

Vacuum technology Kinetic gas theory

Csonka István
Frigyes Dávid

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The goal of kinetic gas theory

- Description of gases/bulk by solving equations of motion of individual particles
- Vast number of particles ($N \sim 10^{23}$): $3N$ differential equations, $6N$ initial values \Rightarrow statistical approach (physical quantities, p, V, T, n, \dots matter rather than ind. trajectories)
- Molecules are described in state space (q, \dot{q}, t) or phase space (q, p, t) by means of probability density functions $f(q, \dot{q}, t)$ or $f(q, p, t)$

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What can we gain?

- Equilibrium is more easily described in the general theory (statistical mechanics)
- The number of collisions is limited in vacuum \Rightarrow individual collisions become important
- Some tricks can help in special calculations
- Transport processes

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Properties of the probability density function

$f(x) \xrightarrow{\sim} f'(y)$

$f(x)dx = f'(x(y)) \frac{dx}{dy} dy$

$f(x)dx = f'(x(y)) |J| dy$

$$|J| = \begin{vmatrix} \frac{\partial x_1}{\partial y_1} & \dots & \frac{\partial x_n}{\partial y_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial x_1}{\partial y_n} & \dots & \frac{\partial x_n}{\partial y_n} \end{vmatrix}$$

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Starting point

- Particle-particle potential decays fast \rightarrow hard sphere model, only collisions
- In equilibrium, in the lack of external potential the distribution of the particles is homogeneous, isotropic

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Determination of the density function I.

- $F(x,y,z,v_x,v_y,v_z) = F(v_x,v_y,v_z) = f_x(v_x)f_y(v_y)f_z(v_z)$
- $\ln F(v_x,v_y,v_z) = \ln f_x(v_x) + \ln f_y(v_y) + \ln f_z(v_z)$ (independent events)

$$\frac{\partial \ln F}{\partial v_x} = \frac{d \ln f_x(v_x)}{dv_x}$$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$\frac{\partial \ln F}{\partial v} \cdot \frac{\partial v}{\partial v_x} = \frac{d \ln f_x(v_x)}{dv_x}$$

$$\frac{\partial \ln F}{\partial v} \cdot \frac{v_x}{v} = \frac{d \ln f_x(v_x)}{dv_x}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$\frac{\partial v^2}{\partial v} \cdot \frac{\partial v}{\partial v_x} = \frac{dv_x^2}{dv_x} = 2v_x$$

$$2v \cdot \frac{\partial v}{\partial v_x} = 2v_x$$

$$\frac{\partial v}{\partial v_x} = \frac{v_x}{v}$$

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Determination of the density function II.

$$\frac{\partial \ln F}{\partial v} \cdot \frac{1}{v} = \frac{d \ln f_x(v_x)}{dv_x} \cdot \frac{1}{v_x} = \frac{d \ln f_y(v_y)}{dv_y} \cdot \frac{1}{v_y} = \dots$$

$$\frac{d \ln f_x(v_x)}{dv_x} \cdot \frac{1}{v_x} = -\beta$$

$$d \ln f_x(v_x) = -\beta \cdot v_x dv_x$$

$$\ln f_x(v_x) = -\frac{\beta}{2} \cdot v_x^2 + \ln a$$

$$f_x(v_x) = \alpha \cdot e^{-\frac{\beta}{2} v_x^2}$$

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Determination of the density function III. (α)

$$f_x(v_x) = \alpha e^{-\frac{\beta}{2} v_x^2}$$

$$1 = \int_{-\infty}^{\infty} f_x(v_x) dx = \alpha \int_{-\infty}^{\infty} e^{-\frac{\beta}{2} v_x^2} dx = \alpha \sqrt{\frac{2\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

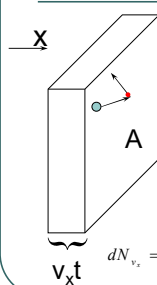
$$f_x(v_x) = \sqrt{\frac{\beta}{2\pi}} \cdot e^{-\frac{\beta}{2} v_x^2}$$

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Determination of the density function IV. (β)



