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Kinetic Theory and Transport Phenomena

Overview of Chapters 1–4

2019-11-04

Chapter 1

Basic concepts

Notations and definitions

- Velocity distribution function $f(\mathbf{r}, \mathbf{c}, t)$

$$\iint f(\mathbf{r}, \mathbf{c}, t)\, \mathrm{d}^3 r\, \mathrm{d}^3 c = N$$

Total number of molecules

- In thermal equilibrium: $f = f(\mathbf{c}) = n\, \hat{f}_{\mathrm{MB}}(\mathbf{c})$, here

$$\hat{f}_{\mathrm{MB}}(\mathbf{c}) = \left(\frac{m}{2\pi k_{\mathrm{B}} T}\right)^{3/2} \exp\left(-\frac{mc^2}{2k_{\mathrm{B}} T}\right)$$

Maxwell–Boltzmann distribution

- Particle density

$$n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{c}, t)\, \mathrm{d}^3 c$$

Notations and definitions

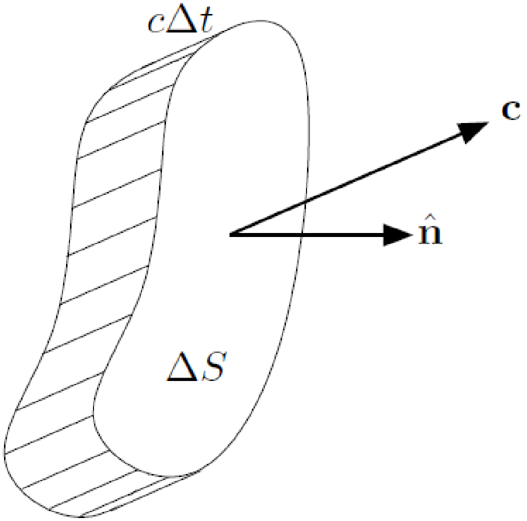
- Particular property $\varphi(\mathbf{c})$:
  - Mass: $\varphi = m$
  - Momentum: $\varphi = m\mathbf{c}$
  - Kinetic energy: $\varphi = \frac{1}{2}mc^2$
- Local average of φ:

$$\langle\varphi\rangle(\mathbf{r},t) = \frac{1}{n(\mathbf{r},t)}\int \varphi(\mathbf{c}) f(\mathbf{r},\mathbf{c},t)\,\mathrm{d}^3c$$

- Local velocity: $\mathbf{v}(\mathbf{r},t) = \frac{1}{n(\mathbf{r},t)}\int \mathbf{c}\, f(\mathbf{r},\mathbf{c},t)\,\mathrm{d}^3c$
- Local temperature:

$$\frac{3}{2}k_{\mathrm{B}}T(\mathbf{r},t) = \left\langle\frac{m(\mathbf{c}-\mathbf{v})^2}{2}\right\rangle$$

Flux



- When particles move, they transfer φ:
  - In time interval Δt surface ΔS is crossed by the molecules from the volume $\Delta\mathcal{V} = \mathbf{c} \cdot \widehat{\mathbf{n}}\, \Delta t \Delta S$
  - Amount of φ transferred:

$$\Delta\varphi = \Delta t \Delta S \int f(\mathbf{r}, \mathbf{c}, t)\varphi(\mathbf{c})\mathbf{c} \cdot \widehat{\mathbf{n}}\, \mathrm{d}^3 c$$

  - Flux:

$$\mathbf{J}_\varphi(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{c}, t)\varphi(\mathbf{c})\mathbf{c}\, \mathrm{d}^3 c$$

Flux

- Mass flux: $\mathbf{J}_m(\mathbf{r},t) = mn(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)$
- Kinetic energy (heat) flux:

$$\mathbf{J}_e(\mathbf{r},t) = \frac{m}{2}\int f(\mathbf{r},\mathbf{c},t)c^2\mathbf{c}\,\mathrm{d}^3c$$

- Momentum flux (tensor)

$$\tilde{P}_{ik}(\mathbf{r},t) = m\int f(\mathbf{r},\mathbf{c},t)c_i c_k\,\mathrm{d}^3c$$

  - $\tilde{P}_{ik} - i^{\text{th}}$ component of momentum that is crosses a unitary surface oriented in k direction per unit time

Stress tensor & energy flux

❖ If the gas has net velocity $\mathbf{v}$ *(convective contribution)*, it is usually subtracted to measure the flux in a frame comoving with the gas:

$$q_i = \frac{m}{2}\int f(\mathbf{r},\mathbf{c},t)(\mathbf{c}-\mathbf{v})^2(c_i - v_i)\ \mathrm{d}^3c$$

$$P_{ik}(\mathbf{r},t) = m\int f(\mathbf{r},\mathbf{c},t)(c_i - v_i)(c_k - v_k)\ \mathrm{d}^3c$$

$i,k = x,y,z$

❖ In thermal equilibrium (MB distribution):

- $q_i = 0$
- $P_{ik} = \delta_{ik} m\int f(\mathbf{r},\mathbf{c},t)(c_i - v_i)^2\ \mathrm{d}^3c = \boxed{nk_\mathrm{B}T}\delta_{ik}$

❖ Definition of pressure:

- $p = \frac{1}{3}P_{ii}\left(\equiv \frac{1}{3}\sum_{i=1}^{3} P_{ii}\right)$

$p = nk_\mathrm{B}T$, holds for the ideal gas even under non-equilibrium

Continuity equations

- Total mass that crosses (inwards) the surface of the commoving volume per unit time:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -\int\int_{(S)} f(\mathbf{r},\mathbf{c},t)m(\mathbf{c}-\mathbf{v})\cdot \mathrm{d}\mathbf{S}\,\mathrm{d}^3c = 0$$

- Total momentum that enters the commoving volume:

$$\boxed{\frac{\mathrm{d}p_i}{\mathrm{d}t}} = -\int\int_{(S)} f(\mathbf{r},\mathbf{c},t)mc_i(\mathbf{c}-\mathbf{v})\cdot \mathrm{d}\mathbf{S}\,\mathrm{d}^3c$$

We can add a zero term $mv_i \int f(\mathbf{r},\mathbf{c},t)(\mathbf{c}-\mathbf{v})\mathrm{d}^3c$

Force in i direction

$$= -\int\int_{(S)} f(\mathbf{r},\mathbf{c},t)m(c_i - v_i)(\mathbf{c}-\mathbf{v})\cdot \mathrm{d}\mathbf{S}\,\mathrm{d}^3c$$

$$= -\int_{(S)} \boxed{P_{ik}}\,\mathrm{d}S_k$$

Stress tensor

Continuity equations

❖ Total energy that enters the commoving volume:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\int\int_{(S)} f(\mathbf{r},\mathbf{c},t)\,\frac{mc^2}{2}(\mathbf{c}-\mathbf{v})\cdot\mathrm{d}\mathbf{S}\,\mathrm{d}^3c$$

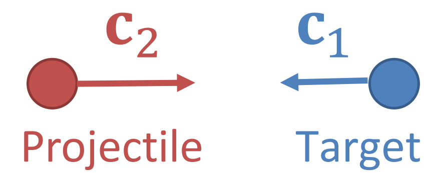
$$c^2 = (\mathbf{c}-\mathbf{v})^2 + 2(\mathbf{c}-\mathbf{v})\cdot\mathbf{v} + v^2$$

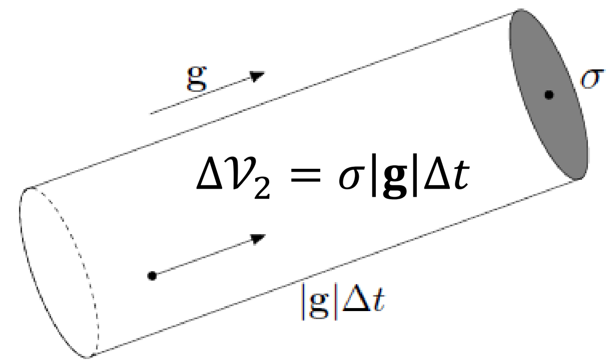
$$\boxed{q_i = \frac{m}{2}\int f(\mathbf{r},\mathbf{c},t)(\mathbf{c}-\mathbf{v})^2(c_i - v_i)\,\mathrm{d}^3c\,, \quad P_{ik}(\mathbf{r},t) = m\int f(\mathbf{r},\mathbf{c},t)(c_i-v_i)(c_k-v_k)\,\mathrm{d}^3c}$$

$$= \underbrace{-\int_{(S)}\mathbf{q}\cdot\mathrm{d}\mathbf{S}}_{\text{Heat flux}} \; \underbrace{-\int\int_{(S)} v_i P_{ik}\cdot\mathrm{d}S_k\,\mathrm{d}^3c}_{\text{Mechanical work per unit time done by external gas}}$$

We get 1st law of thermodynamics!

Collision frequency





- Relative velocity $\mathbf{g} = \mathbf{c}_2 - \mathbf{c}_1$
- Total collision cross-section σ
- Number of projectiles with velocities in the interval $\mathrm{d}^3 c_2$:

$$\Delta N_2 = f(\mathbf{c}_2)\Delta\mathcal{V}_2\,\mathrm{d}^3 c_2$$

- Number of targets: $\Delta N_1 = f(\mathbf{c}_1)\,\mathrm{d}^3 r\,\mathrm{d}^3 c_1$
- Number of collisions: $\Delta N_{\mathrm{coll}} = \Delta N_1 \Delta N_2$
- Collision frequency

$$\nu = \frac{1}{N}\frac{\Delta N_{\mathrm{coll}}}{\Delta t} = \frac{\sigma}{n}\iint f(\mathbf{c}_1) f(\mathbf{c}_2)\,|\mathbf{c}_2 - \mathbf{c}_1|\,\mathrm{d}^3 c_1 \mathrm{d}^3 c_2$$

Collision frequency

- Collision frequency

$$\nu = \frac{1}{N}\frac{\Delta N_{\mathrm{coll}}}{\Delta t} = \frac{\sigma}{n}\iint f(\mathbf{c}_1)f(\mathbf{c}_2)\,|\mathbf{c}_2 - \mathbf{c}_1|\,\mathrm{d}^3c_1\mathrm{d}^3c_2$$

- In thermal equilibrium:
  - New coordinates $\mathbf{C} = \frac{\mathbf{c}_1+\mathbf{c}_2}{2}$ and $\mathbf{g} = \mathbf{c}_2 - \mathbf{c}_1$ (Jacobian = 1)

$$\nu = n\sigma\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^3\int \exp\left(-\frac{mC^2}{k_{\mathrm{B}}T}\right)\mathrm{d}^3C\int \exp\left(-\frac{mg^2}{4k_{\mathrm{B}}T}\right)g\,\mathrm{d}^3g$$

$$= 4n\sigma\sqrt{\frac{k_{\mathrm{B}}T}{\pi m}}$$

$\sim 10^{-10}\ \mathrm{s}^{-1}$ for atmosphere molecules

- Mean free path $\ell = \frac{\langle|\mathbf{c}|\rangle}{\nu} = \frac{1}{\sqrt{2}n\sigma}$ $\sim 10^{-7}$ m for atmosphere molecules

Chapter 2

Distribution functions

Phase space

❖ Hamilton's equations: $\frac{\mathrm{d}q_i}{\mathrm{d}t} = \frac{\partial H}{\partial p_i}, \quad \frac{\mathrm{d}p_i}{\mathrm{d}t} = -\frac{\partial H}{\partial q_i}$

❖ Equation of motion for any function $f(q,p)$:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \underbrace{\{H,f\}}$$

Poisson bracket: $\{H,f\} = \sum_k \left(\frac{\partial H}{\partial p_k} \frac{\partial f}{\partial q_k} - \frac{\partial H}{\partial q_k} \frac{\partial f}{\partial p_k} \right)$

❖ State vector $\Gamma = (q_1, p_1, q_2, p_2, \ldots)$

➢ $\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \{H, \Gamma\}$ – flux vector (generalized velocity of the system in the phase space)

Phase space

- Let's introduce a Gibbs' ensemble of systems, described by a probability density function $F(\Gamma, t)$, given in a Γ-space: $\int F(\Gamma, t)\,\mathrm{d}\Gamma = 1$
- From the continuity equation we get:

$$\frac{\partial F}{\partial t} = -\nabla_\Gamma \cdot \left(F \frac{\mathrm{d}\Gamma}{\mathrm{d}t} \right)$$

$$\boxed{\frac{\partial F(\mathbf{r})}{\partial t} + \nabla(F \cdot \dot{\mathbf{r}}) = 0}$$

- After some manipulations:

$$\boxed{\frac{\partial F}{\partial t} = -\{H, F\}}$$ – Liouville equation

Reduced distributions

- Our initially defined distribution function $F(\Gamma, t)$
- Symmetrized distribution function

$$\hat{F}(\Gamma, t) = \frac{1}{N!}\sum_{P} F(P\Gamma, t)$$

Sum over all permutations

- Reduced *n*-particle distribution function

$$F^{(n)}(1, \dots, n, t) \equiv F^{(n)}(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_n, \mathbf{p}_n, t)$$
$$= \frac{N!}{(N-n)!}\int \hat{F}(\Gamma, t)\ \mathrm{d}^3 r_{n+1}\mathrm{d}^3 p_{n+1} \dots \mathrm{d}^3 r_N \mathrm{d}^3 p_N$$

