\mathrm{eq}})^{3/2}}\exp\left[-\frac{\mathbf{p}^{2}/(2m)+U_{\mathrm{ext}}(\mathbf{r})-U_{\mathrm{ext}}(\mathbf{r}_{0})}{k_{B}T_{\mathrm{eq}}}\right]. \tag{2.8.30}$$

Within the dilute ideal-gas treatment, this has the one-particle canonical Boltzmann form for kinetic energy plus external potential energy. Since f_{eq} counts particles, f_{eq}/N is the corresponding normalized one-particle probability density. In a canonical setting, a heat reservoir fixes T_{eq}; for an isolated gas, its equilibrium temperature is determined by the conserved total energy.

The spatial density variation in (2.8.30) balances acceleration by the external force. For a constant external potential, the density is uniform, and the distribution reduces to the equilibrium Maxwell distribution at rest discussed in §2.5.

As a concrete example, consider a gas in a uniform gravitational field. Let z measure height upwards from the bottom of the container, and let g_{grav} be the magnitude of the gravitational acceleration. Choosing $U_{\mathrm{ext}} = mg_{\mathrm{grav}}z$, equation (2.8.29) gives the equilibrium density and pressure,

$$n_{\mathrm{eq}}(z) = n_{\mathrm{eq}}(0)\exp[-\frac{mg_{\mathrm{grav}}z}{k_BT_{\mathrm{eq}}}], \qquad p_{\mathrm{eq}}(z) = k_BT_{\mathrm{eq}}n_{\mathrm{eq}}(z). \tag{2.8.31}$$

The density decreases with height because raising a particle increases its potential energy. It falls by a factor e over the height $k_BT_{\mathrm{eq}}/(mg_{\mathrm{grav}})$, for which that potential-energy increase equals k_BT_{eq}.

The vertical component of (2.8.25) states that pressure decreases upwards at a rate equal to the local weight per unit volume, $mn_{\mathrm{eq}}g_{\mathrm{grav}}$. The higher pressure below a small gas volume supports its weight. This is a spatially nonuniform thermodynamic equilibrium: the temperature is uniform, while the density and pressure vary to balance gravity.

The Euler equations describe pressure-driven motion and adiabatic temperature changes. To describe viscous momentum transfer and heat conduction during the hydrodynamic evolution, we must retain the anisotropic pressure tensor and heat flux generated by departures from the local Maxwell distribution. Their calculation is the next step.

Small Knudsen number corrections

Physical regime and quantities sought.

We shall use the **Chapman–Enskog method** to derive the first corrections to Euler hydrodynamics. We shall seek a hydrodynamic solution of the Boltzmann equation as an expansion in the Knudsen number. The zeroth-order term is the local Maxwell distribution, which gives **Euler's closures** for the kinetic pressure tensor and heat flux:

$$P_{\alpha\beta}^{\mathrm{kin}} = p\delta_{\alpha\beta}, \qquad q_{\beta}^{\mathrm{kin}} = 0, \qquad p = nk_BT.$$

The first-order correction will be used to determine the viscous stress and heat flux.

Let L be the characteristic length of variation of the hydrodynamic fields and λ_{mfp} the molecular mean free path. We assume

$$\mathrm{Kn} = \frac{\lambda_{\mathrm{mfp}}}{L} \ll 1. \tag{2.8.32}$$

Over one mean free path, the changes in density and temperature are of order $\mathrm{Kn}\,n$ and $\mathrm{Kn}\,T$, respectively. The change in mean velocity is assumed to be of order $\mathrm{Kn}\,v_{\mathrm{th}}$, where $mv_{\mathrm{th}}^2 \sim k_BT$. The external force is assumed to transfer momentum of order $\mathrm{Kn}\,mv_{\mathrm{th}}$ or less during the local relaxation time τ_{loc}.

We first specify the reference Maxwell distribution. The physical density, mean velocity and temperature are defined by the moments of f_1:

$$n = \int d^3p\, f_1,$$
$$mnu_\alpha = \int d^3p\, p_\alpha f_1,$$
$$\frac{3}{2}nk_BT = \int d^3p\, \frac{mc^2}{2} f_1, \qquad \mathbf{c} = \frac{\mathbf{p}}{m} - \mathbf{u}.$$

We choose f_{LE} to be the Maxwell distribution with these same values of $n, \mathbf{u}, T$. Thus, **we impose equality of the density, momentum and internal-energy moments of f_{LE} and f_1**. This is the self-consistent matching condition defining the reference distribution. Distributions with different momentum dependence can share these five moments.

Define the correction by $\delta f = f_1 - f_{\mathrm{LE}}$. Subtracting the matched moments shows that its number, momentum and internal-energy moments are exactly zero.

The order of magnitude of this correction can be estimated using the Boltzmann equation. For molecular velocities of order $v_{\rm th}$ and smooth hydrodynamic evolution, the streaming term evaluated with $f_{\rm LE}$ is of order $v_{\rm th}f_{\rm LE}/L$. The term linear in δf in the collision integral is of order $\delta f/\tau_{\rm loc}$. Equating these orders gives

$$\frac{\delta f}{\tau_{\rm loc}} = O\left(\frac{v_{\rm th}}{L} f_{\rm LE}\right), \qquad \frac{\delta f}{f_{\rm LE}} = O\left(\frac{v_{\rm th}\tau_{\rm loc}}{L}\right) = O(\mathrm{Kn}), \tag{2.8.33}$$

where $\lambda_{\rm mfp} \sim v_{\rm th}\tau_{\rm loc}$. We shall therefore seek the correction in the form

$$f_1 = f_{\rm LE}\big[1 + \mathrm{Kn}\,\chi^{(1)} + O(\mathrm{Kn}^2)\big]. \tag{2.8.34}$$

We shall retain the term proportional to Kn and omit relative corrections of order Kn^2.

The Chapman–Enskog expansion assumes that the distribution's position and time dependence is determined by the current hydrodynamic fields and their spatial gradients. An initially imposed velocity anisotropy can also produce a contribution that relaxes on the collision time. We consider $t - t_0 \gg \tau_{\rm loc}$ and assume that any remaining contribution of this kind is at most $O(\mathrm{Kn}^2 f_{\rm LE})$, so it belongs to the terms that will be omitted.

The matching conditions are imposed at every order of the expansion. At first order, they give

$$\begin{gathered} \int d^3p\, f_{\rm LE}\chi^{(1)} = 0, \\ \int d^3p\, p_\alpha f_{\rm LE}\chi^{(1)} = 0, \qquad \alpha = x,y,z, \\ \int d^3p\, \frac{mc^2}{2} f_{\rm LE}\chi^{(1)} = 0. \end{gathered} \tag{2.8.35}$$

These conditions ensure that the parameters of $f_{\rm LE}$ remain equal to the physical fields of the corrected distribution. The fields are unknown functions of position and time; their evolution and the correction $\chi^{(1)}$ must be determined consistently from the Boltzmann equation.

The flux corrections that we seek are, to first order,

$$\begin{aligned} P^{\rm kin}_{\alpha\beta} - p\delta_{\alpha\beta} &= \mathrm{Kn}\, m\int d^3p\, c_\alpha c_\beta f_{\rm LE}\chi^{(1)}, \\ q^{\rm kin}_\beta &= \mathrm{Kn}\,\frac{m}{2}\int d^3p\, c^2 c_\beta f_{\rm LE}\chi^{(1)}. \end{aligned} \tag{2.8.36}$$

The energy condition in (2.8.35) fixes the trace of the pressure correction to zero, while its anisotropic components remain to be determined. The zero momentum correction likewise leaves the energy-weighted moment defining the heat flux undetermined. Calculating these moments will provide the first-order constitutive relations that replace Euler's closures.

Equation determining the first-order correction.

We substitute the expansion (2.8.34) into the Boltzmann equation and retain terms through first order in Kn. Using the material derivative D_t, we write

$$\begin{gathered} \mathrm{L}_1 f_1 = C[f_1], \\ \mathrm{L}_1 = D_t + c_\beta \frac{\partial}{\partial r_\beta} + F^{\rm ext}_\beta \frac{\partial}{\partial p_\beta}, \\ D_t = \frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial r_\beta}. \end{gathered} \tag{2.8.37}$$

Here $C[f_1]$ is the collision integral. The external force $\mathbf{F}^{\rm ext}(\mathbf{r},t)$ is independent of momentum.