$\Delta(\text{momentum}) = 2mv_x$ (1 molecule)

pressure $p = \frac{F}{A} = \frac{1}{A} \cdot \Delta(\text{momentum})$

$F = \frac{d(\text{momentum})}{dt}$

$p_{v_x} = \frac{F_{v_x}}{A} = 2 \cdot z^{fal} \cdot mv_x$ (Wall-collisions)

$\frac{dN_{v_x}}{V} \cdot A \cdot v_x \cdot t$ Molecules reach the wall

$dN_{v_x} = N \cdot f_x(v_x) dv_x \implies z^{fal} = \frac{N}{V} \cdot f_x(v_x) \cdot v_x dv_x$

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Determination of the density function IV. (β)

$$p_{v_x} = 2 \cdot z^{fal} \cdot m \cdot v_x = 2 \left(\frac{N}{V} \cdot f_x(v_x) dv_x \cdot v_x \right) m v_x = \frac{2N \cdot m}{V} v_x^2 f_x(v_x) dv_x$$

$$pV = 2N \cdot m \int_0^{\infty} v_x^2 f_x(v_x) dv_x = Nm \int_{-\infty}^{\infty} v_x^2 f_x(v_x) dv_x$$

$$pV = \frac{N}{N_A} RT = NkT \implies \int_{-\infty}^{\infty} v_x^2 f_x(v_x) dv_x = \frac{kT}{m}$$

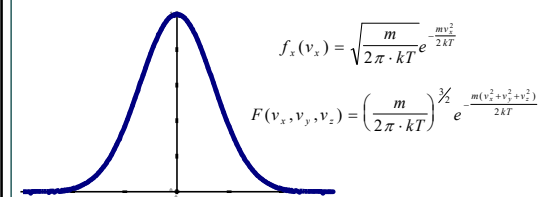
$$\frac{kT}{m} = \sqrt{\frac{\beta}{2\pi}} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{\beta}{2} v_x^2} dv_x = \sqrt{\frac{\beta}{2\pi}} \cdot \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\beta} \implies \beta = \frac{m}{kT}$$

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The density function(s)



Even functions... what's happened?

We are rather interested in $\langle |v| \rangle$!

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Some more functions...

For the distribution of $|v|$ transform it to polar coordinates

$$\hat{f}(v, \vartheta, \varphi) = \left| \frac{\partial F(v)}{\partial v \partial \vartheta \partial \varphi} \right| F(v) =$$

$$= (v^2 \sin \vartheta) \left(\frac{m}{2\pi \cdot kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}}$$

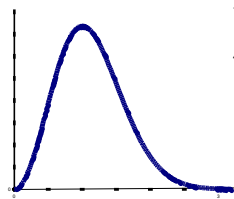
$$f(v) = \int_0^{2\pi} \int_0^\pi \hat{f}(v, \vartheta, \varphi) d\varphi d\vartheta = \int_0^{2\pi} \int_0^\pi \sin \vartheta d\vartheta d\varphi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} =$$

$$= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} \quad \text{Maxwell-velocity distribution}$$

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Getting better...



$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v \cdot v^2 e^{-\frac{mv^2}{2kT}} dv =$$

$$4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2 \left(\frac{m}{2kT} \right)^2} = \sqrt{\frac{8kT}{\pi m}}$$

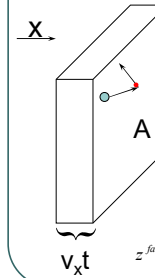
$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

$$v_m = \sqrt{\frac{2kT}{m}}$$

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Number of wall-collisions



$$\frac{dN_{v_x}}{V} \cdot A \cdot v_x t \quad \text{Molecules reach the wall}$$

$$dN_{v_x} = N \cdot f_x(v_x) dv_x \implies z_{v_x}^{fat} = \frac{N}{V} \cdot f_x(v_x) \cdot v_x dv_x$$

$$\int_0^\infty f_x v_x dv_x = \sqrt{\frac{m}{2\pi \cdot kT}} \int_0^\infty v_x e^{-\frac{mv_x^2}{2kT}} dv_x =$$

