

Thermodynamics & Statistical Physics

Chapter 11. Statistical mechanics for non-equilibrium processes

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§11.1 Relaxation time approximation of Boltzmann's equation

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$$= -\frac{\partial}{\partial x}(f v_x) dt d\tau d\omega = -\frac{\partial}{\partial x}(f \dot{x}) dt d\tau d\omega.$$

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- Similar for the velocity if there exists some external force, which makes the velocity changes (equivalently moving in the phase space): $-\frac{\partial}{\partial v_x}(f\dot{v}_x)dtd\tau d\omega$.
- In total, the number for the whole “volume”:

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- $\therefore -\left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + \dot{v}_x \frac{\partial f}{\partial v_x} + \dot{v}_y \frac{\partial f}{\partial v_y} + \dot{v}_z \frac{\partial f}{\partial v_z}\right)dtd\tau d\omega.$

Relaxation time approximation of Boltzmann's equation

- Set $X = \dot{v}_x$, $Y = \dot{v}_y$, $Z = \dot{v}_z$, the number:

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 Notice n, T, v_0 changes with \vec{r} and t .

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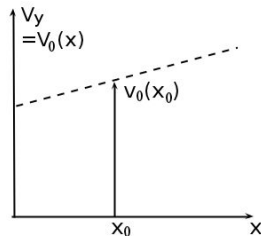
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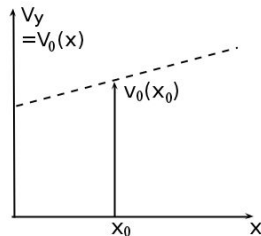
§11.2 Viscous phenomenon of gas

- Gradient in the velocity of gas flowing.
- Newton's viscosity law: $P_{xy} = \eta \frac{dv_0(x)}{dx}$,
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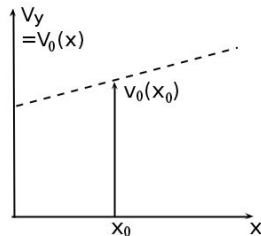
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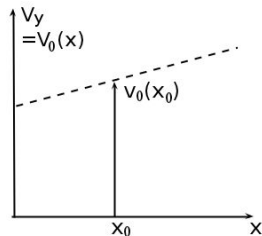
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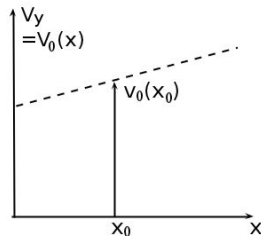
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$$\int_0^\infty dv_x \int_{-\infty}^\infty dv_y \int_{-\infty}^\infty dv_z (mv_y \cdot v_x f) \dots (a)$$

Viscous phenomenon of gas

$$v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} = -\frac{f - f^{(0)}}{\tau_0}$$

- Similarly, from right to the left:

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- Notice $F = \frac{\Delta P}{\Delta t}$, P_{xy} is also the force on unit area (parallel to the surface).

Viscous phenomenon of gas

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- Similarly, from right to the left:

$$-\int_{-\infty}^0 dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z (mv_y \cdot v_x f) \dots (b)$$
- The net momentum from right to the left (b)-(a):

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Viscous phenomenon of gas

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- Notice f is only function of x , without external force ($X = 0, Y = 0, Z = 0$), (11.1.13): $v_x \frac{\partial f}{\partial x} = -\frac{f-f^{(0)}}{\tau_0}.$

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Viscous phenomenon of gas

$$P_{xy} = \eta \frac{dv_0(x)}{dx}$$

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$$= - m \bar{\tau}_0 \int_{-\infty}^{\infty} dv_z dv_x v_x^2 \left[f^{(0)} v_y \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f^{(0)} dv_y \right]$$

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- Approximately, $\bar{\tau}_0$ is the duration between two collisions.