In the gain term, the incoming momenta $\mathbf{p}_1', \mathbf{p}_2'$ produce the momenta $\mathbf{p}_1, \mathbf{p}_2$. At the common collision position and time, we use

$$\begin{gathered} f_{{\rm LE},i} = f_{\rm LE}(\mathbf{r},\mathbf{p}_i,t), \quad f_{{\rm LE},i}' = f_{\rm LE}(\mathbf{r},\mathbf{p}_i',t), \\ \chi_i^{(1)} = \chi^{(1)}(\mathbf{r},\mathbf{p}_i,t), \quad \chi_i^{(1)\prime} = \chi^{(1)}(\mathbf{r},\mathbf{p}_i',t), \qquad i = 1{,}2. \end{gathered}$$

The subscripts identify the collision partners; a prime indicates evaluation at a primed momentum. Conservation of pair momentum and energy gives

$$f_{{\rm LE},1}' f_{{\rm LE},2}' = f_{{\rm LE},1} f_{{\rm LE},2}, \qquad C[f_{\rm LE}] = 0. \tag{2.8.37a}$$

Substitution of (2.8.34) into the collision integral gives

$$\begin{aligned} C[f_1] &= \mathrm{Kn}\, f_{\mathrm{LE},1} C_{\mathrm{lin}}\big[\chi^{(1)}\big] + O\left(\tfrac{\mathrm{Kn}^2 f_{\mathrm{LE},1}}{\tau_{\mathrm{loc}}}\right), \\ C_{\mathrm{lin}}\big[\chi^{(1)}\big] &= \int d^3p_2 \int d\sigma\, g\, f_{\mathrm{LE},2} \times \left(\chi_1^{(1)\prime} + \chi_2^{(1)\prime} - \chi_1^{(1)} - \chi_2^{(1)}\right), \qquad g = \tfrac{|\mathbf{p}_2 - \mathbf{p}_1|}{m}. \end{aligned} \tag{2.8.38}$$

The collision expressions are evaluated at fixed $\mathbf{p}_1$, with integration over $\mathbf{p}_2$ and the cross-section element $d\sigma$. The factor $f_{\mathrm{LE},1}$ is independent of these integration variables and has been extracted from the integral.

For molecular velocities of order v_{th}, the hydrodynamic scales assumed above give

$$\mathrm{L}_1\big(\mathrm{Kn}\, f_{\mathrm{LE}} \chi^{(1)}\big) = O\left(\frac{\mathrm{Kn}^2 f_{\mathrm{LE}}}{\tau_{\mathrm{loc}}}\right).$$

Equations (2.8.37) and (2.8.38) therefore yield

$$\mathrm{Kn}\, C_{\mathrm{lin}}\big[\chi^{(1)}\big] = \tfrac{\mathrm{L}_1 f_{\mathrm{LE}}}{f_{\mathrm{LE}}} + O\left(\tfrac{\mathrm{Kn}^2}{\tau_{\mathrm{loc}}}\right). \tag{2.8.39}$$

Applying L_1 in (2.8.37) to f_{LE} gives the source in (2.8.39). The time and position derivatives act on $\mathbf{u}(\mathbf{r}, t)$ through $\mathbf{c} = \mathbf{p}/m - \mathbf{u}$. We obtain

$$\tfrac{\mathrm{L}_1 f_{\mathrm{LE}}}{f_{\mathrm{LE}}} = D_t \ln n + \mathbf{c} \cdot \nabla_{\mathbf{r}} \ln n + \left(\tfrac{mc^2}{2k_B T} - \tfrac{3}{2}\right)(D_t \ln T + \mathbf{c} \cdot \nabla_{\mathbf{r}} \ln T) + \tfrac{m}{k_B T}\, \mathbf{c} \cdot \left[D_t \mathbf{u} + (\mathbf{c} \cdot \nabla_{\mathbf{r}})\mathbf{u} - \tfrac{\mathbf{F}^{\mathrm{ext}}}{m}\right]. \tag{2.8.40}$$

The fields $n, \mathbf{u}, T$ in (2.8.40) are moments of the full distribution f_1. To express their material derivatives through the fields itself and their spatial gradients, we use continuity (2.8.6), momentum balance (2.8.12) and the temperature equation (2.8.19), derived in subsection "**Conservation equations obtained from the Boltzmann equation**" above:

$$\begin{aligned} D_t n &= -n \frac{\partial u_\beta}{\partial r_\beta}, \\ mn D_t u_\alpha &= n F_\alpha^{\mathrm{ext}} - \frac{\partial P_{\alpha\beta}^{\mathrm{kin}}}{\partial r_\beta}, \\ \frac{3}{2} n k_B D_t T &= -P_{\alpha\beta}^{\mathrm{kin}} \frac{\partial u_\alpha}{\partial r_\beta} - \frac{\partial q_\beta^{\mathrm{kin}}}{\partial r_\beta}. \end{aligned}$$

We recall that the kinetic pressure tensor and heat flux, defined in (2.8.8) and (2.8.13), are

$$P_{\alpha\beta}^{\mathrm{kin}} = m \int d^3p\, c_\alpha c_\beta f_1, \qquad q_\beta^{\mathrm{kin}} = \tfrac{m}{2} \int d^3p\, c^2 c_\beta f_1. \tag{2.8.41}$$

Both quantities depend on the full f_1, so the correction $\chi^{(1)}$ affects the evolution of $\mathbf{u}$ and T through the kinetic pressure tensor and heat flux. Substituting the first-order moments (2.8.36) into the momentum equation (2.8.12) and temperature equation (2.8.19) gives

$$\begin{aligned} mn D_t u_\alpha &= n F_\alpha^{\mathrm{ext}} - \frac{\partial p}{\partial r_\alpha} - \frac{\partial}{\partial r_\beta}\big[\mathrm{Kn}\, m \int d^3p\, c_\alpha c_\beta f_{\mathrm{LE}} \chi^{(1)}\big] + \cdots, \\ \tfrac{3}{2} n k_B D_t T &= -p \frac{\partial u_\beta}{\partial r_\beta} - \mathrm{Kn}\, m \frac{\partial u_\alpha}{\partial r_\beta} \int d^3p\, c_\alpha c_\beta f_{\mathrm{LE}} \chi^{(1)} - \frac{\partial}{\partial r_\beta}\left[\mathrm{Kn}\, \tfrac{m}{2} \int d^3p\, c^2 c_\beta f_{\mathrm{LE}} \chi^{(1)}\right] + \cdots. \end{aligned} \tag{2.8.42}$$

Using $v_{\mathrm{th}} \tau_{\mathrm{loc}} / L \sim \mathrm{Kn}$, equations (2.8.6) and (2.8.42) give

$$D_t n = -n \frac{\partial u_\beta}{\partial r_\beta}, \tag{2.8.43a}$$

$$D_t u_\alpha = \tfrac{F_\alpha^{\mathrm{ext}}}{m} - \tfrac{1}{mn} \frac{\partial p}{\partial r_\alpha} + O\left(\tfrac{\mathrm{Kn}^2 v_{\mathrm{th}}}{\tau_{\mathrm{loc}}}\right), \tag{2.8.43b}$$

$$D_t T = -\tfrac{2}{3} T \frac{\partial u_\beta}{\partial r_\beta} + O\left(\tfrac{\mathrm{Kn}^2 T}{\tau_{\mathrm{loc}}}\right). \tag{2.8.43c}$$

The leading terms in (2.8.43a–c) are the Euler equations, with $p = n k_B T$. The remainder terms in (2.8.43b) and (2.8.43c) contribute only at order $\mathrm{Kn}^2/\tau_{\mathrm{loc}}$ to the source (2.8.40).

Substituting the leading terms of (2.8.43a–c) into (2.8.40) eliminates the force and density-gradient terms. The resulting velocity-gradient term is expressed through the symmetric, traceless tensor

$$S_{\alpha\beta} = \frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} - \frac{2}{3}\delta_{\alpha\beta}\frac{\partial u_\gamma}{\partial r_\gamma}. \tag{2.8.44}$$

The first-order equation (2.8.39) becomes

$$\mathrm{Kn}\, C_{\mathrm{lin}}[\chi^{(1)}] = \frac{m}{2k_BT}\, c_\alpha c_\beta S_{\alpha\beta} + \left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)\frac{c_\beta}{T}\frac{\partial T}{\partial r_\beta}. \tag{2.8.45}$$

The collision equation (2.8.45) does not by itself fix the collision-invariant components of $\chi^{(1)}$. Conservation of momentum and energy results in the following identity

$$C_{\mathrm{lin}}[\chi^{(1)} + \Delta\chi] = C_{\mathrm{lin}}[\chi^{(1)}], \tag{2.8.46}$$

for any $\Delta\chi = a + \mathbf{b}\cdot\mathbf{p} + d\,\frac{\mathbf{p}^2}{2m}$, where a, $\mathbf{b}$ and d may depend on $(\mathbf{r}, t)$, but are independent of $\mathbf{p}$. Thus, if $\chi^{(1)}$ solves (2.8.45), so does $\chi^{(1)} + \Delta\chi$.