  - Normalization: $\int F^{(n)}(1, \dots n, t)\ \mathrm{d}1\ \mathrm{d}2 \dots \mathrm{d}n = \frac{N!}{(N-n)!}$
  - Relation to 1-particle velocity distribution: $f(\mathbf{r}, \mathbf{c}, t) = m^3 F^{(1)}(\mathbf{r}, \mathbf{p}, t)$
  - $\int F^{(1)}(\mathbf{r}, \mathbf{p})\ \mathrm{d}^3 p = \frac{N}{\mathcal{V}} = n$
  - $\int F^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2)\ \mathrm{d}^3 p_1 \mathrm{d}^3 p_2 = \frac{N(N-1)}{\mathcal{V}^2} \xrightarrow{N \gg 1} = n^2$

Average observables

- The ensemble-average of some quantity $A(\Gamma)$ is

$$\langle A\rangle(t) = \int F(\Gamma, t) A(\Gamma)\, \mathrm{d}\Gamma$$

- We will define 3 major types of observables:
  - Global observables
  - Densities
  - Fluxes

Global observables

- Give single value characterizing some properties of the whole system, e.g. kinetic and potential energies
- Kinetic energy $K = \sum_a \frac{p_a^2}{2m}$
  - $$\langle K \rangle = \int F(\Gamma, t) \sum_a \frac{p_a^2}{2m} \,\mathrm{d}\Gamma \ = N \int \hat{F}(\Gamma, t) \frac{p_1^2}{2m} \,\mathrm{d}\Gamma$$
    $$= \int F^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) \frac{p_1^2}{2m} \,\mathrm{d}^3 r_1 \mathrm{d}^3 p_1$$
- Potential energy $U = \sum_{a<b} \phi(\mathbf{r}_a - \mathbf{r}_b)$
  - $$\langle U \rangle = \int F(\Gamma, t) \sum_{a<b} \phi(\mathbf{r}_a - \mathbf{r}_b) \,\mathrm{d}\Gamma$$
    $$= \int F^{(2)}(1,2, t) \phi(\mathbf{r}_1 - \mathbf{r}_2) \,\mathrm{d}1\mathrm{d}2$$

Densities

- For point particles, density of quantity φ (e.g. mass, momentum, energy) is

$$\rho_\varphi(\mathbf{r}) = \sum_a \varphi(\mathbf{r}_a, \mathbf{p}_a)\delta(\mathbf{r} - \mathbf{r}_a)$$

- The phase-space average then is

$$\langle\rho_\varphi\rangle(\mathbf{r}, t) = \int F^{(1)}(\mathbf{r}, \mathbf{p}_1, t)\varphi(\mathbf{r}, \mathbf{p}_1)\,\mathrm{d}^3 p_1$$

Fluxes

- If density field φ is associated with a conserved quantity, we expect that flux field exists and satisfies the conservation equation

$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi = 0$$

- Mass ($\varphi = m$)

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}\sum_a m\delta(\mathbf{r}-\mathbf{r}_a) = -\sum_a m\underbrace{\delta'(\mathbf{r}-\mathbf{r}_a)}_{\nabla\delta(\mathbf{r}-\mathbf{r}_a)} \cdot \frac{\mathrm{d}\mathbf{r}_a}{\mathrm{d}t} = -\nabla \cdot \sum_a \mathbf{p}_a \delta(\mathbf{r}-\mathbf{r}_a)$$

$$\boxed{\mathbf{J} = \sum_a \mathbf{p}_a \delta(\mathbf{r}-\mathbf{r}_a)}$$

Momentum density

  - Average:

$$\langle \mathbf{J} \rangle(\mathbf{r}, t) = \int F^{(1)}(\mathbf{r}, \mathbf{p}_1, t)\mathbf{p}_1 \mathrm{d}^3 p_1$$

Fluxes

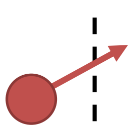
❖ Momentum

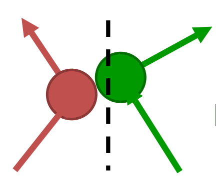
$$\frac{\partial J_i}{\partial t} = \frac{\partial}{\partial t}\sum_a p_{ai}\delta(\mathbf{r}-\mathbf{r}_a)$$

$$= \sum_a \underbrace{\dot{p}_{ai}}_{=f_{ai}=\sum_{b\neq a} f_i^{ab}\ \text{– force acting on } a^{\text{th}} \text{ particle}}\delta(\mathbf{r}-\mathbf{r}_a) - \sum_a p_{ai}\delta'(\mathbf{r}-\mathbf{r}_a)\dot{\mathbf{r}}_a \;= -\nabla_k P_{ik}$$

➢ Components of stress tensor:

$$P_{ik} = \underbrace{\sum_a m c_{ai} c_{ak}\delta(\mathbf{r}-\mathbf{r}_a)}_{\text{Kinetic transfer of momentum through the surface}} + \underbrace{\frac{1}{2}\sum_{\substack{a,b\\ a\neq b}} f_k^{ab}\int_{\mathbf{r}_a}^{\mathbf{r}_b}\delta(\mathbf{r}-\mathbf{s})\,\mathrm{d}s_i}_{\text{Collisional transfer of momentum through the surface}}$$





Fluxes

$$P_{ik} = \sum_{a} m c_{ai} c_{ak} \delta(\mathbf{r} - \mathbf{r}_a) + \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} f_k^{ab} \int_{\mathbf{r}_a}^{\mathbf{r}_b} \delta(\mathbf{r} - \mathbf{s}) \, \mathrm{d}s_i$$

- In homogeneous system, stress tensor can be averaged in space:

$$P_{ik} = \frac{1}{\mathcal{V}} \int P_{ij} \, \mathrm{d}^3 r = \frac{1}{\mathcal{V}} \left[\sum_{a} m c_{ai} c_{ak} + \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} f_k^{ab} r_i^{ab} \right]$$

- Pressure:

$$p = \frac{1}{3} P_{ii} = \frac{1}{3\mathcal{V}} \left[\sum_{a} m \mathbf{c}_a^2 + \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \mathbf{f}^{ab} \cdot \mathbf{r}^{ab} \right]$$

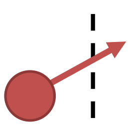
Fluxes

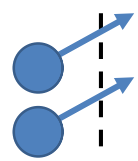
- Energy
  - Density:

$$\rho_e = \sum_a \frac{p_a^2}{2m}\delta(\mathbf{r}-\mathbf{r}_a) + \sum_{a<b}\phi(\mathbf{r}_a-\mathbf{r}_b)\frac{\delta(\mathbf{r}-\mathbf{r}_a)+\delta(\mathbf{r}-\mathbf{r}_b)}{2}$$

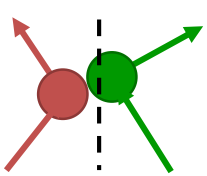
  - Flux:

$$\mathbf{J}_e = \underbrace{\sum_a \frac{p_a^2}{2m}\mathbf{v}_a\delta(\mathbf{r}-\mathbf{r}_a)}_{\text{Kinetic transfer of the kinetic energy}} + \underbrace{\sum_{a<b}\phi(\mathbf{r}_a-\mathbf{r}_b)\frac{\mathbf{v}_a\delta(\mathbf{r}-\mathbf{r}_a)+\mathbf{v}_b\delta(\mathbf{r}-\mathbf{r}_b)}{2}}_{\text{Kinetic transfer of the potential energy of 2 particles}}$$





$$+ \underbrace{\sum_{a<b}\frac{\mathbf{v}_a\cdot\mathbf{f}^{ab}-\mathbf{v}_b\mathbf{f}^{ba}}{2}\int_{\mathbf{r}_a}^{\mathbf{r}_b}\delta(\mathbf{r}-\mathbf{s})\,\mathrm{d}s_i}_{\text{Collisional transfer of the kinetic energy}}$$



BBGKY hierarchy

- *N*-particle distribution function F obeys Liouville equation

$$\frac{\partial F}{\partial t} = -\{H_N, F\},$$

here H_N is full Hamiltonian:

$$H_N = \sum_{a=1}^{N} \underbrace{\left(\frac{p_a^2}{2m} + V(\mathbf{r}_a)\right)}_{h_0(a)} + \sum_{a<b}^{N} \phi(\mathbf{r}_a - \mathbf{r}_b)$$

- What is the equation for the reduced distribution function $F^{(n)}$?

BBGKY hierarchy

❖ Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy

$$\frac{\partial F^{(n)}}{\partial t} = -\left\{H_n, F^{(n)}\right\} - \sum_{a=1}^{n} \int \left\{\phi(a, n+1), F^{(n+1)}\right\} \mathrm{d}(n+1)$$

- Reduced Hamiltonian $H_n = \sum_{a=1}^{n} h_0(a) + \sum_{a<b}^{n} \phi(\mathbf{r}_a - \mathbf{r}_b)$
- System of inter-dependent differential equations equation for $F^{(n)}$ depends on $F^{(n+1)}$

One-particle distribution

- $H_1 = \dfrac{p_1^2}{2m} + V(\mathbf{r}_1)$

$$\{H,f\} = \sum_k \left(\frac{\partial H}{\partial p_k}\frac{\partial f}{\partial q_k} - \frac{\partial H}{\partial q_k}\frac{\partial f}{\partial p_k} \right)$$

- $\left\{H_1, F^{(1)}\right\} = \dfrac{\mathbf{p}_1}{m} \cdot \dfrac{\partial F^{(1)}}{\partial \mathbf{r}_1} + \underbrace{\mathbf{F}_1}_{\mathbf{F}_1 = -\nabla V} \cdot \dfrac{\partial F^{(1)}}{\partial \mathbf{p}_1}$

- BBKGY$_1$ equation:

$$\frac{\partial F^{(1)}}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F^{(1)}}{\partial \mathbf{r}_1} + \mathbf{F}_1 \cdot \frac{\partial F^{(1)}}{\partial \mathbf{p}_1} = -\int \left\{\phi_{12}, F^{(2)}\right\}\, \mathrm{d}^3 r_2 \mathrm{d}^3 p_2$$

- In velocity representation, $f(\mathbf{r}, \mathbf{c}, t) = m^3 F^{(1)}(\mathbf{r}, \mathbf{p}, t)$

$$\boxed{\frac{\partial f}{\partial t} + \mathbf{c}_1 \cdot \frac{\partial f}{\partial \mathbf{r}_1} + \frac{\mathbf{F}_1}{m} \cdot \frac{\partial f}{\partial \mathbf{c}_1} = \int \frac{\partial \phi_{12}}{\partial \mathbf{r}_{12}} \left(\frac{\partial}{\partial \mathbf{c}_1} - \frac{\partial}{\partial \mathbf{c}_2} \right) f^{(2)}(1,2,t)\ \mathrm{d}^3 r_2 \mathrm{d}^3 c_2}$$

Thermal equilibrium

❖ In thermal equilibrium, the system is described by the Gibbs distribution function:

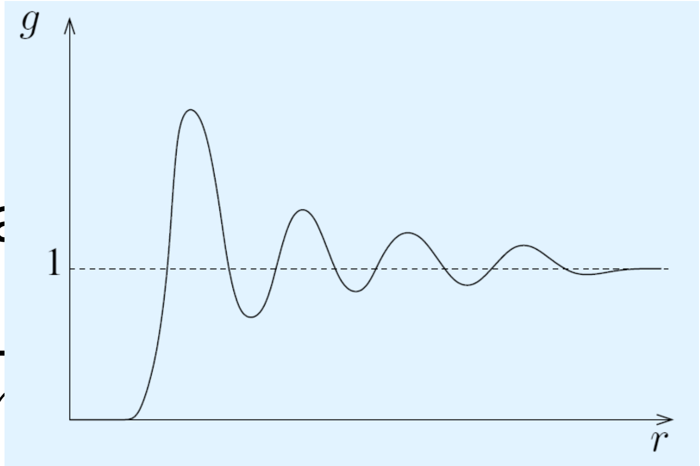
$$F_{\mathrm{eq}}(\Gamma) = \frac{1}{Z}\exp\left(-\frac{H(\Gamma)}{k_{\mathrm{B}}T}\right)$$

❖ Absence of external field → spatial homogeneity

$$H = \sum_{a=1}^{N}\frac{p_a^2}{2m} + \sum_{a<b}^{N}\phi(\mathbf{r}_a$$

❖ 1-particle distribution is Maxwelli

$$F_{\mathrm{eq}}^{(1)}(\mathbf{p}) = \frac{n}{(2\pi m k_{\mathrm{B}}T)^{3/2}}\exp\left(-\frac{}{2r}\right.$$



❖ $F_{\mathrm{eq}}^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2\ ) = F_{\mathrm{eq}}^{(1)}(\mathbf{p}_1)F_{\mathrm{eq}}^{(1)}(\mathbf{p}_2)g^{(2)}(\mathbf{r}_1-\mathbf{r}_2)$

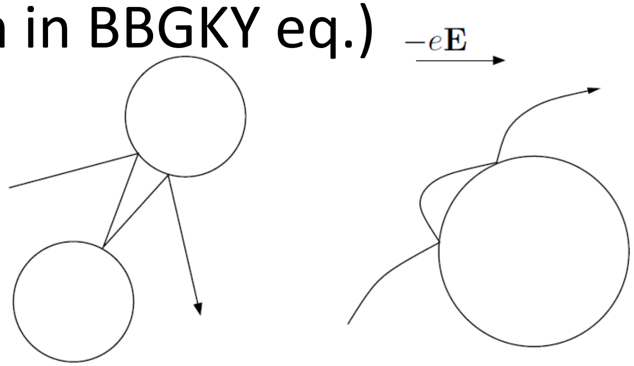
Pair distribution function

Chapter 3

The Lorentz model
for the classical transport of charges

Hypothesis

- Classical model (1905) → no quantum effects
- Free electrons move in a medium between the fixed heavy ions
- Distribution function (*F*) for ions is assumed to be constant
- Electron–electron interaction is neglected
  - Small mass → softer scattering
  - Long-range Coulomb force is compensated by many electrons
  - Small density (we can neglect n_e^2 term in BBGKY eq.)
- Include only 2-particle interactions
- Free flight between two collisions
- No correlations preserved