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 - 11.1 Relaxation time approximation of Boltzmann's equation
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 - 11.5 H theorem
 - 11.6 Detailed balance principle and f in equilibrium

§11.3 Conductivity of metal

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- $$\Rightarrow \sigma = \frac{ne^2\tau_F}{m}.$$

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 - 11.1 Relaxation time approximation of Boltzmann's equation
 - 11.2 Viscous phenomenon of gas
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 - 11.5 H theorem
 - 11.6 Detailed balance principle and f in equilibrium

§11.4 Boltzmann integro-differential equation

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- Before and after the collision, momentum and energy are conserved.

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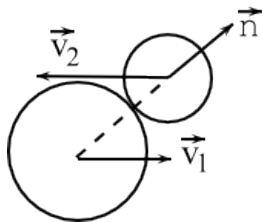
- $m_1\vec{v}_1 + m_2\vec{v}_2 = m_1\vec{v}'_1 + m_2\vec{v}'_2,$
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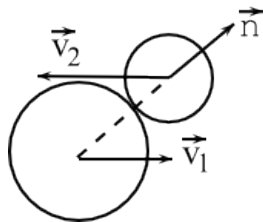
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- The solution:



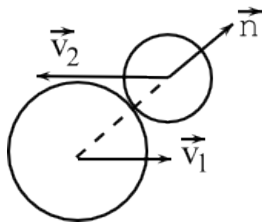
$$\vec{v}'_1 = \vec{v}_1 + \frac{2m_2}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\vec{v}'_2 = \vec{v}_2 - \frac{2m_1}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

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- The solution:

$$\vec{v}'_1 = \vec{v}_1 + \frac{2m_2}{m_1+m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

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- Reverse the solution:

Two-body collision

- $$\begin{aligned}\vec{v}_1 &= \vec{v}_1' + \frac{2m_2}{m_1+m_2} [(\vec{v}_2' - \vec{v}_1') \cdot \vec{n}] \vec{n} \\ \vec{v}_2 &= \vec{v}_2' - \frac{2m_1}{m_1+m_2} [(\vec{v}_2' - \vec{v}_1') \cdot \vec{n}] \vec{n}\end{aligned}$$

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Two-body collision

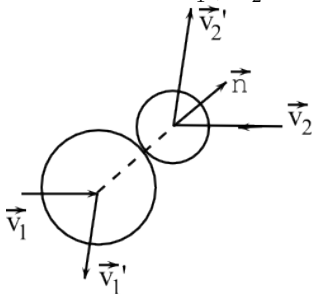
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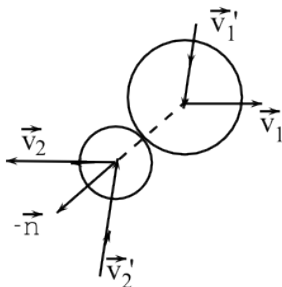
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elementary direct collision

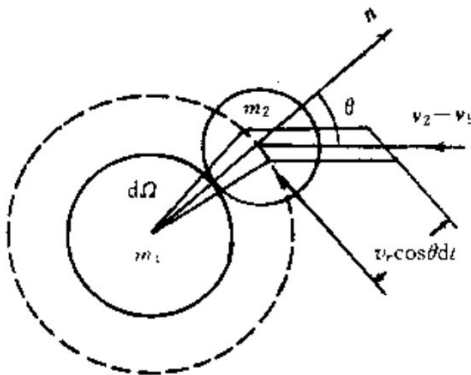


elementary inverse collision

Collision frequency

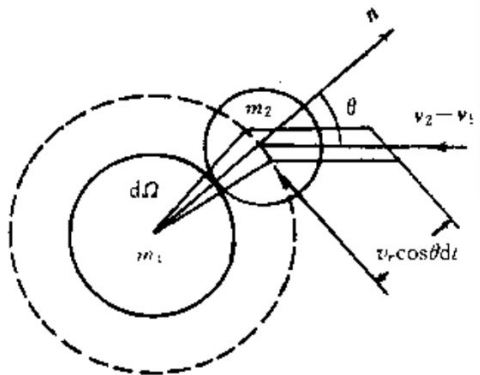
Collision frequency

- To calculate the frequency of collisions.
- Build coordinate at the center of molecule 1.