The matching conditions (2.8.35) remove this freedom. The zero internal-energy moment in (2.8.35) is equivalent to a zero total-kinetic-energy moment because

$$\frac{\mathbf{p}^2}{2m} = \frac{mc^2}{2} + u_\alpha p_\alpha - \frac{mu^2}{2},$$

and the number density and momentum moments of the correction vanish. If $\chi^{(1)}$ and $\chi^{(1)} + \Delta\chi$ both satisfy (2.8.35), subtracting their matching conditions therefore gives

$$\int d^3p\, f_{\mathrm{LE}} \begin{pmatrix} 1 \\ p_\alpha \\ \mathbf{p}^2/(2m) \end{pmatrix} \Delta\chi = 0. \tag{2.8.47}$$

Multiplying the expression for $\Delta\chi$ in (2.8.46) by $f_{\mathrm{LE}}\Delta\chi$ and integrating yields

$$\int d^3p\, f_{\mathrm{LE}}(\Delta\chi)^2 = a\underbrace{\int d^3p\, f_{\mathrm{LE}}\Delta\chi}_{=0} + b_\alpha\underbrace{\int d^3p\, p_\alpha f_{\mathrm{LE}}\Delta\chi}_{=0} + d\underbrace{\int d^3p\, \frac{\mathbf{p}^2}{2m} f_{\mathrm{LE}}\Delta\chi}_{=0} = 0. \tag{2.8.48}$$

Each integral on the right vanishes by (2.8.47). Because $f_{\mathrm{LE}} > 0$ and $\Delta\chi$ is a polynomial in momentum, (2.8.48) implies $\Delta\chi = 0$, hence $a = b_\alpha = d = 0$.

The matching conditions thus fix the collision-invariant components left undetermined by (2.8.45). The moments of $\chi^{(1)}$ entering the pressure correction and heat flux are given in (2.8.36).

From the correction to transport laws.

We now derive the viscous pressure law and Fourier's law from the collision equation (2.8.45) and the momentum integrals (2.8.36).

The source in (2.8.45) contains terms proportional to $S_{\alpha\beta}$ and $\partial T/\,\partial r_\alpha$. Because $S_{\alpha\beta}$ is traceless, the velocity product multiplying $S_{\alpha\beta}$ can be written as

$$Q_{\alpha\beta} = c_\alpha c_\beta - \frac{1}{3}c^2\delta_{\alpha\beta}, \qquad Q_{\alpha\beta}S_{\alpha\beta} = c_\alpha c_\beta S_{\alpha\beta}. \tag{2.8.49}$$

Here $c = |\mathbf{c}|$, where $\mathbf{c} = \mathbf{p}/m - \mathbf{u}$.

For elastic binary collisions whose law is invariant under rotations of the peculiar velocities, and whose only collision invariants are $1, p_\alpha, \mathbf{p}^2/(2m)$, it may be shown that the general first-order hydrodynamic solution of (2.8.45), subject to the matching conditions (2.8.35), has the form

$$\mathrm{Kn}\,\chi^{(1)} = -\frac{m}{2k_BT}A(c)Q_{\alpha\beta}S_{\alpha\beta} - B(c)\frac{c_\beta}{T}\frac{\partial T}{\partial r_\beta}. \tag{2.8.50}$$

The unknown functions $A(c)$ and $B(c)$ depend on the speed c and the local fields n, T. The dependence on the direction of $\mathbf{c}$ is explicit in $Q_{\alpha\beta}$ and c_β.

Substitution of (2.8.50) into (2.8.45), followed by equating the coefficients of the independent gradients, gives

$$C_{\text{lin}}\big[A(c)Q_{\alpha\beta}\big] = -Q_{\alpha\beta}, \tag{2.8.51a}$$

$$C_{\text{lin}}[B(c)c_\alpha] = -\left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)c_\alpha. \tag{2.8.51b}$$

The operator C_{lin} in (2.8.51a–b) is the integral operator (2.8.38). The functions A and B remain inside the collision integrals, evaluated at the speeds corresponding to the primed and unprimed momenta.

The matching conditions (2.8.35) for the number density and momentum density are

$$\int d^3p\, f_{\text{LE}}\chi^{(1)} = 0, \qquad \int d^3p\, p_\alpha f_{\text{LE}}\chi^{(1)} = 0.$$

Since $c_\alpha = p_\alpha/m - u_\alpha$, the matching conditions give

$$\int d^3p\, c_\alpha f_{\text{LE}}\chi^{(1)} = \frac{1}{m}\int d^3p\, p_\alpha f_{\text{LE}}\chi^{(1)} - u_\alpha \int d^3p\, f_{\text{LE}}\chi^{(1)} = 0.$$

At fixed position and time, $d^3p = m^3d^3c$, and f_{LE} depends only on c. Integrals whose integrands change sign under $\mathbf{c} \mapsto -\mathbf{c}$ therefore vanish: opposite peculiar velocities give cancelling contributions.

After substitution of (2.8.50), the $A(c)$ term in the momentum-density matching integral vanishes because $c_\alpha Q_{\gamma\delta}$ changes sign under $\mathbf{c} \mapsto -\mathbf{c}$. For the $B(c)$ term, rotational symmetry gives

$$\int d^3p\, f_{\text{LE}}B(c)c_\alpha c_\beta = \frac{\delta_{\alpha\beta}}{3}\int d^3p\, f_{\text{LE}}B(c)c^2.$$

The factor $1/3$ follows because the three diagonal integrals are equal and their sum is the integral containing c^2. Consequently,

$$0 = \text{Kn}\int d^3p\, c_\alpha f_{\text{LE}}\chi^{(1)} = -\frac{1}{3T}\frac{\partial T}{\partial r_\alpha}\int d^3p\, f_{\text{LE}}B(c)c^2.$$

For momentum-density matching to hold for an arbitrary temperature gradient, $B(c)$ must satisfy

$$\int d^3p\, f_{\text{LE}}B(c)c^2 = 0. \tag{2.8.52}$$

The viscous pressure correction follows by substituting (2.8.50) into the pressure moment (2.8.36). The $B(c)$ term produces an integral proportional to $c_\alpha c_\beta c_\gamma$, which vanishes under reversal of $\mathbf{c}$. Using (2.8.49) for the $A(c)$ term gives

$$P^{\text{kin}}_{\alpha\beta} - p\delta_{\alpha\beta} = -\frac{m^2}{2k_BT}S_{\gamma\delta}\int d^3p\, f_{\text{LE}}A(c)c_\alpha c_\beta c_\gamma c_\delta + O(\text{Kn}^2 p).$$

The fourth velocity moment is rotationally invariant because $f_{\text{LE}}A(c)$ depends only on speed. A rotationally invariant tensor with four indices is a linear combination of the three Kronecker-delta pairings below. Symmetry under interchange of the four indices requires a common coefficient:

$$\int d^3p\, f_{\text{LE}}A(c)c_\alpha c_\beta c_\gamma c_\delta = \frac{\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}}{15}\int d^3p\, f_{\text{LE}}A(c)c^4. \tag{2.8.53}$$

The coefficient $1/15$ is determined by setting $\beta = \alpha$, $\delta = \gamma$, and summing over α, γ. The velocity product becomes c^4, while the three delta products give $9 + 3 + 3 = 15$.

The pressure integral contains $S_{\gamma\delta}$ multiplying the fourth moment (2.8.53). The required index sum is

$$S_{\gamma\delta}\big(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\big) = \delta_{\alpha\beta}S_{\gamma\gamma} + S_{\alpha\beta} + S_{\beta\alpha} = 2S_{\alpha\beta},$$

where the final equality uses the symmetry and zero trace of $S_{\alpha\beta}$.

The pressure correction is therefore proportional to $-S_{\alpha\beta}$. Comparison with the Newtonian viscous-stress law identifies the proportionality coefficient as the **shear viscosity** η:

$$P^{\text{kin}}_{\alpha\beta} = p\delta_{\alpha\beta} - \eta S_{\alpha\beta} + O(\text{Kn}^2 p), \qquad \eta = \frac{m^2}{15k_BT}\int d^3p\, f_{\text{LE}}A(c)c^4. \tag{2.8.54}$$

For example, when $\mathbf{u} = (u_x(y), 0, 0)$, equation (2.8.54) gives $P_{xy}^{\mathrm{kin}} = -\eta\, du_x/dy$. For positive η, the viscous flux transfers x-momentum towards layers with smaller u_x.

The heat flux follows by substituting (2.8.50) into the heat-flux moment (2.8.36). The $A(c)$ term produces an integral proportional to $c^2 c_\alpha Q_{\gamma\delta}$, which changes sign under $\mathbf{c} \mapsto -\mathbf{c}$ and therefore integrates to zero. The $B(c)$ term gives

$$q_\alpha^{\mathrm{kin}} = -\frac{m}{2T}\frac{\partial T}{\partial r_\beta}\int d^3p\, f_{\mathrm{LE}} B(c) c^2 c_\alpha c_\beta + O(\mathrm{Kn}^2 p v_{\mathrm{th}}).$$

Because $f_{\mathrm{LE}} B(c) c^2$ depends only on speed, the second-rank integral is proportional to $\delta_{\alpha\beta}$. Summing over $\alpha = \beta$ determines the coefficient:

$$\int d^3p\, f_{\mathrm{LE}} B(c) c^2 c_\alpha c_\beta = \frac{\delta_{\alpha\beta}}{3}\int d^3p\, f_{\mathrm{LE}} B(c) c^4. \tag{2.8.55}$$

The resulting heat flux is proportional to $-\nabla T$. Comparison with Fourier's law identifies the proportionality coefficient as the **thermal conductivity** κ:

$$q_\alpha^{\mathrm{kin}} = -\kappa\frac{\partial T}{\partial r_\alpha} + O(\mathrm{Kn}^2 p v_{\mathrm{th}}), \qquad \kappa = \frac{m}{6T}\int d^3p\, f_{\mathrm{LE}} B(c) c^4. \tag{2.8.56}$$

The matching condition (2.8.52) sets the c^2-weighted integral of B to zero. The conductivity in (2.8.56) contains the c^4-weighted integral. Thus, the absence of an additional particle current does not require the heat flux to vanish.