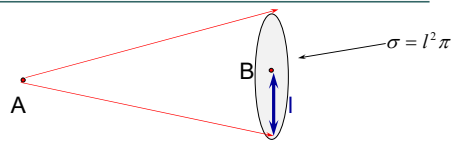
$$= \sqrt{\frac{m}{2\pi \cdot kT}} \frac{kT}{m} = \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{1}{4} \langle v \rangle$$

$$z^{fat} = \frac{N}{4V} \cdot \langle v \rangle = \frac{N}{V} \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{p}{kT} \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{p}{\sqrt{2\pi \cdot mkT}}$$

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Molecular collisions



- Any molecule collides with a maximum of 1 other one
- Relative velocity matters, it has a characteristic distribution, calculated from Maxwell-distribution
- Number of collisions (/s): $\int_0^\infty \sigma v_r \frac{N}{V} f(v_r) dv_r$

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The distribution of the relative velocity

- Look at two molecules. The probability that the velocity of the first one is between v_1 and $v_1 + dv_1$, and the others are between v_2 and $v_2 + dv_2$ (independent events):

$$f_{12}(v_1, v_2) dv_1 dv_2 = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv_1^2}{2kT}} dv_{1x} dv_{1y} dv_{1z} \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv_2^2}{2kT}} dv_{2x} dv_{2y} dv_{2z}$$

- The location vectors of the center-of-mass (r_0) and the relative location vector (r_r):

$$\vec{r}_0 = \frac{1}{2} (\vec{r}_1 + \vec{r}_2) \quad \vec{r}_r = \vec{r}_2 - \vec{r}_1$$

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The distribution of the relative velocity (2)

- The individual velocities:

$$\vec{v}_1 = \dot{\vec{r}}_0 - \frac{1}{2} \vec{v}_r \quad \vec{v}_2 = \dot{\vec{r}}_0 + \frac{1}{2} \vec{v}_r$$

$$m(v_1^2 + v_2^2) = 2m\dot{r}_0^2 + \frac{m}{2} v_r^2$$

$$|J| = 1$$

$$f_{12}(\vec{v}_1, \vec{v}_2) d\vec{v}_1 d\vec{v}_2 = \left(\frac{m}{4\pi kT} \right)^{3/2} e^{-\frac{mv_1^2}{4kT}} dv_{1x} dv_{1y} dv_{1z} \left(\frac{m}{\pi kT} \right)^{3/2} e^{-\frac{mv_r^2}{kT}} dv_{rx} dv_{ry} dv_{rz}$$

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The distribution of the relative velocity (3)

• A product of two factors, depending on relative and center-of-mass, respectively; the first is more important to us:

$$f_r(\vec{v}_r) d\vec{v}_r = \left(\frac{m}{4\pi kT}\right)^{3/2} e^{-\frac{m v_r^2}{4kT}} dv_{rx} dv_{ry} dv_{rz}$$

• And the expected value:

$$\langle v_r \rangle = 4\pi \left(\frac{m}{4\pi kT}\right)^{3/2} \int_0^\infty v_r^3 e^{-\frac{m v_r^2}{4kT}} dv_r = \sqrt{2} \langle v \rangle$$

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Collision number Mean free path

$$Z = \int_0^\infty \sigma v_r \frac{N}{V} f(v_r) dv_r = \frac{N}{V} \sigma \langle v_r \rangle = n \sigma \sqrt{2} \langle v \rangle = \frac{4N}{V} \sigma \sqrt{\frac{kT}{\pi m}} = \sqrt{\frac{16\sigma^2}{kT\pi m}} p$$

• The free path is the ratio of the mean velocity and the collision number (a particle travels $\langle v \rangle$ and collides Z times at a during a time unit):

$$\lambda = \frac{\langle v \rangle}{Z} = \frac{V}{\sqrt{2} N \sigma} = \frac{kT}{\sqrt{2} p \sigma} \quad \left(\frac{V}{N} = \frac{kT}{p}\right)$$

• The time passed between molecular collisions: $\tau = \frac{1}{Z}$

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The distribution of free path