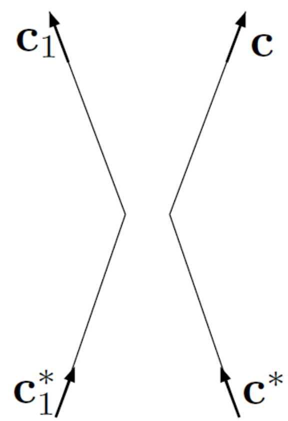
Lorentz kinetic equation

❖ BBGKY equation:

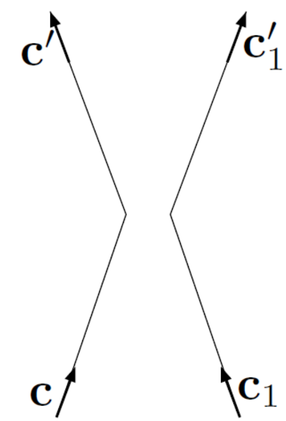
$$\frac{\partial f}{\partial t} + \mathbf{c}_1 \cdot \frac{\partial f}{\partial \mathbf{r}_1} + \frac{\mathbf{F}_1}{m} \cdot \frac{\partial f}{\partial \mathbf{c}_1} = \underbrace{\int \frac{\partial \phi_{12}}{\partial \mathbf{r}_{12}} \left(\frac{\partial}{\partial \mathbf{c}_1} - \frac{\partial}{\partial \mathbf{c}_2} \right) f^{(2)}(1,2,t) \ \mathrm{d}^3 r_2 \mathrm{d}^3 c_2}_{}$$

Collisional source for the change in f
= gain term – loss term

Notation:
$\{\mathbf{r}_1, \mathbf{c}_1\} \rightarrow \{\mathbf{r}, \mathbf{c}\}$ – electrons
$\{\mathbf{r}_2, \mathbf{c}_2\} \rightarrow \{\mathbf{r}_1, \mathbf{c}_1\}$ – ions
$f^{(2)}(1,2,t) \rightarrow f(\mathbf{c}) F(\mathbf{c}_1)$
$\mathbf{F}_1 \rightarrow q\mathbf{E}$

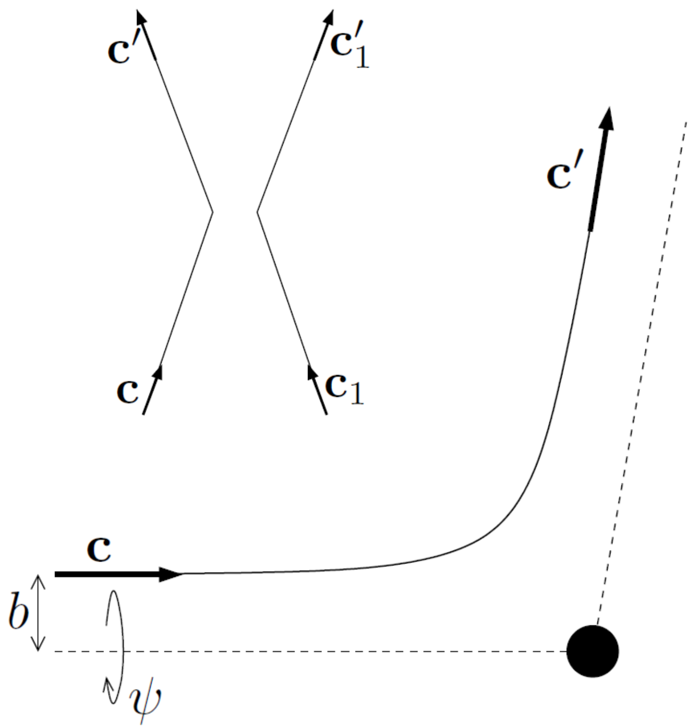


rate $\propto f(\mathbf{c}^*) F(\mathbf{c}_1^*)$

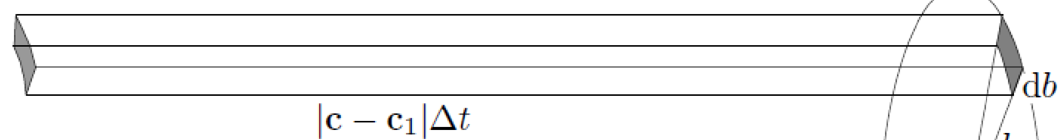


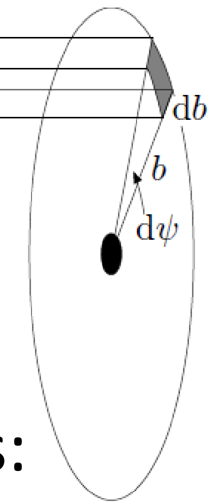
rate $\propto f(\mathbf{c}) F(\mathbf{c}_1)$

Loss term



Electron scattering





- Volume element:

$$\Delta\mathcal{V} = |\mathbf{c}-\mathbf{c}_1|\Delta t \cdot b\mathrm{d}b\mathrm{d}\psi$$

- Number of colliding electrons:

$$\mathrm{d}N_e = f(\mathbf{r},\mathbf{c},t)\,\Delta\mathcal{V}\,\mathrm{d}^3\mathbf{c}$$

- Number of targets (ions):

$$\mathrm{d}N_i = F(\mathbf{r},\mathbf{c}_1,t)\mathrm{d}^3\mathbf{c}_1\mathrm{d}^3\mathbf{r}$$

- Number of collisions per Δt:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{loss}} \mathrm{d}^3c\,\mathrm{d}^3r = -f(\mathbf{r},\mathbf{c},t)F(\mathbf{r},\mathbf{c}_1,t)|\mathbf{c}-\mathbf{c}_1|\cdot b\mathrm{d}b\mathrm{d}\psi\,\mathrm{d}^3\mathrm{c}\,\mathrm{d}^3\mathrm{c}_1\mathrm{d}^3r$$

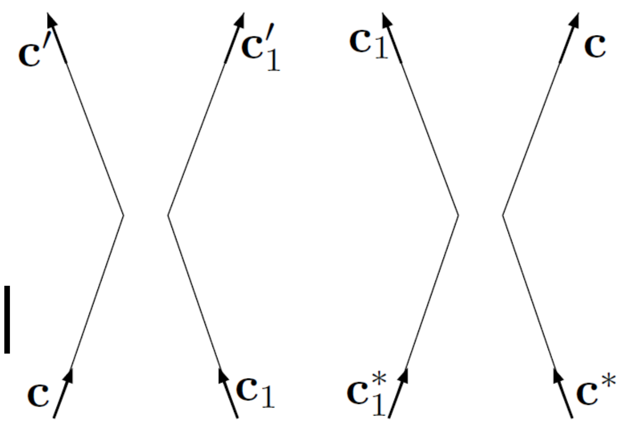
Gain term

$$\left(\frac{\partial f}{\partial t}\right)_{\text{loss}} \mathrm{d}^3 c = -f(\mathbf{r},\mathbf{c},t)F(\mathbf{r},\mathbf{c_1},t)|\mathbf{c}-\mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3 c\ \mathrm{d}^3 c_1$$

❖ Analogically for the gain term:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{gain}} \mathrm{d}^3 c = f(\mathbf{r},\mathbf{c}^*,t)F(\mathbf{r},\mathbf{c}_1^*,t)|\mathbf{c}^*-\mathbf{c}_1^*| \cdot b^*\mathrm{d}b^*\mathrm{d}\psi^*\ \mathrm{d}^3 c^*\ \mathrm{d}^3 c_1^*$$

❖ Energy and angular momentum conservation imply that



$$\mathbf{c}^* = \mathbf{c}',\ \mathbf{c}_1^* = \mathbf{c}_1',\ |\mathbf{c}-\mathbf{c}_1| = |\mathbf{c}'-\mathbf{c}_1'|$$

and

$$b^*\mathrm{d}b^*\mathrm{d}\psi^*\ \mathrm{d}^3\mathbf{c}^*\ \mathrm{d}^3\mathbf{c}_1^* = b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3 c\ \mathrm{d}^3 c_1$$

$$\left(\frac{\partial f}{\partial t}\right)_{\text{gain}} \mathrm{d}^3 c = f(\mathbf{r},\mathbf{c}',t)F(\mathbf{r},\mathbf{c}_1',t)|\mathbf{c}-\mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3 c\ \mathrm{d}^3 c_1$$

Lorentz equation

$$\boxed{\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \underbrace{\int [f' F_1' - f F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d} b \mathrm{d}\psi \, \mathrm{d}^3 c_1}}$$

Collisional operator

$J[f] = J_+[f] - J_-[f]$

here $f = f(\mathbf{r}, \mathbf{c}, t),\ F_1 = F(\mathbf{r}, \mathbf{c}_1, t),$

$f' = f(\mathbf{r}, \mathbf{c}', t),\ F_1' = F(\mathbf{r}, \mathbf{c}_1', t)$

- Ion distribution function – Maxwellian:

$$F(\mathbf{r}, \mathbf{c}_1, t) = F_{\mathrm{MB}}(\mathbf{c}_1) = n_i \left(\frac{M}{2\pi k_{\mathrm{B}} T} \right)^{3/2} \exp\left(-\frac{M c_1^2}{2 k_{\mathrm{B}} T} \right)$$

- Equilibrium solution: $f(\mathbf{r}, \mathbf{c}, t) = f_{\mathrm{MB}}(\mathbf{c})$
  - $\frac{1}{2} m c^2 + \frac{1}{2} M c_1^2 = \frac{1}{2} m c'^2 + \frac{1}{2} M c_1'^2$
  - $f_{\mathrm{MB}}(\mathbf{c}) F_{\mathrm{MB}}(\mathbf{c}_1) = f_{\mathrm{MB}}(\mathbf{c}') F_{\mathrm{MB}}(\mathbf{c}_1')$
  - $J[f_{\mathrm{MB}}] = 0$

Conservation laws

$$\int \mathrm{d}^3c \;\; \varphi(\mathbf{c}) \cdot \left| \; \frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int [f' F_1' - f F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d}b \mathrm{d}\psi \; \mathrm{d}^3 c_1 \right.$$

any function of $\mathbf{c}$

❖ Let's recall:

- Density of φ: $\rho_\varphi(\mathbf{r}, t) = \int \varphi(\mathbf{c}) f(\mathbf{r}, \mathbf{c}, t) \, \mathrm{d}^3 c$
- Flux of φ: $\mathbf{J}_\varphi(\mathbf{r}, t) = \int \varphi(\mathbf{c}) f(\mathbf{r}, \mathbf{c}, t) \mathbf{c} \, \mathrm{d}^3 c$
- Density of $\mathbf{g} = \frac{\partial \varphi}{\partial \mathbf{c}}$: $\rho_{\mathbf{g}}(\mathbf{r}, t) = \int \frac{\partial \varphi}{\partial \mathbf{c}} f(\mathbf{r}, \mathbf{c}, t) \, \mathrm{d}^3 c$

$$\boxed{\frac{\partial \rho_\varphi}{\partial t} + \underbrace{\nabla \cdot \mathbf{J}_\varphi}_{\text{Flux of } \varphi} \underbrace{- \frac{q\mathbf{E}}{m} \cdot \rho_{\mathbf{g}}}_{\substack{\text{Source term} \\ \text{(like mechanical work)}}} = \underbrace{\int \varphi(\mathbf{c}) [f' F_1' - f F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d}b \mathrm{d}\psi \; \mathrm{d}^3 c \mathrm{d}^3 c_1}_{\text{Change in } \varphi \text{ due to collision}}}$$

Conservation laws

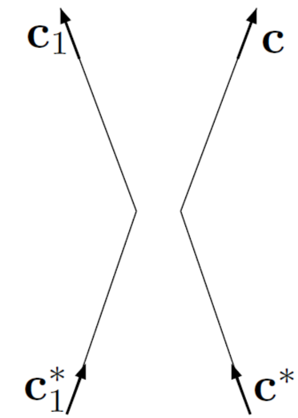
$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi - \frac{q\mathbf{E}}{m} \cdot \rho_\mathbf{g} = \int \varphi(\mathbf{c})[f'F_1' - fF_1]|\mathbf{c} - \mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1$$

❖ Gain term:

$$A = \int \varphi(\mathbf{c})f'F_1' \underbrace{|\mathbf{c} - \mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1}_{= |\mathbf{c}^* - \mathbf{c}_1^*| \cdot b^*\mathrm{d}b^*\mathrm{d}\psi^*\ \boxed{\mathrm{d}^3c^*\mathrm{d}^3c_1^*}}$$

Integration over pre-collisional parameters

Dummy integration variables



$\mathbf{c}^* \to \mathbf{c},\ \mathbf{c}_1^* \to \mathbf{c}_1$ (pre-collisional)

$\mathbf{c} \to \mathbf{c}',\ \mathbf{c}_1 \to \mathbf{c}_1'$ (post-collisional)

$$= \int \varphi(\mathbf{c}')fF_1|\mathbf{c} - \mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1$$

$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi + \frac{q\mathbf{E}}{m} \cdot \rho_\mathbf{g} = \int \underbrace{[\varphi(\mathbf{c}') - \varphi(\mathbf{c})]}_{= 0 \text{ for collisional invariants}} fF_1|\mathbf{c} - \mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1$$

Conservation laws

$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi + \frac{q\mathbf{E}}{m} \cdot \rho_{\mathbf{g}} = \int \underbrace{[\varphi(\mathbf{c}') - \varphi(\mathbf{c})]}_{=\,0 \text{ for collisional invariants}} f F_1 |\mathbf{c} - \mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi \, \mathrm{d}^3 c \mathrm{d}^3 c_1$$