The microscopic calculation of $A(c)$ and $B(c)$ requires the differential collision cross-section $d\sigma$ in (2.8.38). For a specified cross-section, the integral equations (2.8.51a–b), together with (2.8.52), determine the speed functions. Substitution into (2.8.54) and (2.8.56) then gives η and κ.

A standard approximation expands A and B in polynomials of $mc^2/(2k_BT)$. After truncation, substitution into (2.8.51a–b) and evaluation of polynomial moments gives linear algebraic equations for the expansion coefficients. The matching condition (2.8.52) is imposed together with the coefficient equations.

An explicit example is obtained by replacing the Boltzmann collision integral with a model in which collisions relax f_1 towards f_{LE} with a momentum-independent relaxation time τ_R:

$$C[f_1] \simeq -\frac{f_1 - f_{\mathrm{LE}}}{\tau_R}, \qquad \tau_R = \tau_R(n, T) > 0, \qquad \tau_R \sim \tau_{\mathrm{loc}}. \tag{2.8.57}$$

The local Maxwell distribution in (2.8.57) has the same number density, mean velocity and temperature as f_1. The model therefore conserves particle number, momentum and energy.

Substitution of the expansion (2.8.34) into (2.8.57) gives the first-order collision term $-\mathrm{Kn} f_{\mathrm{LE}} \chi^{(1)}/\tau_R$. Using the source in (2.8.45) and comparing with (2.8.50) gives

$$A(c) = \tau_R, \qquad B(c) = \tau_R\left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right). \tag{2.8.58}$$

Substitution of (2.8.58) into the general coefficient formulas (2.8.54) and (2.8.56) requires the Maxwell moments

$$\int d^3p\, f_{\mathrm{LE}} c^4 = 15n\left(\frac{k_BT}{m}\right)^2, \qquad \int d^3p\, f_{\mathrm{LE}} c^6 = 105n\left(\frac{k_BT}{m}\right)^3.$$

The resulting transport coefficients are

$$\eta = p\tau_R, \qquad \kappa = \frac{5k_B}{2m}p\tau_R, \qquad p = nk_BT. \tag{2.8.59}$$

Equation (2.8.59) gives the predictions of the relaxation-time model for a prescribed τ_R. For the full Boltzmann collision integral, the general expressions (2.8.54) and (2.8.56) apply, with A and B determined from the collision cross-section through (2.8.51a–b) and (2.8.52).

Hydrodynamic closure and microscopic content.

The pressure law (2.8.54) and Fourier's law (2.8.56) express $P_{\alpha\beta}^{\mathrm{kin}}$ and $q_{\alpha}^{\mathrm{kin}}$ through $n, \mathbf{u}, T$ and their spatial derivatives. Substitution into continuity (2.8.6), momentum balance (2.8.12) and the temperature equation (2.8.19) gives the **Navier–Stokes–Fourier equations**:

$$D_t n = -n\frac{\partial u_\beta}{\partial r_\beta}, \tag{2.8.60a}$$

$$mnD_t u_\alpha = nF_\alpha^{\mathrm{ext}} - \frac{\partial p}{\partial r_\alpha} + \frac{\partial}{\partial r_\beta}\left(\eta S_{\alpha\beta}\right), \tag{2.8.60b}$$

$$\frac{3}{2}nk_B D_t T = -p\frac{\partial u_\beta}{\partial r_\beta} + \frac{\eta}{2}S_{\alpha\beta}S_{\alpha\beta} + \frac{\partial}{\partial r_\beta}\left(\kappa\frac{\partial T}{\partial r_\beta}\right). \tag{2.8.60c}$$

Here $p = nk_BT$, D_t is the material derivative defined in (2.8.37), and $S_{\alpha\beta}$ is the symmetric, traceless velocity-gradient tensor (2.8.44). In general, $\eta = \eta(n,T)$ and $\kappa = \kappa(n,T)$; the spatial derivatives in (2.8.60b–c) therefore act on the transport coefficients as well as on the gradients.

Equations (2.8.60b–c) retain the pressure tensor and heat flux through first order in Kn. The omitted constitutive corrections are $O(\mathrm{Kn}^2 p)$ in $P_{\alpha\beta}^{\mathrm{kin}}$ and $O(\mathrm{Kn}^2 p v_{\mathrm{th}})$ in q_α^{kin}, as specified in (2.8.54) and (2.8.56).

The term $-p\,\partial u_\beta/\partial r_\beta$ in (2.8.60c) is the pressure work already present in the Euler temperature equation (2.8.43c). Compression, for which $\partial u_\beta/\partial r_\beta < 0$, raises the temperature; expansion lowers the temperature.

The viscous heating term in (2.8.60c) comes from the pressure-work term $-P_{\alpha\beta}^{\mathrm{kin}}\,\partial u_\alpha/\partial r_\beta$ in (2.8.19). Substitution of (2.8.54) gives a viscous contribution $\eta S_{\alpha\beta}\,\partial u_\alpha/\partial r_\beta$. Because $S_{\alpha\beta}$ is symmetric and traceless,

$$S_{\alpha\beta}\frac{\partial u_\alpha}{\partial r_\beta} = \frac{1}{2}S_{\alpha\beta}\left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} - \frac{2}{3}\delta_{\alpha\beta}\frac{\partial u_\gamma}{\partial r_\gamma}\right) = \frac{1}{2}S_{\alpha\beta}S_{\alpha\beta}. \tag{2.8.61}$$

For positive η, the viscous heating rate $\eta S_{\alpha\beta}S_{\alpha\beta}/2$ is nonnegative.

The corresponding transfer of energy from the mean flow follows directly from the momentum equation. The power per unit volume associated with the viscous force in (2.8.60b) is

$$u_\alpha\frac{\partial}{\partial r_\beta}\left(\eta S_{\alpha\beta}\right) = \frac{\partial}{\partial r_\beta}\left(\eta u_\alpha S_{\alpha\beta}\right) - \frac{\eta}{2}S_{\alpha\beta}S_{\alpha\beta}. \tag{2.8.62}$$

The divergence in (2.8.62) accounts for transport of mechanical energy. The negative term $-\eta S_{\alpha\beta}S_{\alpha\beta}/2$ in the mean-flow energy balance is equal in magnitude to the positive viscous heating term in (2.8.60c). Viscosity therefore converts kinetic energy of the mean flow into internal energy.

The heat-conduction term in (2.8.60c) is $-\partial q_\beta^{\mathrm{kin}}/\partial r_\beta$, with q_β^{kin} given by Fourier's law (2.8.56). For positive κ, heat flows towards lower temperature. The divergence of the heat flux determines the local gain or loss of internal energy through heat transport.

The microscopic input required in (2.8.60b–c) is the dependence of η and κ on n, T. For a specified collision cross-section, equations (2.8.51a–b) and the matching condition (2.8.52) determine $A(c)$ and $B(c)$; the integrals (2.8.54) and (2.8.56) then give the transport coefficients. Once $\eta(n,T)$ and $\kappa(n,T)$ are supplied, equations (2.8.60a–c), together with $p = nk_BT$, form a closed system for $n, \mathbf{u}, T$.

Propagation and relaxation of weak hydrodynamic disturbances

After local collisional relaxation, a gas may still have spatial variations of density, mean velocity and temperature. The hydrodynamic equations determine how these variations propagate and decay. We shall examine weak disturbances of a uniform equilibrium state and distinguish the propagation caused by pressure forces from the relaxation produced by viscosity and heat conduction.

We consider weak perturbations depending only on x and t, while retaining all three velocity components. We study the propagation and relaxation of number-density, velocity and temperature perturbations by linearising the Navier–Stokes–Fourier equations (2.8.60a–c) about uniform equilibrium.