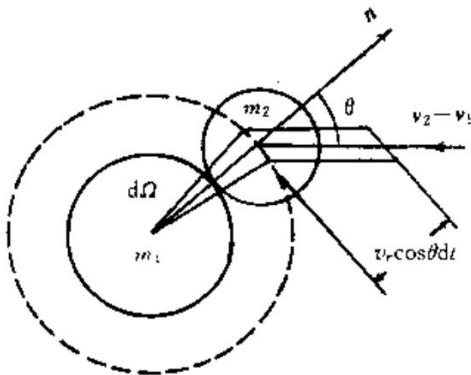
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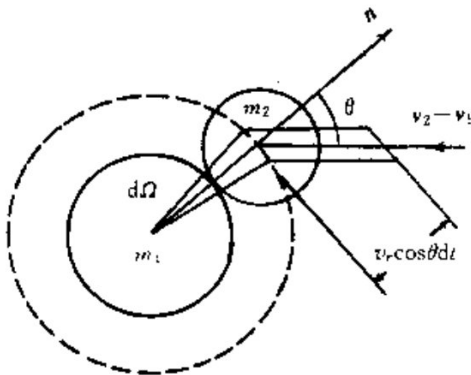
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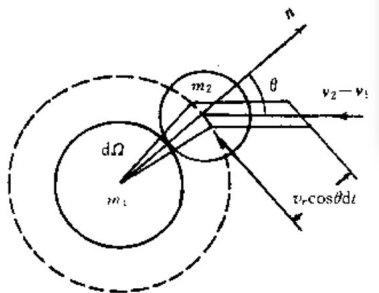
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- The collisions on the surface of m_1 in $d\Omega$, should be on the surface of $d_{12}^2 d\Omega$ for m_2 's center.



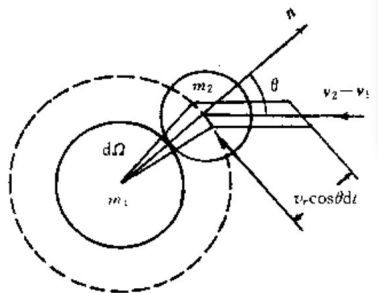
Collision frequency

- Length in dt : $v_r dt$.



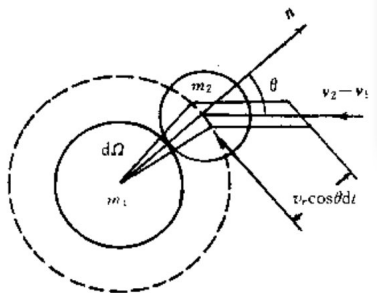
Collision frequency

- Length in dt : $v_r dt$.
- Volume: $d_{12}^2 v_r \cos \theta d\Omega dt$.



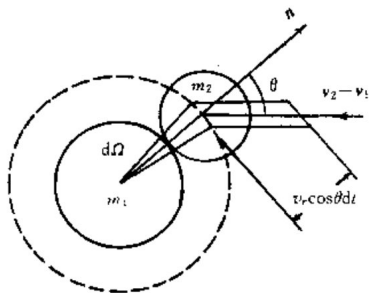
Collision frequency

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- Number in the volume:
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 where $f_2 = f(\vec{r}, \vec{v}_2, t)$ is the
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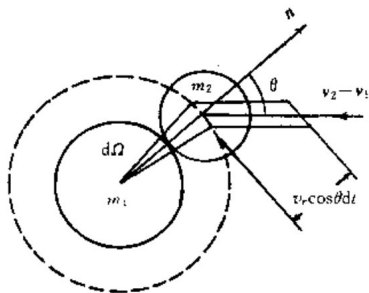
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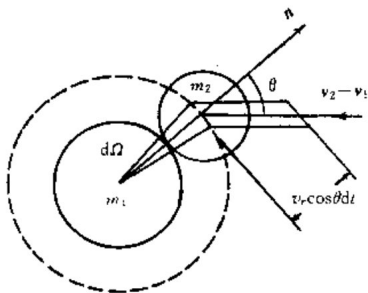
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- Then the number: $f'_1 f'_2 d\omega_1 d\omega_2 \Lambda d\Omega dt d\tau$.
- \therefore the number change because of the collisions:
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- $1 \rightarrow 2, 2 \rightarrow 1$, (11.1.12):