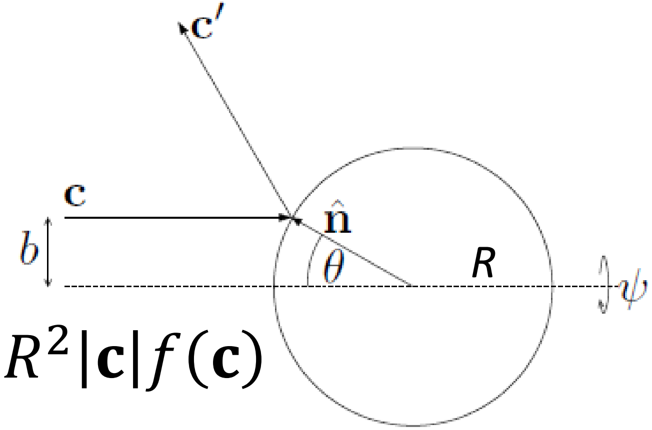
- $\varphi = 1$ or any constant (mass, charge, etc.): $\mathbf{g} = \frac{\partial \varphi}{\partial \mathbf{c}} = 0$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0$$

Conservation law

Kinetic collision models

- Rigid hard spheres
  - Ions: $M = \infty$, radius R, are static ($F(\mathbf{c}_1) = n_i\delta(\mathbf{c}_1)$)
  - $\mathbf{c}' = \mathbf{c} - 2(\mathbf{c}\cdot\hat{\mathbf{n}})\hat{\mathbf{n}}$
  - $b = R\sin\vartheta$
  - Loss term:



$$J_-[f] = \int f F_1 |\mathbf{c}-\mathbf{c}_1| \cdot b\mathrm{d}b\mathrm{d}\psi\, \mathrm{d}^3 c_1 = n_i R^2 |\mathbf{c}| f(\mathbf{c})$$

  - Gain term: $J_+[f] = n_i R^2 |\mathbf{c}| \boxed{\mathbb{P}f(\mathbf{c})}$

Directional average:

$$\mathbb{P}f(\mathbf{c}) = \frac{1}{4\pi}\int f(\mathbf{r},\mathbf{c},t)\,\mathrm{d}^2\hat{\mathbf{c}}$$

  - $J[f] = n_i R^2 |\mathbf{c}|\,(\mathbb{P}f - f)$

"Removes" particles at a rate $n_i R^2|\mathbf{c}|$ and replaces them with an isotropic distribution

Kinetic collision models

- Thermalising ions (BGK model, or relaxation time approximation)
  - Electrons exchange energy with ions
  - After each collision, electrons emerge with velocities described by Maxwell distributions
  - $M \gg m, \ |\mathbf{c} - \mathbf{c}_1| \approx |\mathbf{c}|$
  - Loss term: $J_-[f] = n_i R^2 |\mathbf{c}| f(\mathbf{c})$
  - Gain term: proportional to the Maxwellian flux $|\mathbf{c}|\hat{f}_{\mathrm{MB}}(\mathbf{c})$, should also ensure charge conservation
  - $$J[f] = n_i R^2 c \left[\hat{f}_{\mathrm{MB}}(\mathbf{c}) \frac{\int |\mathbf{c}'| f(\mathbf{c}') \, \mathrm{d}^3 c'}{\int |\mathbf{c}'| \hat{f}_{\mathrm{MB}}(\mathbf{c}') \, \mathrm{d}^3 c'} - f(\mathbf{c}) \right]$$

Methods to solve Lorentz equation

- Linear response
- Frequency response
- Linear operator and eigenvalues
- Chapman–Enskog method

Linear response

$$\boxed{\frac{\partial f}{\partial t} + \mathbf{c}\cdot\frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m}\cdot\frac{\partial f}{\partial \mathbf{c}} = \int [f' F_1' - f F_1] |\mathbf{c}-\mathbf{c}_1| \cdot b\,\mathrm{d}b\,\mathrm{d}\psi\ \mathrm{d}^3 c_1}$$

❖ Weak electric field: $\mathbf{E} = \epsilon \mathbf{E}_0,\ \epsilon \ll 1$

❖ We look for solution of the form:

$$f(\mathbf{c}) = f_{\mathrm{MB}}(\mathbf{c})[1+\epsilon\Phi(\mathbf{c})]$$

❖ $\Phi(\mathbf{c})$ is the response to the external electric field:

$$\Phi(\mathbf{c}) = \phi(c)\,\mathbf{c}\cdot\mathbf{E}_0$$

❖ Terms in LE proportional to ϵ:

$$\underbrace{\frac{q\mathbf{E}_0}{m}\cdot\frac{\partial f_{\mathrm{MB}}}{\partial \mathbf{c}}}_{= -\frac{q}{k_{\mathrm{B}}T} f_{\mathrm{MB}}\,\mathbf{c}\cdot\mathbf{E}_0} = \underbrace{\int f_{\mathrm{MB}}(\mathbf{c}) F_{\mathrm{MB}}(\mathbf{c}_1)[\Phi(\mathbf{c}') - \Phi(\mathbf{c})] |\mathbf{c}-\mathbf{c}_1| \cdot b\,\mathrm{d}b\,\mathrm{d}\psi\ \mathrm{d}^3 c_1}_{= -n_i n_e I[\Phi]}$$

Linear operator acting on correction to $f(\mathbf{c})$

$$\boxed{I[\Phi] = \frac{q}{n_i k_{\mathrm{B}} T}\hat{f}_{\mathrm{MB}}(c)\,\mathbf{c}\cdot\mathbf{E}_0}$$

Linear response

$$\boxed{I[\Phi] = \frac{q}{n_i k_\mathrm{B} T} \hat{f}_\mathrm{MB}(c)\, \mathbf{c} \cdot \mathbf{E}_0}$$

❖ Rigid hard sphere model:

$$I[\Phi] = \pi R^2 \hat{f}_\mathrm{MB} |\mathbf{c}| \, (\Phi - \mathbb{P}\Phi)$$

- here $\Phi(\mathbf{c}) = \phi(c)\, \mathbf{c} \cdot \mathbf{E}_0$ ➡ $\mathbb{P}\Phi = 0$ due to isotropy
- Solution:

$$\phi(c) = \frac{q}{\pi R^2 n_i k_\mathrm{B} T c}$$

❖ Electric current density:

$$\mathbf{J} = q \int \mathbf{c} f_\mathrm{MB} [1 + \epsilon \phi(c)\, \mathbf{c} \cdot \mathbf{E}_0]\, d^3 c = q \int f_\mathrm{MB}(c) \phi(c) \mathbf{c}\, \mathbf{c} \cdot \mathbf{E}\, d^3 c = \sigma \mathbf{E}$$

Conductivity tensor

❖ In isotropic system:

$$\sigma = \frac{1}{3} \sigma_{ii} = \frac{q}{3} \int f_\mathrm{MB}(c) \phi(c) c^2\, d^3 c = \boxed{\frac{q^2 n_e}{3 n_i k_\mathrm{B} T \pi R^2} \sqrt{\frac{8 k_\mathrm{B} T}{\pi m_e}}}$$

Drude formula

Frequency response

- Time-dependent electric field: $\mathbf{E}(t) = \epsilon \mathbf{E}_\omega \mathrm{e}^{-\mathrm{i}\omega t}$
- Linear response: $f(\mathbf{c}, t) = f_{\mathrm{MB}}(\mathbf{c})\left[1 + \epsilon \Phi_\omega(\mathbf{c}) \mathrm{e}^{-\mathrm{i}\omega t}\right]$
- Plugging into LE:

$$I[\Phi_\omega] - \frac{\mathrm{i}\omega}{n_i} \hat{f}_{\mathrm{MB}} \Phi_\omega = \frac{q}{n_i k_{\mathrm{B}} T} \hat{f}_{\mathrm{MB}}\, \mathbf{c} \cdot \mathbf{E}_0$$

- $\Phi_\omega(\mathbf{c}) = \phi_\omega(c)\, \mathbf{c} \cdot \mathbf{E}_\omega$

- Electric current:

$$\mathbf{J} = (\sigma_0 + i\sigma_1) \mathbf{E}_\omega \mathrm{e}^{-\mathrm{i}\omega t} = \boxed{\sigma_\omega} \mathbf{E}_\omega \mathrm{e}^{-\mathrm{i}(\omega t - \boxed{\alpha})}$$

Complex conductivity

$$\sigma_\omega = \sqrt{\sigma_0^2 + \sigma_1^2}$$

Phase delay

$$\alpha = \arctan \frac{\sigma_1}{\sigma_0}$$

Relaxation dynamics

- No external electric field
- Initial distribution – close to, but different from Maxwellian and non-uniform
- Fourier transformation of initial distribution in spatial coordinates → perturbation for single mode:

$$f(\mathbf{r}, \mathbf{c}, t) = f_{\mathrm{MB}}(\mathbf{c})\left[1 + \Phi_{\mathbf{k}}(\mathbf{c}, t)\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\right]$$

- Plugging into LE:

$$f_{\mathrm{MB}} \frac{\partial \Phi_{\mathbf{k}}}{\partial t} = -L_{\mathbf{k}} \Phi_{\mathbf{k}},$$

here operator $L_{\mathbf{k}}\Phi = n_e n_i I[\Phi] + \mathrm{i}\mathbf{k}\cdot\mathbf{c}\, f_{\mathrm{MB}}\Phi$

- $\Phi_{\mathbf{k}}(\mathbf{c}, t) = \Phi_{\mathbf{k}}(\mathbf{c})\mathrm{e}^{-\lambda t}$ ⇒ $\boxed{L_{\mathbf{k}}\Phi_{\mathbf{k}} = \lambda f_{\mathrm{MB}}\Phi_{\mathbf{k}}}$

Operator $L_{\mathbf{k}}$

$$\boxed{L_{\mathbf{k}}\Phi_{\mathbf{k}} = \lambda f_{\mathrm{MB}}\Phi_{\mathbf{k}}}$$

- At longer times, relaxation towards the thermal equilibrium is determined by the **smallest** eigenvalue
- Let's analyze the case of small wavevectors:

$$L_{\mathbf{k}}\Phi = \underbrace{\boxed{n_e n_i I[\Phi]}}_{= L_0\Phi} + \underbrace{\boxed{\mathrm{i}\epsilon\mathbf{k}\cdot\mathbf{c}\, f_{\mathrm{MB}}\Phi}}_{= \mathrm{i}\epsilon L_1\Phi}, \qquad \epsilon \ll 1$$

- Properties of operator L_0:
  - Linear, Hermitian ($\lambda = \lambda^*$), positive semi-definite ($\lambda \geq 0$)
  - The smallest eigenvalue $\lambda = 0$ corresponds to the eigenfunction $\Phi_0 = 1$
- For the smallest eigenvalue of $L_{\mathbf{k}} = L_0 + \mathrm{i}\epsilon L_1$:
  - $\lambda = 0 + \epsilon\lambda_1 + \epsilon^2\lambda_2 + \cdots$
  - $\Phi_{\mathbf{k}} = 1 + \epsilon\Phi_1 + \epsilon^2\Phi_2 + \cdots$

Eigenvalue of $L_{\mathbf{k}}$

$$L_{\mathbf{k}} = L_0 + \mathrm{i}\epsilon L_1$$

$$L_0 = n_e n_i I$$
$$\mathrm{L}_1 = \mathbf{k}\cdot\mathbf{c}\, f_{\mathrm{MB}}$$

- First-order: $L_0\Phi_1 + \mathrm{i}L_1 \overset{=1}{\boxed{\Phi_0}} = f_{\mathrm{MB}}(\overset{=0}{\boxed{\lambda_0}}\Phi_1 + \lambda_1 \overset{=1}{\boxed{\Phi_0}})$
  - $L_0\Phi_1 = \lambda_1 f_{\mathrm{MB}} - \mathrm{i}L_1 \cdot 1$

$$\int (\lambda_1 f_{\mathrm{MB}} - \mathrm{i}L_1)\, \mathrm{d}^3c = \int 1 L_0 \Phi_1\, d^3c = \int \Phi_1 \underbrace{L_0 1}_{=0}\, d^3c = 0$$

$L_1 \propto \mathbf{c}$

L_0 is Hermitian

$$\boxed{\lambda_1 = 0}$$

$$I[\Phi_1] = -\mathrm{i}\frac{f_{MB}}{n_i}\mathbf{c}\cdot\mathbf{k}$$

- Second-order:
  - $L_0\Phi_2 = \lambda_2 f_{\mathrm{MB}} - \mathrm{i}L_1 \cdot \Phi_1$