Linearised hydrodynamic equations

The reference state is an unbounded gas at rest, with constant number density n_0, temperature T_0 and pressure $p_0 = n_0 k_B T_0$. The external force vanishes. The disturbances are defined by

$$n = n_0 + \delta n, \qquad T = T_0 + \delta T, \qquad \mathbf{u} = \delta\mathbf{u}, \qquad p = p_0 + \delta p. \tag{2.8.63}$$

The disturbance amplitudes satisfy

$$\frac{|\delta n|}{n_0} \ll 1, \qquad \frac{|\delta T|}{T_0} \ll 1, \qquad \frac{|\delta\mathbf{u}|}{v_{\mathrm{th}}} \ll 1, \tag{2.8.64}$$

where v_{th} is evaluated at T_0. We retain terms linear in the disturbance amplitudes and omit products of two disturbance amplitudes. Linearisation of the equation of state $p = nk_BT$ gives

$$\delta p = k_B T_0\, \delta n + n_0 k_B\, \delta T. \tag{2.8.65}$$

All disturbances depend on x and t, while the velocity may have three components. The component δu_x is longitudinal, parallel to the direction of spatial variation; δu_y and δu_z are transverse, perpendicular to that direction. The definition (2.8.44) gives

$$S_{xx} = \frac{4}{3}\frac{\partial \delta u_x}{\partial x}, \qquad S_{yx} = \frac{\partial \delta u_y}{\partial x}, \qquad S_{zx} = \frac{\partial \delta u_z}{\partial x}.$$

The convective terms $\delta u_x\, \partial_x \delta n$, $\delta u_x\, \partial_x \delta u_\alpha$ and $\delta u_x\, \partial_x \delta T$ are quadratic in the disturbance amplitudes and are omitted. The viscous heating term $\eta S_{\alpha\beta} S_{\alpha\beta}/2$ in (2.8.60c) is also quadratic and is omitted.

In the transport terms, the coefficients are evaluated at the reference state:

$$\eta = \eta(n_0, T_0), \qquad \kappa = \kappa(n_0, T_0).$$

Changes in η and κ are linear in $\delta n, \delta T$; multiplication by a velocity or temperature gradient therefore produces quadratic terms. Likewise, the products $nD_t u_\alpha$ and $p\ \partial_x u_x$ retain only $n_0\, \partial_t \delta u_\alpha$ and $p_0\, \partial_x \delta u_x$.

Substitution into continuity (2.8.60a), momentum balance (2.8.60b) and the temperature equation (2.8.60c) gives

$$\frac{\partial \delta n}{\partial t} = -n_0 \frac{\partial \delta u_x}{\partial x}, \tag{2.8.66a}$$

$$m n_0 \frac{\partial \delta u_x}{\partial t} = -\frac{\partial \delta p}{\partial x} + \frac{4}{3}\eta \frac{\partial^2 \delta u_x}{\partial x^2}, \tag{2.8.66b}$$

$$m n_0 \frac{\partial \delta u_y}{\partial t} = \eta \frac{\partial^2 \delta u_y}{\partial x^2}, \tag{2.8.66c}$$

$$m n_0 \frac{\partial \delta u_z}{\partial t} = \eta \frac{\partial^2 \delta u_z}{\partial x^2}, \tag{2.8.66d}$$

$$\frac{3}{2} n_0 k_B \frac{\partial \delta T}{\partial t} = -p_0 \frac{\partial \delta u_x}{\partial x} + \kappa \frac{\partial^2 \delta T}{\partial x^2}. \tag{2.8.66e}$$

Equations (2.8.65) and (2.8.66a–e) form a closed linear system for $\delta n, \delta\mathbf{u}, \delta T$. The transverse velocities evolve independently according to (2.8.66c–d). The longitudinal velocity, number-density disturbance and temperature disturbance are coupled through (2.8.65), (2.8.66a), (2.8.66b) and (2.8.66e).

Equations (2.8.65) and (2.8.66a–e) are linear with constant coefficients, so spatial Fourier harmonics evolve independently. We therefore analyse one harmonic of wave number k:

$$\delta n(x,t) = \mathrm{Re}\big[N_k(t) e^{ikx}\big], \qquad \delta\mathbf{u}(x,t) = \mathrm{Re}\big[\mathbf{U}_k(t) e^{ikx}\big], \qquad \delta T(x,t) = \mathrm{Re}\big[\Theta_k(t) e^{ikx}\big].$$

Substitution into (2.8.65) and (2.8.66a–e) gives ordinary differential equations for the amplitudes $N_k(t)$, $\mathbf{U}_k(t)$ and $\Theta_k(t)$. General spatial profiles evolve by superposition of the independently evolving harmonics.

The hydrodynamic description requires

$$k\lambda_{\mathrm{mfp}} \ll 1. \tag{2.8.67}$$

The small-amplitude conditions (2.8.64) justify linearisation; condition (2.8.67) justifies the hydrodynamic gradient approximation.

Shear relaxation

The initial perturbation is a transverse velocity harmonic of amplitude U_0,

$$\delta u_y(x,0) = U_0 \cos kx,$$

with $\delta u_x, \delta u_z, \delta n, \delta T$ initially zero. Equations (2.8.65) and (2.8.66a–b,d–e) preserve these zero values. The evolution of δu_y is therefore governed independently by the transverse momentum equation (2.8.66c).

For $\delta u_y(x,t) = \mathrm{Re}\left[U_{y,k}(t) e^{ikx}\right]$, equation (2.8.66c) gives

$$\frac{dU_{y,k}}{dt} = -\nu k^2 U_{y,k}, \qquad U_{y,k}(0) = U_0, \qquad \nu = \frac{\eta}{m n_0}. \tag{2.8.68}$$

The coefficient ν is the **kinematic viscosity**, equal to the shear viscosity divided by the mass density. In the relaxation-time model, the expression $\eta = p_0 \tau_R$ from (2.8.59) gives

$$\nu = \frac{k_B T_0}{m} \tau_R, \qquad \tau_R = \tau_R(n_0, T_0).$$

Integration of (2.8.68) gives the velocity profile

$$\delta u_y(x,t) = U_0 \cos kx \, e^{-t/\tau_\nu}, \qquad \tau_\nu = \frac{1}{\nu k^2}. \tag{2.8.69}$$

The decay results from viscous transport of momentum. For the velocity profile (2.8.69), the pressure law (2.8.54) gives the flux of y-momentum in the x-direction:

$$P_{yx}^{\mathrm{kin}} = -\eta \frac{\partial \delta u_y}{\partial x} = \eta k U_0 \sin kx \, e^{-t/\tau_\nu}. \tag{2.8.70}$$

The viscous flux transfers y-momentum from layers with larger δu_y towards layers with smaller δu_y, reducing the velocity differences. The negative divergence of this momentum flux determines the local rate of change of momentum density:

$$m n_0 \frac{\partial \delta u_y}{\partial t} = -\frac{\partial P_{yx}^{\mathrm{kin}}}{\partial x} = \eta \frac{\partial^2 \delta u_y}{\partial x^2} = -\eta k^2 \delta u_y. \tag{2.8.71}$$

Collisions conserve momentum locally; equation (2.8.71) describes redistribution of momentum between neighbouring layers.

Within the dilute-gas approximation, internal energy is represented by the kinetic energy of motion relative to the local mean velocity, $e_{\mathrm{int}} = 3 n k_B T/2$. Viscous relaxation transfers mean-flow kinetic energy into this thermal energy. The associated temperature increase is quadratic in U_0 and is omitted from the linearised temperature equation.

Sound propagation

For perturbations depending only on x, the wave vector is $\mathbf{k} = k\mathbf{e}_x$. The velocity component $\delta u_x(x,t)$, parallel to $\mathbf{k}$, is the **longitudinal velocity perturbation**. We now study its coupling to the number-density, temperature and pressure perturbations.

Differentiating the pressure relation (2.8.65) with respect to time and substituting the continuity and temperature equations (2.8.66a,e) gives

$$\frac{\partial \delta p}{\partial t} = -\frac{5}{3} p_0 \frac{\partial \delta u_x}{\partial x} + \frac{2}{3} \kappa \frac{\partial^2 \delta T}{\partial x^2}. \tag{2.8.72}$$

We first obtain the sound speed and the leading travelling-wave solution. The longitudinal viscous term in (2.8.66b) produces a relaxation rate $4\nu k^2/3$, while the conduction term in (2.8.66e) produces a relaxation rate $2\kappa k^2/(3 n_0 k_B)$. Both rates are proportional to k^2. The sound frequency is $c_s k$, where c_s is determined below in (2.8.74). For sufficiently small k, both dissipative rates are therefore small compared with the sound frequency.

Neglecting dissipation in this limit gives the leading propagation equations:

$$m n_0 \frac{\partial \delta u_x}{\partial t} = -\frac{\partial \delta p}{\partial x}, \tag{2.8.73a}$$

$$\frac{\partial \delta p}{\partial t} = -\frac{5}{3} p_0 \frac{\partial \delta u_x}{\partial x}. \tag{2.8.73b}$$

Taking the time derivative of (2.8.73b) and substituting (2.8.73a) eliminates δu_x:

$$\frac{\partial^2 \delta p}{\partial t^2} = c_s^2 \frac{\partial^2 \delta p}{\partial x^2}, \qquad c_s^2 = \frac{5p_0}{3mn_0} = \frac{5k_B T_0}{3m}. \tag{2.8.74}$$

The coefficient c_s is the sound speed. A travelling harmonic has the form

$$\delta p(x,t) = P_0 \cos(kx \mp c_s k t), \tag{2.8.75}$$

where P_0 is the pressure amplitude. The upper sign describes propagation in the positive x direction; the lower sign describes propagation in the negative x direction.