$p(x)$ is the probability that a particle travels a distance x without collision

$$p(x+dx) = p(x)p(dx) = p(x) + \frac{dp}{dx} dx$$

The probability $\tilde{p}(dx)$ that the particle collides at path dx is proportional to dx

$$\tilde{p}(dx) = \alpha dx$$

$$p(dx) = 1 - \tilde{p}(dx) = 1 - \alpha dx$$

$$p(x+dx) = p(x) + \frac{dp}{dx} dx = p(x)(1 - \alpha dx)$$

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The distribution of free path (2)

$$\frac{dp}{dx} = -\alpha p(x) \implies p(x) = A e^{-\alpha x} \quad (\text{limits} \implies A=1)$$

dP is the probability that the particle travels freely path x then collides on distance dx :

$$dP = p(x)\tilde{p}(dx) = p(x)\alpha dx = \alpha e^{-\alpha x} dx$$

$$\lambda = \int_0^\infty x dP = \int_0^\infty x \alpha e^{-\alpha x} dx = \frac{1}{\alpha}$$

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The distribution of free path (3)

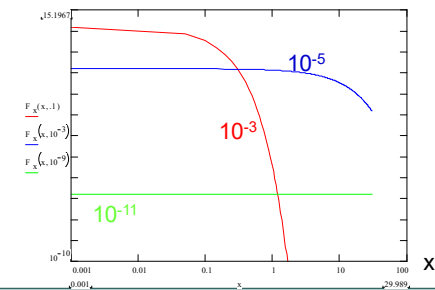
$$dP = \frac{1}{\lambda} e^{-\frac{1}{\lambda}x} dx \implies F(x) = \frac{1}{\lambda} e^{-\frac{1}{\lambda}x}$$

The time passed between collisions can be calculated analogously, only the integral is different:

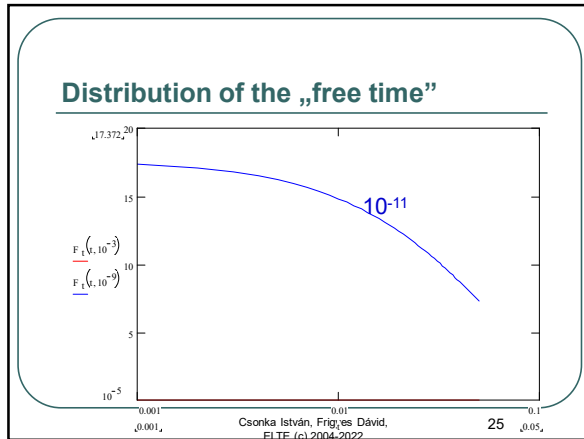
$$F_i(t) = Z e^{-Zt}$$

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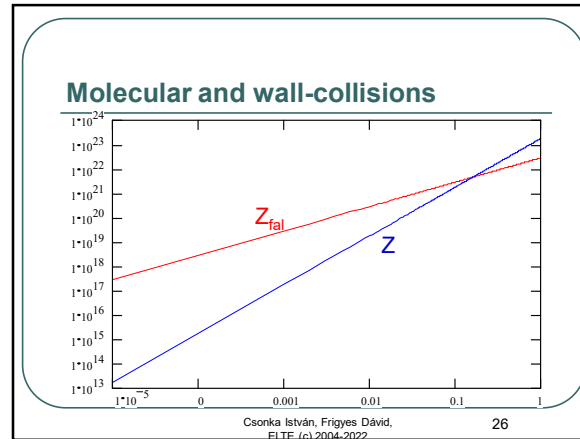
Distribution of the free path (4)



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Transport phenomena

- Close to equilibrium but a physical quantity is not homogeneous
- p (momentum): viscosity
- c: diffusion
- T: thermal conductance
- Can be described by means of collision numbers