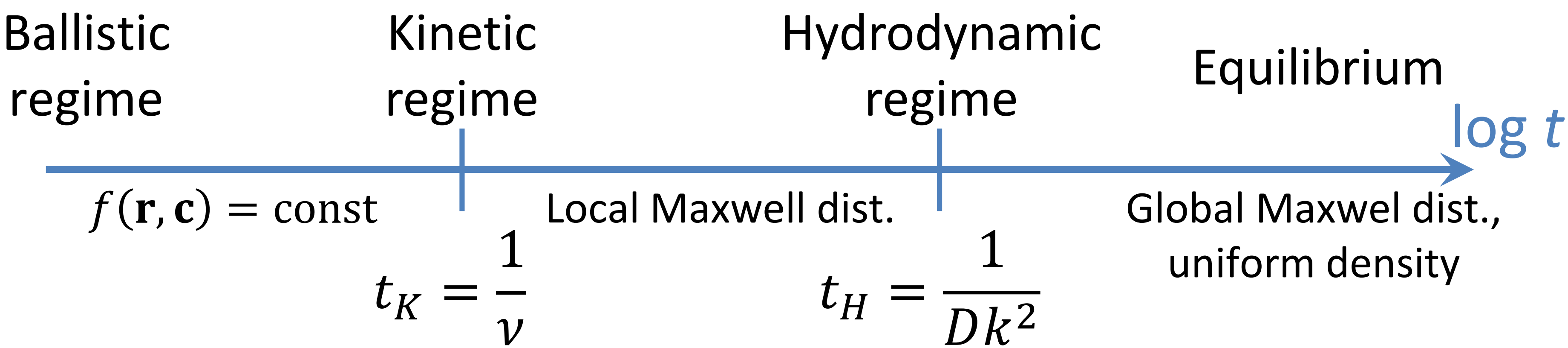
$$\lambda_2 = \mathrm{i}\frac{\int L_1\Phi_1\, \mathrm{d}^3c}{\int f_{\mathrm{MB}}\, \mathrm{d}^3c} = \mathrm{i}\frac{\int L_1\Phi_1\, \mathrm{d}^3c}{n_e} = \boxed{\left(\frac{k_B T\sigma}{n_e q^2}\right)k^2}$$

Diffusive behavior

- $\lambda = \left(\frac{k_B T \sigma}{n_e q^2}\right) k^2$
- By integrating LE over $\mathrm{d}^3 c$ and calculating inverse Fourier transform we obtain the diffusion equation:

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho$$

- Diffusion coefficient $D = \frac{k_B T \sigma}{n_e q^2} = \frac{\ell \langle |\mathbf{c}| \rangle}{3}$



Chapman–Enskog method

- A method to obtain hydrodynamic equations by time scale separation
- In the hydrodynamic regime, f depends on **c**, **r** and t not separately, but via $n(\mathbf{r}, t)$:
$$f(\mathbf{r}, \mathbf{c}, t) = h\big(\mathbf{c}; n(\mathbf{r}, t)\big)$$
- Expand h as power series:
$$h = h_0 + \epsilon h_1 + \epsilon^2 h_2 + \cdots$$

We also assume that $\mathbf{E}$ and ∇n are **first-order** in ϵ

- Introducing time scales:
$$t_0 = t, \qquad t_1 = \epsilon t, \qquad t_2 = \epsilon^2 t, \qquad \ldots$$
  - For *very* small t, $t_1 = t_2 = 0$, and h depends only on t_0
  - At larger times, stationary state for the t_0 timescale is reached, and h starts to depend on t_1, etc.

Chapman–Enskog method

- $n = n(\mathbf{r}, t_0, t_1, t_2, \dots)$

$$\frac{\partial n}{\partial t} \to \frac{\partial n}{\partial t_0} + \epsilon \frac{\partial n}{\partial t_1} + \epsilon^2 \frac{\partial n}{\partial t_2} + \cdots$$

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int [f' F_1' - f F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c_1$$

- Zeroth-order in ϵ:

$$\frac{\partial h_0}{\partial n} \frac{\partial n}{\partial t_0} = \int [h_0' F_1' - h_0 F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c_1$$

  - Integral over $\mathrm{d}^3 c$ is equal to 0 $\Rightarrow$ $\dfrac{\partial n}{\partial t_0} = 0$
  - $h_0 = n \hat{f}_{\mathrm{MB}}$

$$n = n(\mathbf{r}, t_1, t_2, \dots)$$

Chapman–Enskog method

$$\frac{\partial f}{\partial t} + \mathbf{c}\cdot\frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m}\cdot\frac{\partial f}{\partial \mathbf{c}} = \int [f'F_1' - fF_1]|\mathbf{c}-\mathbf{c}_1|\cdot b\mathrm{d}b\mathrm{d}\psi\,\mathrm{d}^3c_1$$

- First-order in ϵ:

$$\frac{\partial h_1}{\partial n}\cancel{\frac{\partial n}{\partial t_0}} + \frac{\partial h_0}{\partial n}\cancel{\frac{\partial n}{\partial t_1}} + \mathbf{c}\cdot\nabla h_0 + \frac{q\mathbf{E}}{m}\cdot\frac{\partial h_0}{\partial \mathbf{c}}$$

$$= \int [h_1'F_1' - h_1F_1]|\mathbf{c}-\mathbf{c}_1|\cdot b\mathrm{d}b\mathrm{d}\psi\,\mathrm{d}^3c_1$$

- Integral over d^3c is equal to 0 $\Rightarrow$ $\frac{\partial n}{\partial t_1} = 0$

$n = n(\mathbf{r}, t_2, \dots)$

Density evolves at the slowest time scale!

- $h_1 = h_0\Phi$

$$I[\Phi] = \frac{\hat{f}_{\mathrm{MB}}(c)}{k_{\mathrm{B}}T}\mathbf{c}\cdot\left[\frac{q\mathbf{E}}{m} - \frac{k_{\mathrm{B}}T\nabla n}{nn_i}\right]$$

- Eq. of the same form as we had before for linear response

Chapman–Enskog method

$$\boxed{\frac{\partial f}{\partial t} + \mathbf{c}\cdot\frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m}\cdot\frac{\partial f}{\partial \mathbf{c}} = \int [f'F_1' - fF_1]|\mathbf{c}-\mathbf{c}_1|\cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c_1}$$

❖ Second-order in ϵ:

$$\frac{\partial h_2}{\partial n}\cancel{\frac{\partial n}{\partial t_0}} + \frac{\partial h_1}{\partial n}\cancel{\frac{\partial n}{\partial t_1}} + \overbrace{\boxed{\frac{\partial h_0}{\partial n}}}^{=\hat{f}_{\mathrm{MB}}}\frac{\partial n}{\partial t_2} + \mathbf{c}\cdot\nabla h_1 + \frac{q\mathbf{E}}{m}\cdot\frac{\partial h_1}{\partial \mathbf{c}}$$

$$= \int [h_2'F_1' - h_2F_1]|\mathbf{c}-\mathbf{c}_1|\cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c_1$$

➢ Integral over d^3c is equal to 0 ➡ $\frac{\partial n}{\partial t_2} + \nabla\int \mathbf{c}h_1\, d^3c = 0 \Big| \cdot q$

➢ $\frac{\partial \rho}{\partial t_2} + \nabla\mathbf{J} = 0$

➢ $\mathbf{J} = \sigma\mathbf{E} - D\nabla\rho$ ➡ $\boxed{\frac{\partial \rho}{\partial t_2} + \nabla(\sigma\mathbf{E}) = D\nabla^2\rho}$

Chapter 4

The Boltzmann equation for dilute gases

The Boltzmann equation

- Formulated in 1872
- Describes evolution of classical gases
- Explains:
  - Origin of the irreversible behavior of macroscopic systems
  - Relates the macroscopic coefficients (viscosity, thermal conductivity, diffusion coefficient) to the interatomic interactions
- Valid for dilute gas

The Boltzmann equation

- Dilute gas:
  - N molecules in a volume $\mathcal{V}$, density $n = \frac{N}{\mathcal{V}}$
  - Molecules interact via potential with range r_0
  - Cross-section $\sigma \sim r_0^2$
  - Fraction of volume occupied by all molecules (assuming them to be spheres of radius r_0) is $\phi = \frac{4}{3}\pi n r_0^3 \ll 1$
  - Transport coefficients are proportional to the mean free path $\ell \sim \frac{1}{n\sigma} \sim \frac{1}{n r_0^2}$
  - Number of molecules within the mean free path volume $N_\ell = n\ell^3 \gg 1$,
    so that statistical description by using distribution functions is valid

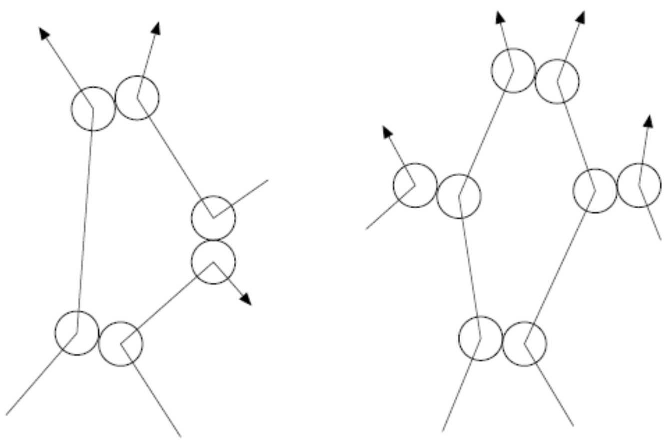
In the atmosphere under normal conditions:

- $n = 2{,}7 \cdot 10^{25}\ \mathrm{m}^{-3}$
- $r_0 \sim 1\ \text{Å}$
- $\ell \sim 8 \cdot 10^{-8}\ \mathrm{m}$
- $\phi \sim 10^{-4}$
- $N_\ell \sim 1.4 \cdot 10^4$

- Boltzmann–Grad limit: $r_0 \to 0,\ n \to \infty$ while $\mathcal{V}$ is finite

Assumptions

- $r_0 \to 0, n \to \infty$ while $\mathcal{V}$ is finite
- Colliding particles are statistically independent
  - No re-collisions or pre-collisional correlations



BBKGY$_1$ equation:

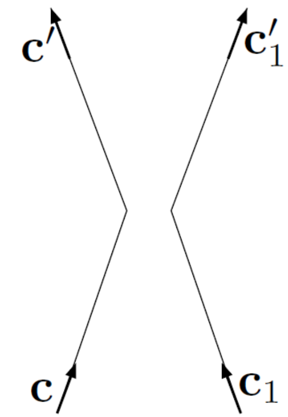
$$\frac{\partial f}{\partial t} + \mathbf{c}_1 \cdot \frac{\partial f}{\partial \mathbf{r}_1} + \frac{\mathbf{F}_1}{m} \cdot \frac{\partial f}{\partial \mathbf{c}_1} = \int \frac{\partial \phi_{12}}{\partial \mathbf{r}_{12}} \left(\frac{\partial}{\partial \mathbf{c}_1} - \frac{\partial}{\partial \mathbf{c}_2} \right) \underbrace{f^{(2)}(1,2,t)}_{} \ \mathrm{d}^3 r_2 \mathrm{d}^3 c_2$$

Molecular chaos hypothesis $\quad f^{(2)}(\mathbf{c}_1, \mathbf{c}_2)_{\text{precoll}} = f(\mathbf{c}_1) f(\mathbf{c}_2)$

- All derived equation are valid on the mesoscale
  - Time and length scales $\geq$ mean free time & path
  - Duration of the collision is much shorter
  - No effect of the external forces during the collision

Boltzmann kinetic equation

- Derivation similar to that of the Lorentz equation, but now particle collide between themselves and not with (almost) stationary ions



$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \underbrace{\int [f' f_1' - f f_1] |\mathbf{g}| \cdot b \mathrm{d}b \mathrm{d}\psi \; \mathrm{d}^3 c_1}_{\substack{\text{Collisional operator} \\ J[f,f]}}$$

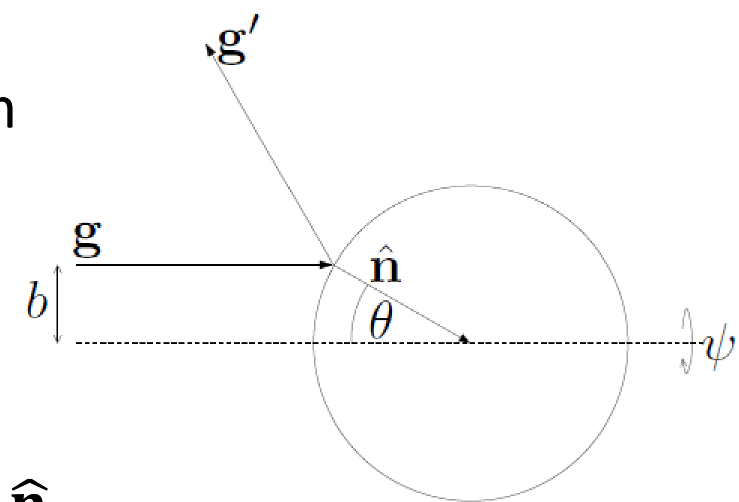
here $f = f(\mathbf{r}, \mathbf{c}, t),\ f_1 = f(\mathbf{r}, \mathbf{c_1}, t),$

$$f' = f(\mathbf{r}, \mathbf{c}', t),\ f_1' = f(\mathbf{r}, \mathbf{c}_1', t)$$

$$\mathbf{g} = \mathbf{c} - \mathbf{c}_1$$

Hard sphere model

- Molecules are hard spheres of radius r_0
  - They meet at a distance $D = 2r_0$
  - From the energy and momentum conservation laws:
    $\mathbf{c}' = \mathbf{c} - [(\mathbf{c} - \mathbf{c}_1) \cdot \hat{\mathbf{n}}]\,\hat{\mathbf{n}}$
    $\mathbf{c}_1' = \mathbf{c}_1 - [(\mathbf{c} - \mathbf{c}_1) \cdot \hat{\mathbf{n}}]\,\hat{\mathbf{n}}$
  - Post-collisional relative velocity:
    $$\mathbf{g}' = \mathbf{g} - 2(\mathbf{g} \cdot \hat{\mathbf{n}})\,\hat{\mathbf{n}}$$
  - $b = R \sin \vartheta$
  - $|\mathbf{g}| \cdot b\mathrm{d}b\mathrm{d}\psi = D^2 |\mathbf{g}| \sin\vartheta \cos\vartheta \, \mathrm{d}\vartheta \mathrm{d}\psi = D^2 (\mathbf{g} \cdot \hat{\mathbf{n}})\, \mathrm{d}^2\hat{\mathbf{n}}$