For either travelling sound harmonic, substitution into (2.8.66a), (2.8.66e) with the conduction term omitted, and (2.8.73a) gives

$$\frac{\delta n}{n_0} = \frac{3}{5}\frac{\delta p}{p_0}, \tag{2.8.76a}$$

$$\frac{\delta T}{T_0} = \frac{2}{5}\frac{\delta p}{p_0} = \frac{2}{3}\frac{\delta n}{n_0}, \tag{2.8.76b}$$

$$\delta u_x = \pm \frac{\delta p}{m n_0 c_s}. \tag{2.8.76c}$$

The signs in (2.8.76c) correspond to the propagation directions specified after (2.8.75). Compression increases both number density and temperature, giving

$$\frac{\delta p}{p_0} = \frac{5}{3}\frac{\delta n}{n_0}. \tag{2.8.77}$$

The factor $5/3$ is the ratio of specific heats for the monatomic ideal gas.

The approximation used in (2.8.73a–b) requires

$$\frac{4\nu k}{3c_s} \ll 1, \qquad \frac{2\kappa k}{3n_0 k_B c_s} \ll 1. \tag{2.8.78}$$

These inequalities compare the dissipative rates directly with $c_s k$. Under (2.8.78), viscosity and heat conduction change the sound amplitude only slightly during one oscillation. Retaining the dissipative terms gives sound attenuation.

Thermal relaxation

We seek the relaxation rate of a temperature harmonic and the accompanying number-density, longitudinal-velocity and pressure perturbations. The governing equations are (2.8.66a,b,e), together with the pressure relation (2.8.65).

For a harmonic of wave number $k > 0$, an exponentially decaying solution is written as

$$\delta T(x,t) = \Theta \cos(kx) e^{-\Gamma_T t}, \tag{2.8.79a}$$

$$\delta n(x,t) = N \cos(kx) e^{-\Gamma_T t}, \tag{2.8.79b}$$

$$\delta u_x(x,t) = U \sin(kx) e^{-\Gamma_T t}, \tag{2.8.79c}$$

$$\delta p(x,t) = P \cos(kx) e^{-\Gamma_T t}. \tag{2.8.79d}$$

Here $\Gamma_T > 0$ is the thermal decay rate. Substitution into the continuity equation (2.8.66a), the longitudinal momentum equation (2.8.66b), the temperature equation (2.8.66e), and the pressure relation (2.8.65) gives

$$\Gamma_T N = n_0 k U, \tag{2.8.80a}$$

$$m n_0 \left(\frac{4}{3}\nu k^2 - \Gamma_T\right) U = kP, \tag{2.8.80b}$$

$$\frac{3}{2} n_0 k_B \Gamma_T \Theta = p_0 k U + \kappa k^2 \Theta, \tag{2.8.80c}$$

$$P = k_B T_0 N + n_0 k_B \Theta. \tag{2.8.80d}$$

Eliminating U between (2.8.80a) and (2.8.80b) gives

$$\frac{P}{p_0} = \frac{m\Gamma_T\left(\frac{4}{3}\nu k^2 - \Gamma_T\right)}{k_B T_0 k^2}\,\frac{N}{n_0}. \tag{2.8.81}$$

For a decay rate proportional to k^2, the coefficient multiplying N/n_0 tends to zero as k^2. We therefore seek a thermal solution with $\Gamma_T = O(k^2)$; its decay rate will be determined below.

Equation (2.8.81) implies that the pressure perturbation is small compared with the separate pressure changes produced by N and Θ. Consequently, the pressure relation (2.8.80d) gives, to leading order,

$$\frac{\delta n}{n_0} \simeq -\frac{\delta T}{T_0}. \tag{2.8.82}$$

To obtain a closed equation for δT, we use (2.8.82) to eliminate δn from the continuity equation. Differentiating (2.8.82) **with respect to time** and substituting (2.8.66a) gives

$$\frac{\partial \delta n}{\partial t} = -n_0 \frac{\partial \delta u_x}{\partial x} \simeq -\frac{n_0}{T_0}\frac{\partial \delta T}{\partial t}.$$

Consequently,

$$\frac{\partial \delta u_x}{\partial x} \simeq \frac{1}{T_0}\frac{\partial \delta T}{\partial t}. \tag{2.8.83}$$

The longitudinal velocity gradient in the pressure-work term of the temperature equation (2.8.66e) can therefore be expressed through $\partial_t \delta T$:

$$-p_0 \frac{\partial \delta u_x}{\partial x} \simeq -n_0 k_B \frac{\partial \delta T}{\partial t}.$$

Substitution into (2.8.66e) gives

$$\frac{3}{2} n_0 k_B \frac{\partial \delta T}{\partial t} \simeq -n_0 k_B \frac{\partial \delta T}{\partial t} + \kappa \frac{\partial^2 \delta T}{\partial x^2},$$

or

$$\frac{5}{2} n_0 k_B \frac{\partial \delta T}{\partial t} \simeq \kappa \frac{\partial^2 \delta T}{\partial x^2}.$$

The leading temperature evolution is therefore diffusive:

$$\frac{\partial \delta T}{\partial t} \simeq D_T \frac{\partial^2 \delta T}{\partial x^2}, \qquad D_T = \frac{2\kappa}{5 n_0 k_B}. \tag{2.8.84}$$

The thermal diffusivity D_T includes the effect of pressure work during the expansion and compression required by (2.8.83).

The decay rate with both viscosity and heat conduction retained follows by eliminating N, U, P from the full amplitude equations (2.8.80a–d):

$$c_s^2 k^2 (\Gamma_T - D_T k^2) + \Gamma_T \left(\Gamma_T - \frac{4}{3}\nu k^2\right)\left(\Gamma_T - \frac{5}{3} D_T k^2\right) = 0. \tag{2.8.85}$$

For the thermal root, substitution of $\Gamma_T = O(k^2)$ into (2.8.85) gives

$$\Gamma_T = D_T k^2 + O(k^4), \qquad \tau_T = \frac{1}{\Gamma_T} \simeq \frac{1}{D_T k^2}. \tag{2.8.86}$$

The assumed k^2 dependence is therefore consistent. Within the linearised Navier–Stokes–Fourier equations, viscosity contributes to the thermal decay rate beyond the leading k^2 term.

The leading temperature, number-density and velocity profiles are

$$\delta T(x,t) \simeq \Theta \cos(kx) e^{-D_T k^2 t}, \tag{2.8.87a}$$

$$\delta n(x,t) \simeq -\frac{n_0 \Theta}{T_0} \cos(kx) e^{-D_T k^2 t}, \tag{2.8.87b}$$

$$\delta u_x(x,t) \simeq -\frac{D_T k \Theta}{T_0} \sin(kx) e^{-D_T k^2 t}. \tag{2.8.87c}$$

Heat conduction reduces the temperature variation. The longitudinal flow changes the number-density variation so that the pressure remains approximately uniform. A thermal harmonic requires the accompanying number-density and velocity profiles in (2.8.87b,c), including their values at $t = 0$.

The leading expressions (2.8.87a–c) apply when $D_T k/c_s \ll 1$ and $\nu k/c_s \ll 1$. In particular,

$$\frac{(c_s k)^{-1}}{(D_T k^2)^{-1}} = \frac{D_T k}{c_s} \ll 1,$$

so thermal relaxation is slow compared with sound propagation over the distance $1/k$. The small pressure perturbation is determined by (2.8.81), and the decay rate at finite k by (2.8.85).

The shear, sound and thermal solutions describe distinct contributions to a weak hydrodynamic perturbation. Comparing their time scales shows how propagation and relaxation depend on wavelength.

Characteristic times

For the same wave number k, the characteristic times are

$$\tau_s = \frac{1}{c_s k}, \qquad \tau_\nu = \frac{1}{\nu k^2}, \qquad \tau_T \simeq \frac{1}{D_T k^2}. \tag{2.8.88}$$

Here τ_s is the sound propagation time over the distance $1/k$ (the characteristic gradient length of the harmonic, whose wavelength is $2\pi/k$); the sound oscillation period is $2\pi\tau_s$. The shear relaxation time τ_ν is the characteristic time for viscosity to redistribute transverse momentum over the distance $1/k$. Similarly, the thermal relaxation time τ_T is the characteristic time for heat conduction to reduce temperature differences over the distance $1/k$. Consequently,

$$\frac{\tau_s}{\tau_\nu} = \frac{\nu k}{c_s}, \qquad \frac{\tau_s}{\tau_T} \simeq \frac{D_T k}{c_s}. \tag{2.8.89}$$

Both ratios tend to zero as $k \to 0$. At sufficiently long wavelengths, sound therefore undergoes many oscillations during one shear or thermal relaxation time.

The hydrodynamic description also requires the local molecular relaxation time τ_{loc} to be short compared with the evolution times of the hydrodynamic fields. Together with the long-wavelength conditions in (2.8.89), this gives

$$\tau_{\mathrm{loc}} \ll \tau_s \ll \tau_\nu, \tau_T. \tag{2.8.90}$$

This hierarchy compares distinct processes; it does not specify successive stages through which every perturbation passes. A pure shear disturbance relaxes without generating sound. In a general weak perturbation, the sound, shear and thermal contributions evolve simultaneously, with the different time scales in (2.8.88).