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Number of wall-collisions

Molecules reach the wall

$$\frac{dN_{v_x}}{V} \cdot A \cdot v_x t$$

$$dN_{v_x} = N \cdot f_x(v_x) dv_x \implies z^{fal} = \frac{N}{V} \cdot f_x(v_x) \cdot v_x dv_x$$

$$\int_0^\infty f_x v_x dv_x = \sqrt{\frac{m}{2\pi \cdot kT}} \int_0^\infty v_x e^{-mv_x^2/2kT} dv_x = \sqrt{\frac{m}{2\pi \cdot kT}} \frac{kT}{m} = \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{1}{4} \langle v \rangle$$

$$z^{fal} = \frac{N}{4V} \cdot \langle v \rangle = \frac{N}{V} \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{p}{kT} \sqrt{\frac{kT}{2\pi \cdot m}} = \frac{p}{\sqrt{2\pi \cdot mkT}}$$

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Viscosity – transport of momentum

$$\eta = \frac{F_x}{A \cdot \frac{u_{max}}{d}}$$

Number of particles reaching the wall (t/A): $z^{fal} = \frac{\langle v \rangle N}{4V}$

Their momentum in direction x: $\frac{\langle v \rangle N}{4V} m u_{max} \frac{\lambda_0}{d} \approx \frac{\langle v \rangle}{3} \rho u_{max} \frac{\lambda}{d}$

The force: $\frac{F_x}{A} = \frac{\langle v \rangle}{3} \rho u_{max} \frac{\lambda}{d} \implies \eta = \frac{\langle v \rangle}{3} \rho \lambda \sim \sqrt{T}$

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Discussion

- This formula holds except for
 - High pressure (starting point of kinetic gas theory is not true), but this is not the case in vacuum
 - Low pressure: when $\lambda > d$, the actual value of λ does not matter

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Viscosity at pure molecular flow

- The particle travels without collisions, thus there is no linear velocity distribution in direction y but the particle obtains the momentum of the surfaces:

$$\frac{F_x}{A} = \frac{1}{\beta} \frac{\langle v \rangle}{4} \rho u_{\max}$$

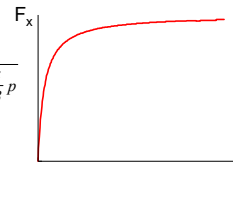
Close to 1

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Transition (Knudsen) range

- The two effects (free travel between walls and linear velocity distribution) apply together

$$\frac{F_x}{A} = \frac{1}{\beta + \alpha \frac{d}{\lambda}} \langle v \rangle \rho \cdot u_{\max} \sim \frac{p}{1 + \frac{\alpha}{\beta} p}$$



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Thermal conductivity The transport of kinetic energy

Heat flux/hőáramsűrűség $j_q = \frac{P}{A} = -\kappa \frac{\Delta T}{d}$ power

$\kappa = \frac{5}{6} k \lambda \langle v \rangle \frac{N}{V}$: independent of pressure (limits)

$\langle v_x^2 \rangle = \frac{kT}{m}$ $\langle E_{kin} \rangle = \frac{3}{2} NkT \rightarrow c_v = \frac{C}{V} = \frac{E}{TV} = \frac{3}{2} \frac{Nk}{V}$

$\kappa = \frac{5}{9} \lambda \langle v \rangle c_v$ κ is proportional to η ; c_v breaks the law at higher range

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Free molecular thermal conductivity

The particle obtains part of the energy of the heated surface.
Accommodation coefficient:

$$\alpha = \frac{T_r - T_1}{T_2 - T_1}$$

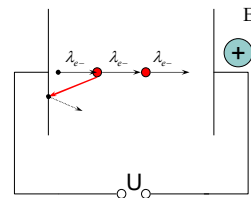
α	H ₂	N ₂
plain Pt	0,36	0,89
Pt black	0,71	0,95
W	0,20	0,57

$$j_q = \frac{P}{A} = \frac{\langle v \rangle_1}{4} \frac{N}{V} 2k(T_r - T_1) = \frac{\langle v \rangle_1}{2} \frac{p}{T_1} (T_r - T_1) = \frac{\alpha \langle v \rangle_1}{2} \frac{p}{T_1} (T_2 - T_1)$$