$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = D^2 \int [f' f_1' - f f_1](\mathbf{g} \cdot \hat{\mathbf{n}}) \Theta(\mathbf{g} \cdot \hat{\mathbf{n}})\, \mathrm{d}^2\hat{\mathbf{n}} \mathrm{d}^3 c_1$$

Conservation laws

$$\int \mathrm{d}^3 c \;\; \varphi(\mathbf{c}) \cdot \left| \; \frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{q\mathbf{E}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int [f' F_1' - f F_1] |\mathbf{c} - \mathbf{c}_1| \cdot b \mathrm{d} b \mathrm{d} \psi \; \mathrm{d}^3 c_1 \right.$$

❖ Let's recall:

- Density of φ: $\rho_\varphi(\mathbf{r}, t) = \int \varphi(\mathbf{c}) f(\mathbf{r}, \mathbf{c}, t) \, \mathrm{d}^3 c$
- Flux of φ: $\mathbf{J}_\varphi(\mathbf{r}, t) = \int \varphi(\mathbf{c}) f(\mathbf{r}, \mathbf{c}, t) \mathbf{c} \, \mathrm{d}^3 c$
- Source due to external force: $S_\varphi(\mathbf{r}, t) = \int \frac{\mathbf{F}}{m} \cdot \frac{\partial \varphi}{\partial \mathbf{c}} f(\mathbf{r}, \mathbf{c}, t) \, \mathrm{d}^3 c$

$$\boxed{\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi - S_\varphi = \int \varphi(\mathbf{c}) [f' f_1' - f f_1] |\mathbf{g}| \cdot b \mathrm{d} b \mathrm{d} \psi \; \mathrm{d}^3 c \mathrm{d}^3 c_1}$$

Conservation laws

$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi - S_\varphi = \int \varphi(\mathbf{c})[f'f_1' - ff_1]|\mathbf{g}| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1$$

$$= \frac{1}{2}\int \big(\varphi(\mathbf{c}) + \varphi(\mathbf{c}_1)\big)[f'f_1' - ff_1]|\mathbf{g}| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1$$

Relabel variables: $\mathbf{c} \leftrightarrow \mathbf{c}'$ and $\mathbf{c}_1 \leftrightarrow \mathbf{c}_1'$

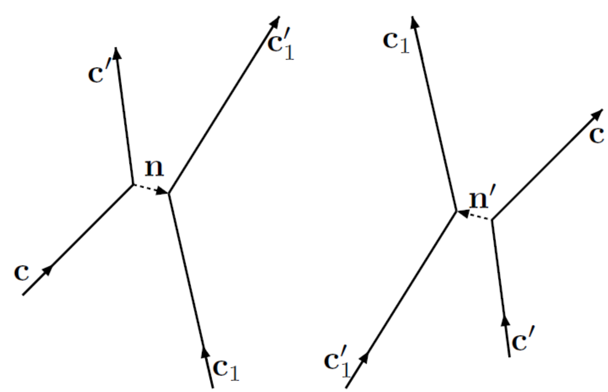
Now ' denote post-collisional velocities

$$= \frac{1}{2}\int \big(\varphi(\mathbf{c}') + \varphi(\mathbf{c}_1')\big)[ff_1 - f'f_1']\underbrace{|\mathbf{g}'| \cdot b'\mathrm{d}b'\mathrm{d}\psi'\ \mathrm{d}^3c'\mathrm{d}^3c_1'}_{=\ |\mathbf{g}| \cdot b\mathrm{d}b\mathrm{d}\psi\ \mathrm{d}^3c\mathrm{d}^3c_1}$$

$$= \frac{1}{4}\int \underbrace{(\varphi + \varphi_1 - \varphi' - \varphi_1')[f'f_1'}\, - ff_1]|\mathbf{g}'| \cdot b'\mathrm{d}b'\mathrm{d}\psi'\ \mathrm{d}^3c'\mathrm{d}^3c_1'$$

Re-do the same trick

$$= \frac{1}{2}\int \underbrace{(\varphi' + \varphi_1' - \varphi - \varphi_1)}_{=\ 0 \text{ for collisional invariants}} ff_1|\mathbf{g}'| \cdot b'\mathrm{d}b'\mathrm{d}\psi'\ \mathrm{d}^3c'\mathrm{d}^3c_1'$$



Conservation laws

Equations are not closed!
(P_{ik} and $\mathbf{q}$ are not specified)

$$\frac{\partial \rho_\varphi}{\partial t} + \nabla \cdot \mathbf{J}_\varphi - S_\varphi = \frac{1}{2}\int (\varphi' + \varphi_1' - \varphi - \varphi_1) f f_1 |\mathbf{g}'| \cdot b' \mathrm{d}b' \mathrm{d}\psi' \, \mathrm{d}^3 c' \mathrm{d}^3 c_1'$$

$$\mathbf{J}_\varphi(\mathbf{r},t) = \int \varphi(\mathbf{c}) f(\mathbf{r},\mathbf{c},t)\mathbf{c} \, \mathrm{d}^3 c$$

$$S_\varphi(\mathbf{r},t) = \int \frac{\mathbf{F}}{m} \cdot \frac{\partial \varphi}{\partial \mathbf{c}} f(\mathbf{r},\mathbf{c},t) \, \mathrm{d}^3 c$$

- Mass ($\varphi = m$):

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

- Momentum ($\varphi = mc$):
  - $\tilde{P}_{ik}(\mathbf{r},t) = m\int f(\mathbf{r},\mathbf{c},t) c_i c_k \, \mathrm{d}^3 c \; = \boxed{P_{ik}} + \rho v_i v_k$

Stress tensor $P_{ik}(\mathbf{r},t) = m\int f(\mathbf{r},\mathbf{c},t)(c_i - v_i)(c_k - v_k) \, \mathrm{d}^3 c$

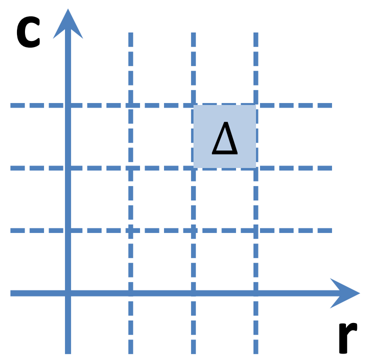
$$\frac{\partial}{\partial t}(\rho v_i) + \frac{\partial}{\partial x_k}(P_{ik} + \rho v_i v_k) - \rho \frac{F_i}{m} = 0$$

- Energy ($\varphi = mc^2/2$):

Heat flux $q_i = \frac{m}{2}\int f(\mathbf{r},\mathbf{c},t)(\mathbf{c} - \mathbf{v})^2 (c_i - v_i) \, \mathrm{d}^3 c$

$$\frac{3}{2} k_\mathrm{B} \rho \left(\frac{\partial T}{\partial t} + (\mathbf{v} \cdot \nabla) T \right) = -\nabla \cdot \mathbf{q} - P_{ik} \frac{\partial v_i}{\partial x_k} = 0$$

H-theorem



- Let's divide 1-particle phase space into parcels of size Δ
- Number of particles in the k^{th} parcel is
$$N_k = f_k \Delta$$
- Total number of configurations is $\Omega = \dfrac{N!}{N_1! N_2! \cdots N_k! \cdots}$, here $N = \sum_k N_k$
- Entropy of such macroscopic state is
$$S = k_B \ln \Omega \overset{N \gg 1}{\simeq} -k_B \sum_k N_k \ln \frac{N_k}{N}$$
$$\simeq -k_B \int f(\mathbf{r}, \mathbf{c}) \ln \frac{f(\mathbf{r}, \mathbf{c})\Delta}{N} \, \mathrm{d}^3 r \mathrm{d}^3 c$$

H-theorem

- For homogeneous gas we can define the functional

$$H[f](t) = \int f(\mathbf{c},t) \ln \frac{f(\mathbf{c},t)}{f_0} \, \mathrm{d}^3 c$$

- From the Boltzmann equation we obtain:

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int \left[\ln \frac{f(\mathbf{c})}{f_0} + 1\right] \boxed{\frac{\partial f}{\partial t}} \, \mathrm{d}^3 c$$

$$\frac{\partial f}{\partial t} = -\int [f' f_1' - f f_1] |\mathbf{g}| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c_1$$

$$= -\int \boxed{[\ln(f f_1) - \ln(f' f_1')][f f_1 - f' f_1']} |\mathbf{g}| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c \mathrm{d}^3 c_1$$

Argument is of the form $(\ln x - \ln y)(x - y) \geq 0$ ➡ $\boxed{\dfrac{\mathrm{d}H}{\mathrm{d}t} \leq 0}$

- It can be proven that lower boundary exists

- Steady state: $\dfrac{\mathrm{d}H}{\mathrm{d}t} = 0$ ➡ $f f_1 = f' f_1'$
  - Steady-state distribution f should be collisional-invariant

H-theorem

- We can expand $\ln f_{\mathrm{st}}(\mathbf{c})$ in terms of collisional invariants:

$$\ln f_{\mathrm{st}} = \alpha m + \boldsymbol{\beta} \cdot m\mathbf{c} + \gamma \frac{mc^2}{2}$$

$$\Downarrow$$

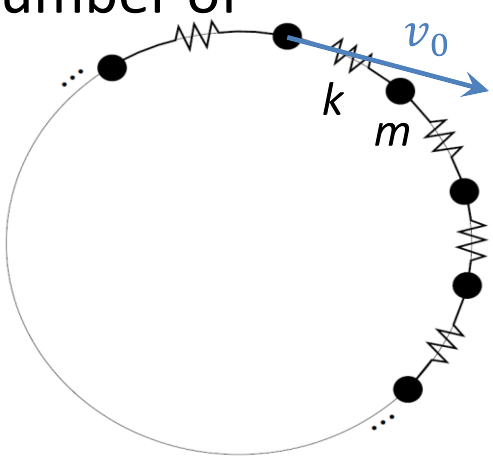
- We obtain Maxwell-Boltzmann distribution:

$$f_{\mathrm{st}}(\mathbf{c}) = n\left(\frac{m}{2\pi k_{\mathrm{B}} T}\right)^{3/2} \exp\left(-\frac{m(\mathbf{c}-\mathbf{v})^2}{2k_{\mathrm{B}} T}\right)$$

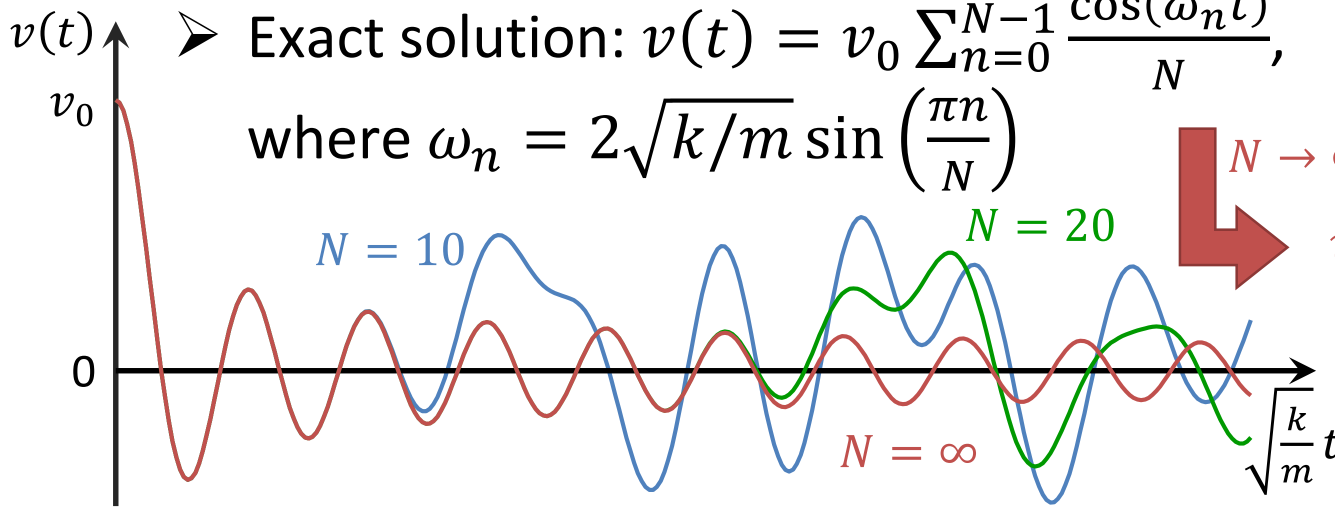
- How does irreversible evolution towards MB distribution appear, when we start from the time-reversible equations of motion?