Relaxation times and the scope of the hydrodynamic description

The preceding application makes the distinction between local relaxation and equilibration of the gas as a whole quantitative. Collisions establish a nearly Maxwellian momentum distribution on the time scale τ_{loc}, while spatial variations of number density, mean velocity and temperature persist. Pressure disturbances propagate on the time scale τ_s; shear and thermal disturbances decay on the time scales τ_ν and τ_T. Equation (2.8.90) shows that all these hydrodynamic times are much longer than τ_{loc} when $k\lambda_{\mathrm{mfp}} \ll 1$.

This separation explains the successive reductions developed in §§2.4–2.8. At the kinetic stage, Bogoliubov's hypothesis states that, after an initial relaxation of correlations, the higher distribution functions $f_s(t)$, $s \geq 2$, are determined by the current one-particle distribution $f_1(t)$. The higher distributions still contain correlations generated by interactions. The assumption is that, to the accuracy of the kinetic approximation, $f_s(t)$ no longer depends separately on the initial higher distributions $f_2(t_0), f_3(t_0), \ldots$. Consequently, the subsequent kinetic evolution requires an equation for f_1, without separate evolution equations for every f_s. The kinetic equation still determines the full momentum dependence of f_1.

A further reduction becomes possible after local collisional relaxation. The local Maxwell distribution is specified by the five fields $n, \mathbf{u}, T$. Spatial transport continually produces a small correction to this distribution, whose first-order contribution determines the viscous stress and heat flux. Under the conditions of the hydrodynamic approximation, the Chapman–Enskog expansion (2.8.34) therefore expresses f_1 through $n, \mathbf{u}, T$ and their spatial gradients to the retained accuracy. The continuity, momentum and temperature equations (2.8.60a–c) determine the subsequent evolution of $n, \mathbf{u}, T$.

Whether the hydrodynamic evolution approaches equilibrium or maintains transport depends on the boundary conditions and external constraints. Moving walls or walls maintained at different temperatures can sustain velocity gradients or heat flow. Equilibrium at rest has no mean flow, $\mathbf{u} = 0$, uniform temperature and zero heat flux, while its number density may remain nonuniform in an external potential, as in (2.8.29). Local equilibrium alone imposes neither uniform temperature across the gas nor the absence of mean flow. Figure 2.8.1 summarises the successive descriptions and the possible long-time outcomes.

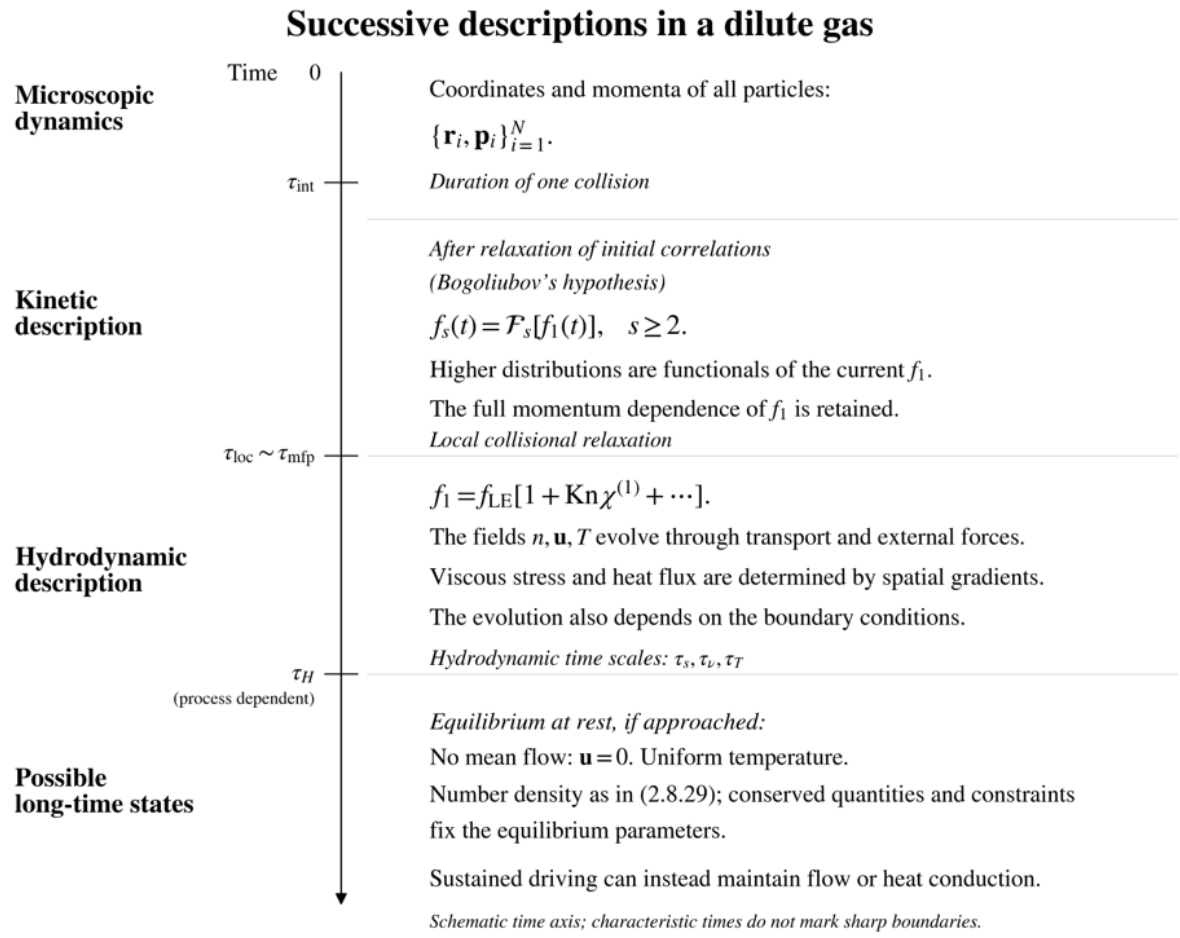


Figure 2.8.1. Successive descriptions and characteristic relaxation times. The dilute-gas estimates of §2.4 give a collision duration $\tau_{int} \simeq 7 \times 10^{-13}\ s$ and a local relaxation time $\tau_{loc} \sim \tau_{mfp} \simeq 1.4 \times 10^{-10}\ s$. As an illustration of the much longer hydrodynamic relaxation, a shear disturbance of wavelength $2\ mm$, with $\nu = 1.4 \times 10^{-5}\ m^2\ s^{-1}$, has $\tau_\nu \simeq 7.2 \times 10^{-3}\ s$. The time axis is schematic; characteristic times do not mark sharp boundaries. The hydrodynamic time depends on the process, and equilibrium is a possible long-time outcome rather than an automatic consequence of local relaxation.

Conditions and limitations of the approximations

The dilute-gas approximation and the hydrodynamic approximation involve different comparisons of lengths:

$$\varepsilon = nd^3 \ll 1, \qquad \mathrm{Kn} = \frac{\lambda_{\mathrm{mfp}}}{L} \ll 1. \tag{2.8.91}$$

Here d is the interaction range and L is the characteristic length over which the hydrodynamic fields vary. The first condition concerns the number of particles within a volume comparable to the interaction volume. Under the assumptions of §2.4, diluteness justifies describing collisions by isolated two-particle dynamics. The second condition requires the hydrodynamic fields to vary little over a mean free path. Together with the slow temporal evolution specified in (2.8.1), small Kn justifies expressing f_1 as a local Maxwell distribution plus small gradient corrections.

The consequences of violating (2.8.91) depend on which condition fails. Spatial variations on the scale of the mean free path require the momentum dependence of f_1 to be followed with a kinetic equation. For a sufficiently dilute gas satisfying the assumptions of §2.4, the Boltzmann equation remains applicable in this regime. Increasing density instead requires reconsideration of the isolated binary collision approximation.

Retaining higher powers of Kn in a solution of the Boltzmann equation gives further gradient corrections while retaining the same binary collision integral. Improving the collision integral requires a different calculation: contributions involving three or more particles to the pair distribution must also be retained.

For example, if particle 3 exerts forces on particles 1 or 2 during their collision, the momenta of particles 1 and 2 evolve under forces involving all three particles. The corresponding contribution to the equation for f_2 involves f_3.

Correlations involving three particles also arise through successive binary collisions. Particle 1 first collides with particle 2, and particle 2 subsequently collides with particle 3. Particles 1 and 3 can then become correlated through their interactions with particle 2, even without a direct collision between particles 1 and 3. A subsequent collision between particles 1 and 3 therefore need not begin with a factorised pair distribution, although the preceding collisions occurred separately in time.

Four-particle correlations arise in the same way. Collisions within the pairs 1,2 and 3,4, followed by a collision between particles 2 and 3, can correlate the states of all four particles. Their joint statistics are described by f_4. No additional three-particle or four-particle forces are required: the pair forces already present in the Hamiltonian generate the correlations. Contributions from higher distributions to f_2, and hence to the collision integral, are calculated by retaining the corresponding higher BBGKY equations and comparing powers of ε, as outlined in §2.4.