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Electrical conductivity

$$\lambda_{ion} = \sqrt{2} \lambda \quad \lambda_{e^-} = 4 \lambda \quad \langle KE_e \rangle = e \frac{\lambda_{e^-}}{d} U$$



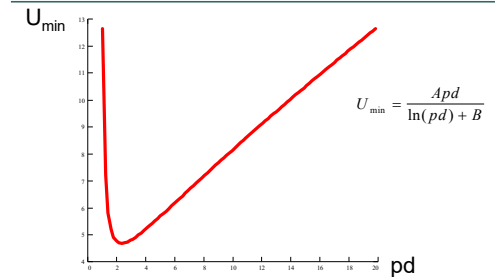
Electron avalanche: $IE \leq e \frac{\lambda_{e^-}}{d} U$

$$U_{\min} = \frac{IE \cdot d}{\lambda \cdot e} \sim pd$$

Continuous discharge:
avalanche + electron supply
Low pressure: lack of charge carrier

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Paschen-curve



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Types of electric discharge

- Spark (short time, e.g., conductors moving away)
- Arc (continuous electron supply)
- Glow discharge (low pressure, glow)
- Corona discharge (partial discharge around sharp conductor)

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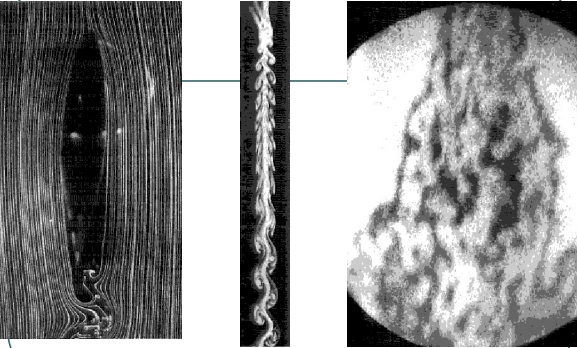
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Gas flow – particle transport

- Viscous flow: Reynolds-number:
 - Laminar flow ($Re < 1200$)
 - Turbulent flow ($Re > 2200$)
$$Re = \frac{du\rho}{\eta}$$
- Knudsen-number:
 - Molecular flow ($Kn > 1$)
 - Transition regime ($1 > Kn > 0,01$)
 - Viscous flow ($Kn < 0,01$)
$$Kn = \frac{\lambda}{d}$$

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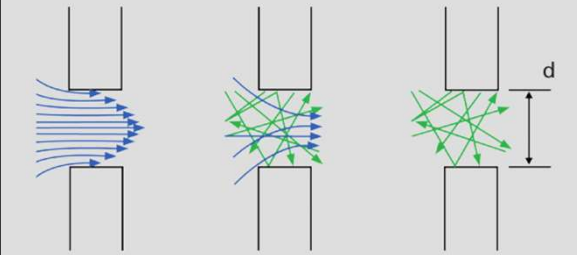
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laminar transition turbulent

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Continuous flow
 $Kn < 0.01$
Low vacuum

Knudsen flow
 $0.01 < Kn < 0.5$
Medium vacuum

Molecular flow
 $Kn > 0.5$
High/ Ultra-high vacuum

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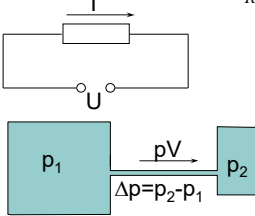
	Viscous flow	Knudsen flow	Molecular flow
Pressure range [hPa]	$10^3 \dots 1$	$1 \dots 10^{-3}$	High // Ultra-high vacuum
Pressure range [Pa]	$10^5 \dots 10^2$	$10^2 \dots 10^{-1}$	$< 10^{-3}$ // $< 10^{-7}$
Knudsen number	$Kn < 0.01$	$0.01 < Kn < 0.5$	$Kn > 0.5$
Reynolds number	$Re < 2,300$: laminar $Re > 4,000$: turbulent		
$p \cdot d$ [hPa cm]	$p \cdot d > 0.6$	$0.6 > p \cdot d > 0.01$	$p \cdot d < 0.01$