Irreversibility problem

- Poincaré recurrence theorem:
  - After a long but finite time any classical system obeying microscopic reversible dynamics will return close to any initial condition
  - The recurrence time $\sim 2^N$, where N is the number of degrees of freedom



- Example: oscillator chain on a ring
  - Initially, one ball is given velocity v_0
  - Exact solution: $v(t) = v_0 \sum_{n=0}^{N-1} \frac{\cos(\omega_n t)}{N}$, where $\omega_n = 2\sqrt{k/m}\,\sin\left(\frac{\pi n}{N}\right)$



$N \to \infty$

$$v(t) = v_0 J_0\left(2\sqrt{\frac{k}{m}}\,t\right)$$

(damped oscillations)

Dynamics close to equilibrium

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int [f' f_1' - f f_1] |\mathbf{g}| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c_1$$

- Eventually, the gas state will approach thermal equilibrium. Let's study the later stage of its evolution, when it is already close to equilibrium
- $f(\mathbf{c}) = f_{\mathrm{MB}}(\mathbf{c})[1 + \Phi(\mathbf{c})]$
- $J[f, f] \approx -n^2 \underbrace{\int \hat{f}_{\mathrm{MB}} \hat{f}_{\mathrm{MB}1} [\Phi + \Phi_1 - \Phi' - \Phi_1'] \, |\mathbf{g}| \cdot b \mathrm{d}b \mathrm{d}\psi \, \mathrm{d}^3 c_1}_{= I[\Phi]}$
- $I[\Phi]$ – linear, Hermitian, positive semidefinite operator:
  - Bracket product $[\Psi, \Phi] = \int \Psi^*(\mathbf{c}) I[\Phi](\mathbf{c}) \, \mathrm{d}^3 c$
  - $[\Psi, \Phi] = [\Phi, \Psi]^*, \quad [\Phi, \Phi] \geq 0$
  - $[\Psi, \Phi] = 0$ if either Ψ or Φ is a collisional invariant

Eigenvalue analysis

- Consider gas close to equilibrium with no external forces
- Perturbation for a single Fourier mode:
$$f(\mathbf{r},\mathbf{c},t) = f_{\mathrm{MB}}(\mathbf{c})\left[1 + \Phi_{\mathbf{k}}(\mathbf{c},t)\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\right]$$
- From BE:
$$f_{\mathrm{MB}}\frac{\partial \Phi_{\mathbf{k}}}{\partial t} + \mathrm{i}\mathbf{k}\cdot\mathbf{c}f_{\mathrm{MB}}\Phi_{\mathbf{k}} = -n^2 I[\Phi_{\mathbf{k}}]$$
- Linear operator $L_{\mathbf{k}} = n^2 I + \mathrm{i}\mathbf{k}\cdot\mathbf{c}f_{\mathrm{MB}}$
  - Eigenvalue equation: $L_{\mathbf{k}}\Phi_{\mathbf{k},j} = -\lambda_{\mathbf{k},j}f_{\mathrm{MB}}\Phi_{\mathbf{k},j}$
  - $f(\mathbf{r},\mathbf{c},t) = f_{\mathrm{MB}}(\mathbf{c})\left[1 + \sum_j A_{\mathbf{k},j}\Phi_{\mathbf{k}}(\mathbf{c})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}-\lambda_{\mathbf{k},j}\boldsymbol{t}}\right]$

Eigenvalue analysis

- When $\mathbf{k}=0$, operator $L_0 = n^2 I$ is Hermitian and positive semidefinite ($\lambda \geq 0$)
- The smallest eigenvalue $\lambda_0 = 0$ corresponds to 5 different eigenfunctions (collisional invariants):
  - $\Phi = \left\{1, c_x, c_y, c_z, \mathbf{c}^2\right\}$
  - Each Fourier component $\Phi_{\mathbf{k}}$ will have 5 different modes
- Spectrum of the operator $L_{\mathbf{k}}$ for small $\mathbf{k} = k\hat{\mathbf{x}}$:

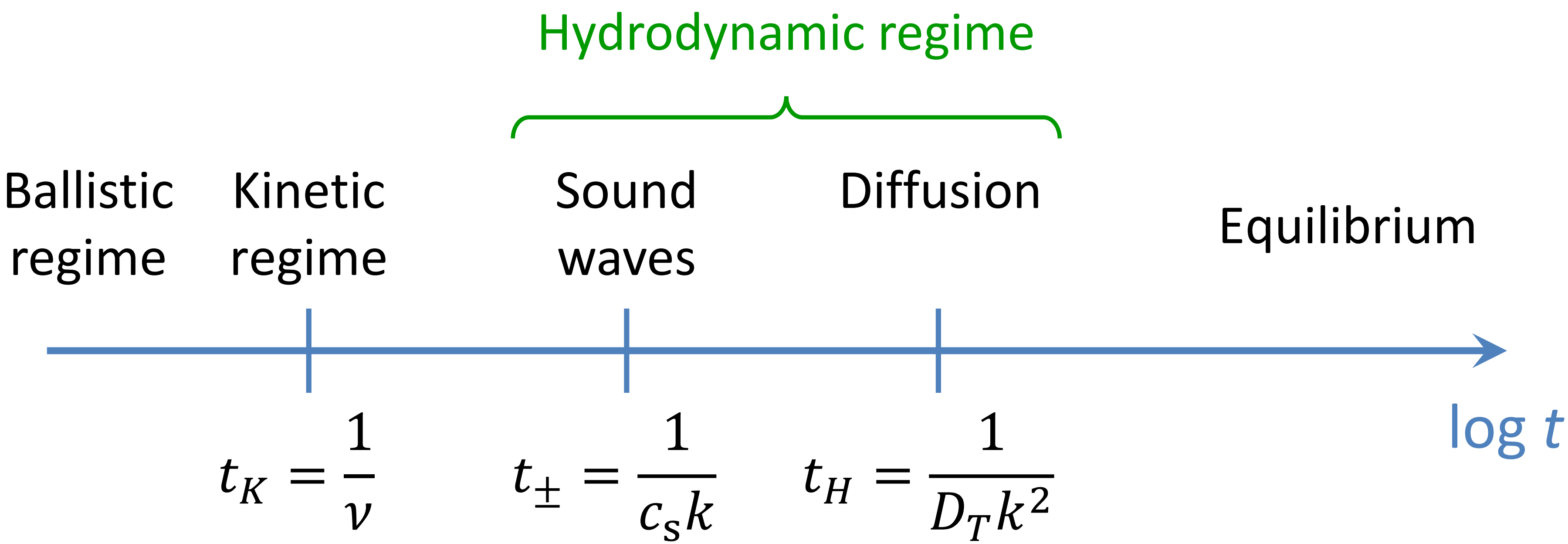
  Momentum diffusion (viscosity)

  - 2 transverse modes: $\lambda_{\perp}^{(y,z)} = \nu k^2, \; \Phi = c_{y,z} + \mathcal{O}(k)$
  - 2 sound modes: $\lambda_{\pm} = \pm \mathrm{i} c_s k + \Gamma k^2, \; \Phi = c_x + \mathcal{O}(k)$
  - 1 heat mode: $\lambda_{\mathrm{H}} = \boxed{D_T k^2}, \; \Phi = \frac{mc^2}{2} - \frac{3}{2} k_{\mathrm{B}} T + \mathcal{O}(k)$

  Heat diffusion (heat conductivity)

- In all cases: $\mathrm{Re}\,\lambda > 0$ ⇒ relaxation to a homogeneous equilibrium
- Sound modes: $\mathrm{e}^{\mathrm{i}k(x \mp c_s t)}$ ⇒ damping longitudinal sound waves

Time scales


Hydrodynamic regime
Ballistic regime
Kinetic regime
Sound waves
Diffusion
Equilibrium
log t
$t_K = \frac{1}{\nu}$
$t_\pm = \frac{1}{c_s k}$
$t_H = \frac{1}{D_T k^2}$

BGK model

- Boltzmann equation gives accurate description of gases, but is too complicated for the detailed calculations
- Any simplified description should still include irreversible evolution towards the equilibrium and preserve collisional invariants
- Bhatnagar–Gross–Krook (BGK) model:

$$J_{\mathrm{BGK}}[f] = \nu\{f_{\mathrm{MB}}(\mathbf{c}; n[f], \mathbf{v}[f], T[f]) - f(\mathbf{r}, \mathbf{c}, t)\}$$

  - $n[f](\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{c}, t)\, \mathrm{d}^3 c$
  - $\mathbf{v}[f](\mathbf{r}, t) = \frac{1}{n(\mathbf{r},t)} \int \mathbf{c}\, f(\mathbf{r}, \mathbf{c}, t)\, \mathrm{d}^3 c$
  - $\frac{3}{2} k_{\mathrm{B}} T[f](\mathbf{r}, t) = \frac{1}{n(\mathbf{r},t)} \int \frac{m(\mathbf{c}-\mathbf{v}[f])^2}{2} f(\mathbf{r}, \mathbf{c}, t)\, \mathrm{d}^3 c$

Linear BGK model

- Linear BGK operator is notably simpler
- $f(\mathbf{r},\mathbf{c},t) = f_{\mathrm{MB}}(\mathbf{c})[1+\Phi(\mathbf{c},t)]$
  - $n[f](t) = n_0\left[1+\int \hat{f}_{\mathrm{MB}}(\mathbf{c})\Phi(\mathbf{c},t)\,\mathrm{d}^3c\right]$
  - $\mathbf{v}[f](t) = n_0\int \hat{f}_{\mathrm{MB}}(\mathbf{c})\Phi(\mathbf{c},t)\mathbf{c}\,\mathrm{d}^3c$
  - $T[f](t) = T_0\left[1+\frac{2}{3}\int \hat{f}_{\mathrm{MB}}(\mathbf{c})\Phi(\mathbf{c},t)\left(\frac{mc^2}{2k_{\mathrm{B}}T}-\frac{3}{2}\right)\,\mathrm{d}^3c\right]$
- Collision operator:

$$n_0 I_{\mathrm{BGK}}[\phi] = \nu\widehat{f}_{\mathrm{MB}}(\mathbf{c})\Phi(\mathbf{c}) - \nu\widehat{f}_{\mathrm{MB}}(\mathbf{c})\left[\int \widehat{f}_{\mathrm{MB}}(\mathbf{c}')\Phi(\mathbf{c}')\,\mathrm{d}^3c' + \frac{m\mathbf{c}}{k_{\mathrm{B}}T_0}\cdot\int \widehat{f}_{\mathrm{MB}}(\mathbf{c}')\Phi(\mathbf{c}')\mathbf{c}'\,\mathrm{d}^3c' + \frac{2}{3}\left(\frac{mc^2}{2k_{\mathrm{B}}T_0}-\frac{3}{2}\right)\int \widehat{f}_{\mathrm{MB}}(\mathbf{c}')\Phi(\mathbf{c}')\left(\frac{mc'^2}{2k_{\mathrm{B}}T_0}-\frac{3}{2}\right)\,\mathrm{d}^3c'\right]$$

Hydrodynamic regime

❖ Fourier law for the heat flux:

$$\mathbf{q} = -\boxed{\kappa}\,\nabla T$$

Thermal conductivity

❖ Newton's law for the stress tensor:

$$\mathbb{P} = \boxed{p}\,\mathbb{I} - \boxed{\eta}\left[(\nabla\mathbf{v}) + (\nabla\mathbf{v})^{\mathrm{T}} - \frac{2}{3}(\nabla\cdot\mathbf{v})\mathbb{I}\right]$$

Pressure $= nk_{\mathrm{B}}T$ Shear viscosity

❖ Conservation laws:

- $\dfrac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0$
- $\rho\dfrac{\partial v_i}{\partial t} + \rho(\mathbf{v}\cdot\nabla)v_i = -\dfrac{\partial P_{ik}}{\partial x_k} + \rho\dfrac{F_i}{m} = 0$
- $\dfrac{3}{2}k_{\mathrm{B}}\rho\left(\dfrac{\partial T}{\partial t} + (\mathbf{v}\cdot\nabla)T\right) = -\nabla\cdot\mathbf{q} - mP_{ik}\dfrac{\partial v_i}{\partial x_k} = 0$

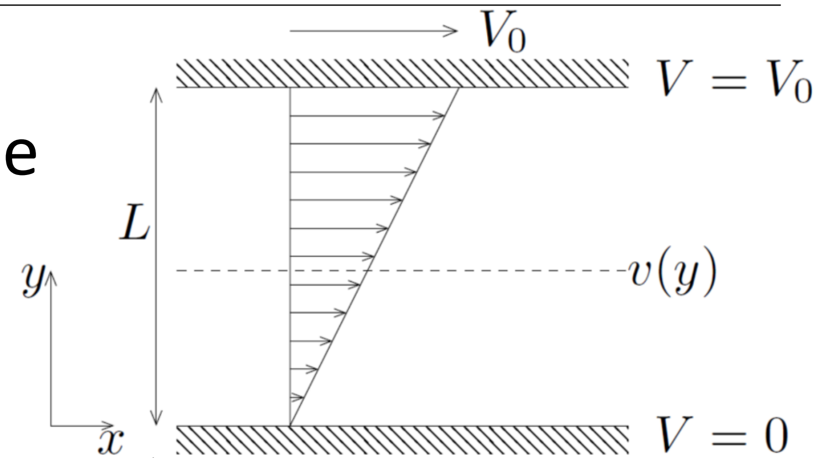
Hydrodynamic equations

- Perturbations (with no external forces):
  - $n = n_0 + \epsilon n_1(\mathbf{r}, t)$
  - $\mathbf{v} = \epsilon \mathbf{v}_1(\mathbf{r}, t)$
  - $T = T_0 + \epsilon T_1(\mathbf{r}, t)$
- Substituting into the conservation laws:
  - $\frac{\partial n_1}{\partial t} = -n_0 \nabla \cdot \mathbf{v}_1 = 0$
  - $m n_0 \frac{\partial \mathbf{v}_1}{\partial t} = -k_\mathrm{B} \nabla (n_0 T_1 + T_0 n_1) + \eta_0 \nabla^2 \mathbf{v}_1$
  - $\frac{3}{2} k_\mathrm{B} m n_0 \frac{\partial T_1}{\partial t} = \kappa_0 \nabla^2 T_1 + m p_0 \nabla \cdot \mathbf{v} = 0$

  here $p_0 = k_\mathrm{B} n_0 T_0, \eta_0 = \eta(n_0, T_0),\ \kappa_0 = \kappa(n_0, T_0)$
- Fourier mode analysis yields:
  - $\nu = \frac{\eta_0}{m n_0}$
  - $\Gamma = \frac{2\kappa_0}{15 k_\mathrm{B} T} + \frac{2\eta_0}{m n_0}$
  - $D_T = \frac{3\kappa_0}{5 k_\mathrm{B} T}$
  - $c_\mathrm{s} = \sqrt{\frac{5 k_\mathrm{B} T}{3m}}$