A higher gradient correction improves physical accuracy only when the effects omitted from the collision integral are smaller than the correction being calculated. Increasing the number of terms in the expansion in Kn alone does not establish this accuracy.

The relaxation-time model introduces a separate approximation. For example, the single relaxation time used in (2.8.57) gives $\nu = D_T$, as follows from (2.8.59), (2.8.68) and (2.8.84). Further gradient corrections within that model preserve its assumed collision term. Determining the transport coefficients from the actual collision law instead requires solving the integral equations (2.8.51a–b) and evaluating the expressions for η and κ in (2.8.54) and (2.8.56).

Irreversibility and the H-theorem

Irreversibility already appears at the kinetic stage, before the hydrodynamic approximation is introduced. Under the assumptions of §2.5, the ordinary Boltzmann equation gives

$$\mathrm{L}_1 f_1 = C[f_1], \qquad \frac{dH}{dt} \leq 0. \tag{2.8.92}$$

Here L_1 is the streaming operator in (2.8.37), and H is the functional of the one-particle distribution defined in (2.5.1). Periodic boundaries or stationary walls with elastic, mirror-like reflection produce no net streaming contribution to dH/dt. The nonpositive collision contribution, derived in (2.5.7–9), establishes the Boltzmann H-theorem.

The molecular collision laws are reversible. Why, then, does the closed kinetic equation select decreasing H? The distinction enters through the condition used to calculate the pair distribution.

In §2.4, weakening of correlations was applied to widely separated particle states **before their collision**. Their joint distribution was factorised there, and the interacting pair dynamics determined the correlations generated during and after the collision. **The asymptotic boundary**

condition thus treats the past and future differently: factorisation is imposed on incoming states, while outgoing correlations are calculated from the collision dynamics.

The factorisation assumption discards specific information. Knowledge of f_1 specifies the single-particle statistics; knowledge of f_2 additionally specifies the statistical dependence between two particle states. Replacing the incoming joint distribution by a product of one-particle distributions neglects incoming correlations, including correlations produced by earlier collision sequences.

Starting from the factorised incoming distribution, the interacting pair dynamics determines the distribution during and after the collision. The outgoing momenta become correlated because both momenta depend on the same collision. Thus, incoming factorisation assumes statistically independent incoming states; it does not impose factorisation on the outgoing states.

Reversible pair dynamics also permits the incoming distribution to be calculated from a specified outgoing distribution. Imposing factorisation on widely separated states **after the collision** therefore selects the time-reversed construction. Evolution backwards through the collision determines the incoming correlations required to produce the factorised outgoing distribution.

Incoming and outgoing factorisation consequently neglect different information: incoming factorisation neglects correlations before the collision, while outgoing factorisation neglects correlations after it. Within the same binary collision approximation, outgoing factorisation gives the **anti-Boltzmann equation**

$$\mathrm{L}_1 f_1 = -C[f_1], \qquad \frac{dH}{dt} \geq 0. \tag{2.8.93}$$

The collision functional C has the same definition in (2.8.92) and (2.8.93). Its opposite sign reverses the collision contribution to dH/dt.

The irreversible kinetic equation follows from combining the kinetic temporal resolution with incoming factorisation. Choosing a temporal resolution and integrating over the positions and momenta of the other particles do not, by themselves, imply factorisation of the incoming pair distribution. Incoming factorisation is the additional assumption used to close the kinetic equation and obtain the H-theorem. The hydrodynamic approximation subsequently determines the slower evolution of $n, \mathbf{u}, T$ from a kinetic equation that already selects a direction of relaxation.

Momentum reversal and the role of correlations

An exact momentum-reversal experiment clarifies why incoming factorisation is an additional assumption. Suppose that N particles evolve under Hamilton equations with time-independent interactions depending only on their positions. At time t_R, every momentum is replaced by its negative, while every position is left unchanged:

$$\mathbf{p}_i \mapsto -\mathbf{p}_i, \qquad i = 1, \ldots, N.$$

The subsequent Hamiltonian motion retraces the preceding trajectories, with all momenta reversed.

For an ensemble, momentum inversion is applied to every microscopic state represented by its distribution. To distinguish exact Hamiltonian evolution from the Boltzmann approximation, the exact one-particle marginal of ρ_N is denoted by f_1^{ex}. At elapsed time s after reversal,

$$f_{1,\mathrm{rev}}^{\mathrm{ex}}(\mathbf{r}, \mathbf{p}, s) = f_1^{\mathrm{ex}}(\mathbf{r}, -\mathbf{p}, t_R - s).$$

This equality expresses retracing of the sequence of one-particle distributions, with momenta inverted. It does not assert that the one-particle distribution is constant along a molecular trajectory. Liouville's constancy statement concerns the full N-particle density along a trajectory in $6N$-dimensional phase space. The evolution of its one-particle marginal instead involves the pair distribution through the first BBGKY equation.

Since momentum inversion leaves the integral defining H unchanged,

$$H^{\mathrm{ex}}_{\mathrm{rev}}(s) = H^{\mathrm{ex}}(t_R - s).$$

If H^{ex} decreases over an interval of the original evolution, it increases over the corresponding interval after exact reversal. Hamiltonian mechanics alone does not require H^{ex} to decrease in the original evolution; the statement is conditional.

There is no conflict with conservation of the Gibbs functional

$$\int d\Gamma\, \rho_N \ln \rho_N.$$

The Gibbs functional uses the full N-particle distribution and remains constant under Hamiltonian evolution. By contrast, H^{ex} uses only the one-particle marginal and contains no information about pair and higher correlations.

A pair separating after a collision before momentum inversion becomes an approaching pair after inversion. When the two particles meet again, their motion retraces the same collision in reverse. The correlations between the outgoing particle states before inversion become correlations between the incoming particle states after inversion: reversing the momenta does not remove their statistical dependence. The exactly reversed pair distribution therefore need not satisfy the incoming factorisation used to derive the ordinary Boltzmann equation. Replacing this correlated incoming distribution by a product of one-particle distributions would discard correlations required to retrace the original collision and would change the exactly reversed ensemble.

The exact reversal argument thus identifies the limitation of the ordinary Boltzmann description: reversible mechanics permits correlated incoming states that its factorisation assumption excludes. This does not make the ordinary Boltzmann equation time-reversal invariant; its formal time reverse is the anti-Boltzmann equation (2.8.93).

Finally, the Boltzmann H-theorem alone does not establish convergence to equilibrium. In the homogeneous setting of §2.5, the conserved particle number, momentum and energy provide a finite lower bound for H. Monotonic decrease then implies a limiting value of H, but does not alone prove convergence of f_1 to the equilibrium Maxwell distribution or determine a relaxation time. The shear and thermal relaxation times obtained above follow from the hydrodynamic equations for the specified disturbances.

Conclusion to Section 2

The BBGKY hierarchy couples the evolution of the one-particle distribution to pair statistics, whose evolution depends on higher distributions. Bogoliubov's kinetic hypothesis permits a reduction: after an initial relaxation of correlations, the higher distributions are approximated as functionals of the current one-particle distribution. Collision-generated correlations remain included, but separate dependence on the initial higher distributions is neglected. For a dilute gas, isolated binary collision dynamics, together with factorisation of the incoming pair distribution, leads to the Boltzmann equation. For a weakly coupled plasma, retaining the self-consistent electric field while neglecting the correlation contribution gives the Vlasov equation, which describes screening and collisionless collective evolution.

A further reduction becomes possible when local collisional relaxation is fast compared with changes in number density, mean velocity and temperature, and these fields vary little over a mean free path. The momentum distribution is then approximately Maxwellian at each position. Local equilibrium still permits spatial variations and flow, so the gas can continue to evolve on much longer time scales. Momentum integration of the Boltzmann equation, weighted by particle number, momentum and energy, gives the corresponding local conservation equations. The densities and fluxes entering these equations are moments of the one-particle distribution. Evaluating the pressure tensor and heat flux with the local Maxwell distribution gives Euler's

closures. The first-order Chapman–Enskog correction gives viscous stress and Fourier's law, closing the Navier–Stokes–Fourier equations. The transport coefficients connect molecular collision dynamics with the propagation and decay of macroscopic disturbances.

Conservation of particle number, momentum and energy does not determine the direction of relaxation: both the Boltzmann and anti-Boltzmann equations respect these conservation laws, yet predict opposite directions of entropy change. The direction is selected by imposing factorisation on incoming rather than outgoing particle states. Incoming factorisation treats the past and future differently; temporal coarse resolution alone does not impose this assumption. Under the conditions of §2.5, the Boltzmann H-theorem establishes nondecreasing kinetic entropy; zero collisional entropy production corresponds to the local Maxwell form. Monotonicity alone does not prove convergence to global equilibrium.

In the quantum description, the Pauli master equation governs the populations of many-particle states at the kinetic time resolution established in §2.7. With symmetric transition rates, every nonstationary contribution decays. If sequences of transitions with nonzero rates connect all states within the prescribed energy interval, the unique normalised stationary distribution is microcanonical. If the transitions leave disconnected groups of states, the total probability within each group remains fixed by the initial ensemble.