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Conductance

Analogy:



$$R = \frac{U}{I} \quad G = \frac{1}{R} = \frac{I}{U}$$

$$I = \frac{dQ}{dt} = G\Delta U = \frac{\Delta U}{R}$$

$$\frac{d}{dt} pV = \frac{\Delta p}{Z} = C\Delta p$$

$$[C] = \frac{[V]}{[t]} = \frac{l}{s}$$

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Resultant conductance

Series: $\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \dots$

Parallel: $C = C_1 + C_2 + \dots$

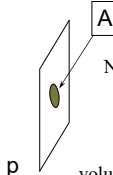
Conductance depends on:

- Type of flow (molecular, Knudsen, laminar, turbulent)
- pressure (independent in molecular flow)
- M
- T

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Flow through a hole (molecular!!!)



Number of particles / time unit: $z^{fal} = A \frac{N}{4V} \cdot \langle v \rangle$

mass: $m z^{fal} = A \frac{N}{4V} m \cdot \langle v \rangle = A \frac{\langle v \rangle}{4} \rho$

volume: $A \frac{\langle v \rangle}{4}$ Gas amount: $Q = pV = pA \frac{\langle v \rangle}{4}$

Flowing into non-zero p (backflow):

$$Q = A \frac{\langle v \rangle}{4} \Delta p = \frac{\langle v \rangle}{4} \frac{d^2 \pi}{4} \Delta p = A \frac{1}{4} \sqrt{\frac{8kT}{\pi m}} \Delta p$$

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Examples

- Long tube, laminar flow, Poiseuille-law:

$$Q = \frac{\pi \cdot d^4}{128 \eta \cdot L} C (p_1 - p_2)$$

- Long tube, molecular flow:

$$C = \frac{16}{3} \sqrt{\frac{kT}{2m\pi}} \frac{A^2}{o} L$$

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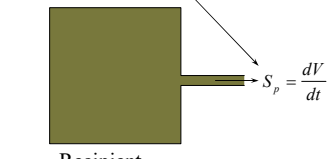
Flow through hole (23°C, air)

- Viscous flow ($p_1/p_2=0,5$): $C_{viszk} = 40 A \frac{l}{s}$
- Viscous flow ($p_1/p_2=1$): $C_{viszk} = 20 A \frac{l}{s}$
- Molecular flow: $C_{mol} = 11,6 A \frac{l}{s}$

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Pumping speed, Throughput



Recipient

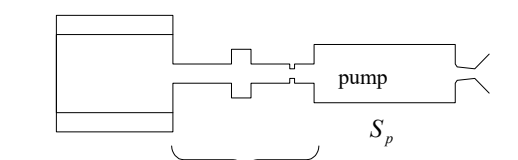
Throughput is identical in the whole instrument (energy dimension)

$$S_p = \frac{dV}{dt} \quad Q = pS_p = p \frac{dV}{dt} = C\Delta p$$

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Effective pumping speed



Important in design/implementation!

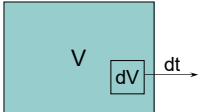
$$\frac{1}{S_{eff}} = \frac{1}{S_p} + \frac{1}{C_{tot}}$$

$$\frac{1}{C_{tot}} = \frac{1}{C_1} + \frac{1}{C_2} + \dots$$

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Pumping speed



$$S = \frac{dV}{dt}$$

$$dp = -\frac{dV}{V} \cdot p = -\frac{S dt}{V} \cdot p$$

$$p = p_0 e^{-\frac{S}{V} t} \xrightarrow{(t=\frac{V}{S})} p = \frac{p_0}{e}$$

Pumps

- compression
- trapping

True only when volume pumping (outgassing!!!)

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Basic equation of vacuum technology

$$V \frac{dp}{dt} = I_{be} - pS_p$$

I_{be}

- holes
- desorption
- evaporation

gas load
Statical/dynamic vacuum system

Final vacuum:
Pressure is no longer decreasing:

$$V \frac{dp}{dt} = I_{be} - pS_p = 0$$

$$I_{be} = pS_p \quad \text{ill.:} \quad I_{be} = pS_{eff}$$

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