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- $1 \rightarrow 2, 2 \rightarrow 1$, (11.1.12): $\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z}$
 $+ X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} = \iint (f' f'_1 - f f_1) d\omega_1 \Lambda d\Omega$.

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§11.5 H theorem

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- $$\begin{aligned} & \frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \\ &= \iint (f' f'_1 - f f_1) d\omega_1 \Lambda d\Omega. \end{aligned}$$

§11.5 H theorem

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§11.5 H theorem

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- Define $H \equiv \iint f \ln f d\tau d\omega.$
- $$\frac{dH}{dt} = \frac{d}{dt} \iint f \ln f d\tau d\omega$$

§11.5 H theorem

- $$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} = \iint (f' f'_1 - f f_1) d\omega_1 \Lambda d\Omega.$$
- Define $H \equiv \iint f \ln f d\tau d\omega$.
- $$\frac{dH}{dt} = \frac{d}{dt} \iint f \ln f d\tau d\omega = \iint \frac{\partial}{\partial t} (f \ln f) d\tau d\omega$$

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 $= - \iint (1 + \ln f) (v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z}) d\tau d\omega \quad (1)$
 $- \iint (1 + \ln f) (X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z}) d\tau d\omega \quad (2)$
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$$= \iint (1 + \ln f) \frac{\partial f}{\partial t} d\tau d\omega$$

$$= - \iint (1 + \ln f) \left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} \right) d\tau d\omega \quad (1)$$

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- Inside (1), $\int (1 + \ln f) (\vec{v} \cdot \nabla f) d\tau = \int \nabla \cdot (\vec{v} f \ln f) d\tau$

$$= \oint d\vec{\Sigma} \cdot \vec{v} f \ln f$$

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$$- \iint (1 + \ln f) (X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z}) d\tau d\omega \quad (2)$$

$$- \iiint (1 + \ln f) (f f_1 - f' f'_1) d\tau d\omega_1 \Lambda d\Omega \quad (3).$$
- Inside (1), $\int (1 + \ln f) (\vec{v} \cdot \nabla f) d\tau = \int \nabla \cdot (\vec{v} f \ln f) d\tau$
 $= \oint d\vec{\Sigma} \cdot \vec{v} f \ln f = 0$, as \oint represents the integration along the surface of the container.

H theorem

- Inside (2), $\int (1 + \ln f) \left(X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) d\omega$

H theorem

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- $\frac{dH}{dt} = - \int (1 + \ln f) (ff_1 - f'f'_1) d\tau d\omega d\omega_1 \Lambda d\Omega$

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- Inside (2), $\int (1 + \ln f) \left(X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) d\omega$
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- Inside (2), $\int (1 + \ln f) (X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z}) d\omega$
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- $\frac{dH}{dt} = - \int (1 + \ln f) (ff_1 - f'f'_1) d\tau d\omega d\omega_1 \Lambda d\Omega \dots =$
 $-\frac{1}{4} \iiint [\ln(ff_1) - \ln(f'f'_1)] (ff_1 - f'f'_1) d\omega d\omega_1 \Lambda d\Omega d\tau.$

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- Inside (2), $\int (1 + \ln f) \left(X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) d\omega$
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H theorem

- Inside (2), $\int (1 + \ln f) \left(X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) d\omega$
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 $\therefore \frac{dH}{dt} \leq 0$, **H theorem.**

H theorem

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Direction of the f in collisions. (Movement does not change f .)