Viscosity

- Velocity profile: $\mathbf{v} = V' y \hat{\mathbf{x}}$, here $V' = V_0/L$ is a shear rate
- By definition: $P_{xy} = -\eta \dfrac{\partial v_x}{\partial y}$



- Linear response:

$$f(\mathbf{r}, \mathbf{c}) = f_{\mathrm{MB}}\big(\mathbf{c}; n_0, T_0, \mathbf{v}(\mathbf{r})\big)[1 + \Phi(\mathbf{c})]$$

- Boltzmann eq.: $\dfrac{\partial f}{\partial t} + \mathbf{c} \cdot \dfrac{\partial f}{\partial \mathbf{r}} + \dfrac{\mathbf{F}}{m} \cdot \dfrac{\partial f}{\partial \mathbf{c}} = J[f, f]$
  - $\dfrac{f_{\mathrm{MB}} V'}{k_{\mathrm{B}} T} (c_x - v_x) c_y = -n_0^2 I[\Phi]$

(Switch to the commoving frame)

  - Ansatz: $\Phi(\mathbf{c}) = -\dfrac{V'}{n_0} \widehat{\Phi}(\mathbf{c})$ ➡ $I\big[\widehat{\Phi}\big] = \dfrac{\hat{f}_{\mathrm{MB}}}{k_{\mathrm{B}} T} m c_x c_y$
  - $P_{xy} = \int f(\mathbf{c}) m c_x c_y \, \mathrm{d}^3 c = -V' \int \hat{f}_{\mathrm{MB}}(\mathbf{c}) \widehat{\Phi}(\mathbf{c}) m c_x c_y \, \mathrm{d}^3 c$

$$\boxed{\eta = \int \hat{f}_{\mathrm{MB}}(\mathbf{c}) \widehat{\Phi}(\mathbf{c}) m c_x c_y \, \mathrm{d}^3 c}$$

Viscosity: variational principle

$$\boxed{\eta = \int \hat{f}_{\mathrm{MB}}(\mathbf{c})\widehat{\Phi}(\mathbf{c}) m c_x c_y \, \mathrm{d}^3 c}$$

$$I\left[\widehat{\Phi}\right] = \frac{\hat{f}_{\mathrm{MB}}}{k_{\mathrm{B}}T} m c_x c_y$$

- Recall bracket product:

$$\eta = k_{\mathrm{B}}T \int \widehat{\Phi}(\mathbf{c}) I\left[\widehat{\Phi}\right] \mathrm{d}^3 c \equiv k_{\mathrm{B}}T \left[\widehat{\Phi}, \widehat{\Phi}\right]$$

- Let's assume we can find another function $\widehat{\Psi}$ – such that $\left[\widehat{\Psi}, \widehat{\Psi}\right] = \left[\widehat{\Psi}, \widehat{\Phi}\right] = \frac{m}{k_{\mathrm{B}}T} \int \widehat{\Psi}(\mathbf{c}) \hat{f}_{\mathrm{MB}}(\mathbf{c}) c_x c_y \, \mathrm{d}^3 c$
- $0 \leq k_{\mathrm{B}}T\left[\widehat{\Psi} - \widehat{\Phi}, \widehat{\Psi} - \widehat{\Phi}\right] = -k_{\mathrm{B}}T\left[\widehat{\Phi}, \widehat{\Psi}\right] + k_{\mathrm{B}}T\left[\widehat{\Phi}, \widehat{\Phi}\right]$

$$\Rightarrow \quad \eta \geq k_{\mathrm{B}}T\left[\widehat{\Psi}, \widehat{\Psi}\right]$$

- Polynomial ansatz

Leave just a single term:

  - $\widehat{\Psi} = c_x c_y\left(a_0 + a_1 c^2 + a_2 (c^2)^2 + \cdots\right) = a_0 c_x c_y$
  - $\Rightarrow \quad a_0^2\left[c_x c_y, c_x c_y\right] = \frac{m a_0}{k_{\mathrm{B}}T} \int \hat{f}_{\mathrm{MB}}(\mathbf{c}) c_x^2 c_y^2 \, \mathrm{d}^3 c$

Viscosity: variational principle

$$a_0 = \frac{m}{k_\mathrm{B}T}\frac{\int \hat{f}_\mathrm{MB}(\mathbf{c})c_x^2c_y^2\,\mathrm{d}^3c}{\left[c_xc_y, c_xc_y\right]}$$

❖ Lower bound for the viscosity:

$$\eta \geq \eta_0 = k_\mathrm{B}T\left[\widehat{\Psi}, \widehat{\Psi}\right] = k_\mathrm{B}Ta_0^2\left[c_xc_y, c_xc_y\right]$$

$$= \frac{4m^2}{k_\mathrm{B}T}\frac{\left(\int \hat{f}_\mathrm{MB}(\mathbf{c})c_x^2c_y^2\,\mathrm{d}^3c\right)^2}{\int \left(\boxed{\Delta c_xc_y}\right)^2 \hat{f}_\mathrm{MB}(\mathbf{c})\hat{f}_\mathrm{MB}(\mathbf{c}_1)|\mathbf{g}|\cdot b\mathrm{d}b\mathrm{d}\psi\,\mathrm{d}^3c\mathrm{d}^3c_1}$$

$$= c'_xc'_y + c'_{x1}c'_{y1} - c_xc_y - c_{x1}c_{y1}$$

❖ Hard sphere model:

$$\boxed{\eta_0^{(\mathrm{HS})} = \frac{5}{16D^2}\sqrt{\frac{mk_\mathrm{B}T}{\pi}}}$$

Chapman–Enskog method

- $f(\mathbf{r},\mathbf{c},t) = h\big(\mathbf{c}; n(\mathbf{r},t), \mathbf{v}(\mathbf{r},t), T(\mathbf{r},t)\big)$
- $h = h_0 + \epsilon h_1 + \epsilon^2 h_2 + \cdots$
- $t_0 = t,\ t_1 = \epsilon t,\ t_2 = \epsilon^2 t,\ \ldots$
  - $\frac{\partial}{\partial t} \to \frac{\partial}{\partial t_0} + \epsilon \frac{\partial}{\partial t_1} + \epsilon^2 \frac{\partial}{\partial t_2} + \cdots$
- Zeroth-order
  - $\frac{\partial h_0}{\partial n}\frac{\partial n}{\partial t_0} + \frac{\partial h_0}{\partial \mathbf{v}} \cdot \frac{\partial \mathbf{v}}{\partial t_0} + \frac{\partial h_0}{\partial T}\frac{\partial T}{\partial t_0} = J[h_0, h_0]$
  - $n, \mathbf{v}$ and T do not depend on t_0 ⇨ $J[h_0, h_0] = 0$
  - Solution – local Maxwellian: $h_0 = f_{\mathrm{MB}}$
- First-order
  - $\frac{\partial h_0}{\partial t_1} + \mathbf{c} \cdot \nabla h_0 = -I[\Phi]$, here $h_1 = h_0 \Phi$

Chapman–Enskog method: 1st order

- Heat flux and stress tensor: $\mathbf{q} = 0, \quad \mathbb{P} = nk_{\mathrm{B}}T\mathbb{I}$
- Conservation laws:

Euler equations for compressible gas

$$\begin{cases} \dfrac{\partial \rho}{\partial t_1} + \nabla \cdot (\rho \mathbf{v}) = 0, \\ \rho \left(\dfrac{\partial \mathbf{v}}{\partial t_1} + (\mathbf{v} \cdot \nabla)\mathbf{v} \right) = -\nabla p + \rho \mathbf{F}/m, \\ \dfrac{3}{2} k_{\mathrm{B}} \rho \left(\dfrac{\partial T}{\partial t_1} + (\mathbf{v} \cdot \nabla) T \right) = -p \nabla \cdot \mathbf{v}, \end{cases}$$

- Substitution into BE:

Here $\mathbf{C} = \mathbf{c} - \mathbf{v}$

$$n^2 I[\Phi] = -\left[\left(\frac{mC^2}{2k_{\mathrm{B}}T} - \frac{5}{2} \right) \mathbf{C} \cdot \nabla \ln T + \frac{m}{k_{\mathrm{B}}T} \left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I} \right) : \nabla \mathbf{v} \right] f_{\mathrm{MB}}(c)$$

$$\Rightarrow \quad \Phi = -\frac{1}{n} A(C) \mathbf{C} \cdot \nabla \ln T - \frac{1}{n} B(C) \left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I} \right) : \nabla \mathbf{v}$$

Chapman–Enskog method: 2nd order

- Heat flux and stress tensor: $\mathbf{q}_1 = -\kappa\nabla T$,

$$\mathbb{P}_1 = -\eta\left[(\nabla\mathbf{v}) + (\nabla\mathbf{v})^{\mathrm{T}} - \frac{2}{3}(\nabla\cdot\mathbf{v})\mathbb{I}\right]$$

- Conservation laws:

$$\frac{\partial\rho}{\partial t_2} = 0, \qquad \rho\frac{\partial\mathbf{v}}{\partial t_2} = -\nabla\cdot\mathbb{P}_1, \qquad \frac{3}{2}k_{\mathrm{B}}\rho\frac{\partial T}{\partial t_2} = -\nabla\cdot\mathbf{q}_1$$

- Transport coefficients:
  - $\eta = \frac{k_{\mathrm{B}}T}{10}\left[B\left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I}\right), B\left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I}\right)\right]$
  - $\kappa = \frac{k_{\mathrm{B}}}{T}[A\mathbf{C}, A\mathbf{C}]$

  here *A* and *B* are functions that obey

$$I[A(C)\mathbf{C}] = -\left(\frac{mC^2}{2k_{\mathrm{B}}T} - \frac{5}{2}\right)\mathbf{C}\widehat{f}_{\mathrm{MB}}(C) \qquad I\left[B(C)\left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I}\right)\right] = -\frac{m}{k_{\mathrm{B}}T}\left(\mathbf{CC} - \frac{C^2}{3}\mathbb{I}\right)\widehat{f}_{\mathrm{MB}}(C)$$

Hard sphere model

- $\eta_0^{(\mathrm{HS})} = \dfrac{5}{16D^2}\sqrt{\dfrac{mk_\mathrm{B}T}{\pi}}$
- $\kappa_0^{(\mathrm{HS})} = \dfrac{75k_\mathrm{B}}{64D^2}\sqrt{\dfrac{k_\mathrm{B}T}{\pi m}}$
- Prandit number $\mathrm{Pr} = \dfrac{c_p\eta}{\kappa}$
  - c_p – heat capacity per unit mass
  - For ideal gas:

$$c_p = \frac{k_\mathrm{B}}{2m}\cdot\begin{cases}5, & \text{monoatomic gas}\\ 7, & \text{diatomic gas}\\ 8, & \text{polyatomic gas}\end{cases} \Rightarrow \mathrm{Pr} = \frac{2}{15}\cdot\begin{Bmatrix}5\\7\\8\end{Bmatrix} \approx \begin{cases}\boxed{0.667}\\ 0.933\\ 1.067\end{cases}$$

Table 1.1 Prandtl number (Pr) for various gases at 20 °C.

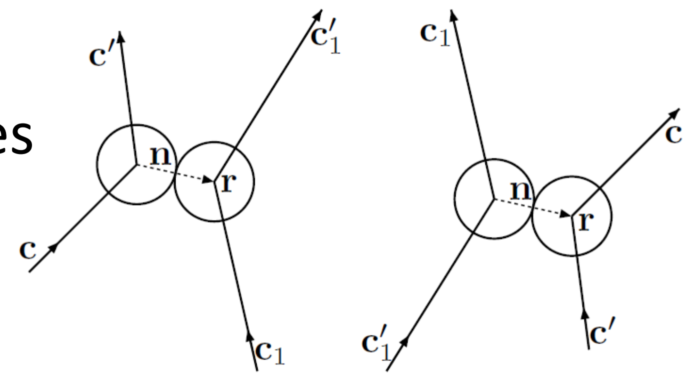
		Pr
Monoatomic gases	He	0.69
	Ne	0.66
	Ar	0.67
Diatomic gases	N_2	0.72
	O_2	0.72
	NO	0.75
	CO	0.75

Beyond BE

❖ Boundary conditions (collisions with the walls)

❖ Dense gases

➢ Enskog model for hard sphere gases



$$J[f] = D^2 \int \Big[f^{(2)}(\mathbf{r}, \mathbf{c}', \mathbf{r} - \mathbf{n}, \mathbf{c}_1') - $$
$$- f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r} + \mathbf{n}, \mathbf{c}_1)\Big] (\mathbf{g} \cdot \widehat{\mathbf{n}})\Theta(\mathbf{g} \cdot \widehat{\mathbf{n}}) \mathrm{d}^2\widehat{\mathbf{n}}\, \mathrm{d}^3 c_1$$

➢ Pair distribution function

$$f^{(2)}(\mathbf{r}_1, \mathbf{c}_1, \mathbf{r}_2, \mathbf{c}_2)\Big|_{|\mathbf{r}_1 - \mathbf{r}_2| = D} = f(\mathbf{r}_1, \mathbf{c}_1) f(\mathbf{r}_2, \mathbf{c}_2) \cdot \chi(|\mathbf{r}_2 - \mathbf{r}_1|)$$

❖ Virial expansion

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} = J[f, f] + K[f, f, f] + L[f, f, f, f,] + \cdots$$

❖ Inelastic collisions, etc.