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- $\frac{dH}{dt} = 0$ only if $ff_1 = f'f'_1$,

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§11.6 Detailed balance principle and the distribution function in equilibrium

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§11.6 Detailed balance principle and the distribution function in equilibrium

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Boltzmann integro-differential equation (11.4.16) \rightarrow

$$v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} = 0,$$

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- $ff_1 = f'f'_1 \Rightarrow \ln f_1 + \ln f_2 = \ln f'_1 + \ln f'_2$.

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§11.6 Detailed balance principle and the distribution function in equilibrium

- $ff_1 = f'f'_1$ is the detailed balance, means in equilibrium, the f changed by collisions is canceled.
- $ff_1 = f'f'_1 \Leftrightarrow$ overall equilibrium.
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- Means before and after the collision, something is conserved. Number, momentum, energy.

The distribution function in equilibrium

- Particular solutions: $\ln f = 1, mv_x, mv_y, mv_z, \frac{1}{2}mv^2$.

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where \vec{v} is arbitrary.

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Meaning: Temperature is uniform in equilibrium.

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- For a_1 , i.e., $\nabla (\ln n - \frac{m}{2kT} v_0^2) - \frac{m}{kT} \vec{F} = 0$. Notice $\vec{F} = -\nabla \varphi$, where φ is kind of potential energy.

The distribution function in equilibrium

$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

- For a_2 , i.e., $\vec{v} \cdot \nabla \left[\frac{m}{kT} (\vec{v} \cdot \vec{v}_0) \right] = 0$. Solution is $\vec{v}_0 = \vec{a} + \vec{\omega} \times \vec{r}$, where \vec{a} and $\vec{\omega}$ are constant vectors.
Meaning: To be in equilibrium, the whole motion can only be uniformly moving or/and rotating with constant angular velocity.
- For a_1 , i.e., $\nabla (\ln n - \frac{m}{2kT} v_0^2) - \frac{m}{kT} \vec{F} = 0$.
Notice $\vec{F} = -\nabla \varphi$, where φ is kind of potential energy.
 $\Rightarrow \nabla (\ln n - \frac{m}{2kT} v_0^2 + \frac{m}{kT} \varphi) = 0$.

The distribution function in equilibrium

$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

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$$\Rightarrow \nabla \left(\ln n - \frac{m}{2kT} v_0^2 + \frac{m}{kT} \varphi \right) = 0.$$

$\Rightarrow \ln n - \frac{m}{2kT} v_0^2 + \frac{m}{kT} \varphi = \ln n_0$, where $\ln n_0$ is the integration constant.

The distribution function in equilibrium

$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

- $\Rightarrow n = n_0 e^{\frac{m}{2kT} v_0^2 - \frac{m}{kT} \varphi}.$

The distribution function in equilibrium

$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

- $\Rightarrow n = n_0 e^{\frac{m}{2kT} v_0^2 - \frac{m}{kT} \varphi}.$

Meaning: number of density can change with place.
(\vec{v}_0 and φ can vary with coordinate.)

The distribution function in equilibrium

$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

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Meaning: the whole motion must be perpendicular to the external force.

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$$\vec{v} \cdot \nabla \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{m}{2kT} (\vec{v} - \vec{v}_0)^2 \right] - \frac{m}{kT} \vec{F} \cdot (\vec{v} - \vec{v}_0) = 0$$

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- For a_0 , $\vec{v}_0 \cdot \vec{F} = 0$.

Meaning: the whole motion must be perpendicular to the external force.

- To have equilibrium, the 4 conditions (properties) above should all be satisfied. $\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = \frac{\partial T}{\partial z} = 0$;
 $\vec{v}_0 = \vec{a} + \vec{\omega} \times \vec{r}$; $n = n_0 e^{\frac{m}{2kT} v_0^2 - \frac{m}{kT} \varphi}$ and $\vec{v}_0 \cdot \vec{F} = 0$.

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