Kinetičko-molekularna teorija plinova

Rudolf Clausius, 1857

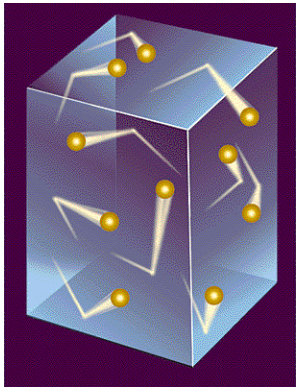
Pretpostavke:

- Plinovi se sastoje od velikog broja molekula (ili atoma-u slučaju plemenitih plinova) koje se neprestano gibaju
- Volumen svih molekula plina je zanemariv u usporedbi s ukupnim volumenom spremnika u kojem se plin nalazi
- Privlačne i odbojne sile između molekula plina su zanemarive

- Prosječna kinetička energija molekula se ne mijenja s vremenom (pri konstantnoj temperaturi). Energija se izmjenjuje (prenosi) između molekula tijekom sudara. Sudari su potpuno elastični.

- Prosječna kinetička energija molekula proporcionalna je apsolutnoj temperaturi

Tlak plina-posljedica je sudara molekula sa stjenkom spremnika (Iznos tlaka ovisi o tome kako jako i kako često molekule udaraju u stjenku)



Pretpostavimo :

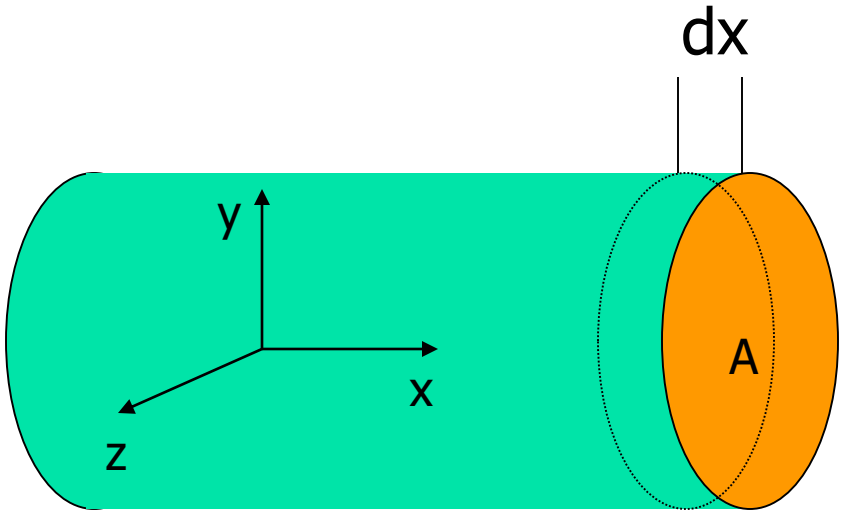
Plin se sastoji od N molekula

(N je veliki broj, reda veličine Avogadrovog broja N_A=6,023 10^{23} molekula/mol

Molekule imaju masu m

Molekule se nalaze u volumenu V i pri temperaturi T

"Brojčana gustoća" N/V



Kako definirati brzinu gibanja u?

Velik broj čestica-čestice se gibaju u smjeru osi x, y i z

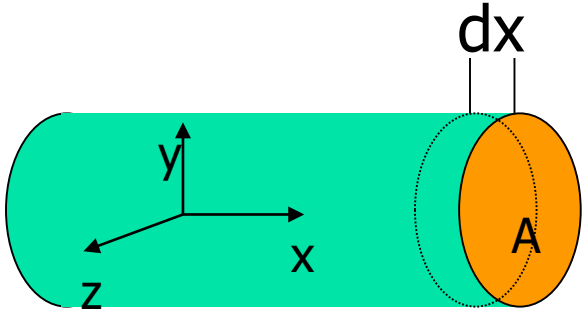
Srednja (prosječna) brzina gibanja može se prostorno rastaviti na tri međusobno okomite komponente:

$$\bar{u}^2 = \bar{u}_x^2 + \bar{u}_y^2 + \bar{u}_z^2$$

Statistički, u smjeru osi x (y, z) giba se N/3 čestica

1/2 od N/3 (N/6) se giba u desno

N/6 se giba u lijevo



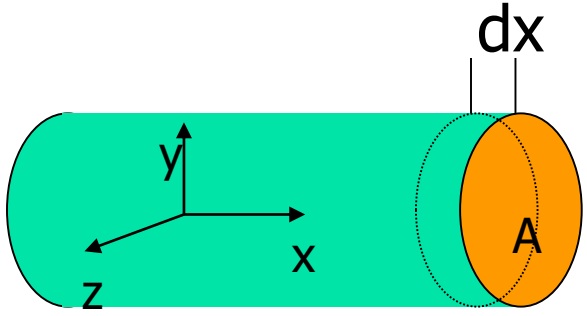
Koliko će molekula udariti u klip u malom odsječku vremena dt?

Udarit će one koje su blizu klipu (volumen na udaljenosti dx)

$$\bar{u}_x = \frac{dx}{dt} \qquad dx = \bar{u}_x dt$$

Udaljenost dx i površina A kreiraju volumen Adx koji sadrži

$$\frac{N}{V} A\bar{u}_x dt$$ molekula



Broj čestica koje u vremenu dt udaraju na površinu klipa

$$\frac{N}{V} A\bar{u}_x dt \cdot \frac{1}{6}$$

Impuls koji klip dobiva od svih molekula u vremenu dt:

$$dI = \frac{N}{V} A\bar{u}_x dt \cdot \frac{1}{6} \cdot 2m\bar{u}_x$$

Elastični sudar: pri sudaru i pri odbijanju molekula predaje klipu impuls mu_x

$$dI = \frac{1}{3}\frac{N}{V} A\bar{u}_x^2 m \cdot dt$$

$$\frac{dI}{dt} = F = \frac{1}{3}\frac{N}{V} A \bar{u}_x^2 m$$

$$\bar{u}_x = \bar{u}$$

(Komponente brzine $\bar{u}_y$ i $\bar{u}_z$ za promatrane molekule jednake su nuli)

Tlak

$$p = \frac{F}{A} = \frac{1}{3}\frac{N}{V} m \cdot \bar{u}^2 \qquad /\cdot V_m$$

$$p \cdot V_m = \frac{1}{3} \frac{N}{V} \cdot V_m \cdot m \cdot \bar{u}^2$$

$$n = \frac{V}{V_m}$$

$$p \cdot V_m = \frac{1}{3} \frac{N}{n} \cdot m \cdot \bar{u}^2$$

$$\rightarrow N_A$$

$$p \cdot V_m = \frac{1}{3} N_A \cdot m \cdot \bar{u}^2$$

$$p \cdot V_m = \frac{1}{3} M \bar{u}^2$$

$$p \cdot V_m = RT$$

$$\frac{1}{3} M \bar{u}^2 = RT$$

$$\bar{u} = \sqrt{\frac{3RT}{M}}$$

$$M \bar{u}^2 = 3RT \qquad / \cdot \frac{1}{2}$$

$$\bar{E}_{kin} = \frac{1}{2} M \bar{u}^2 = \frac{3}{2} RT$$

Srednja kinetička energija 1 mola plina

Dijeljenjem gornje jednadžbe s Avogadrovim brojem dobiva se srednja kinetička energija jedne molekule plina

$$\bar{\varepsilon}_{kin} = \frac{1}{2} m \cdot \bar{u}^2 = \frac{3}{2} kT \longrightarrow \frac{R}{N_A} = k$$

Budući da je

$$\overline{E}_{kin} = \frac{1}{2} M\overline{u}^2 = \frac{3}{2} RT$$

$$\overline{u}^2 = \overline{u}_x^2 + \overline{u}_y^2 + \overline{u}_z^2$$

Vrijedi da je

$$\frac{1}{2} M\overline{u}_x^2 + \frac{1}{2} M\overline{u}_y^2 + \frac{1}{2} M\overline{u}_z^2 = \frac{3}{2} RT$$

Prema statistici

$$\frac{1}{2} M\overline{u}_x^2 = \frac{1}{2} RT$$

$$\frac{1}{2} M\overline{u}_y^2 = \frac{1}{2} RT$$

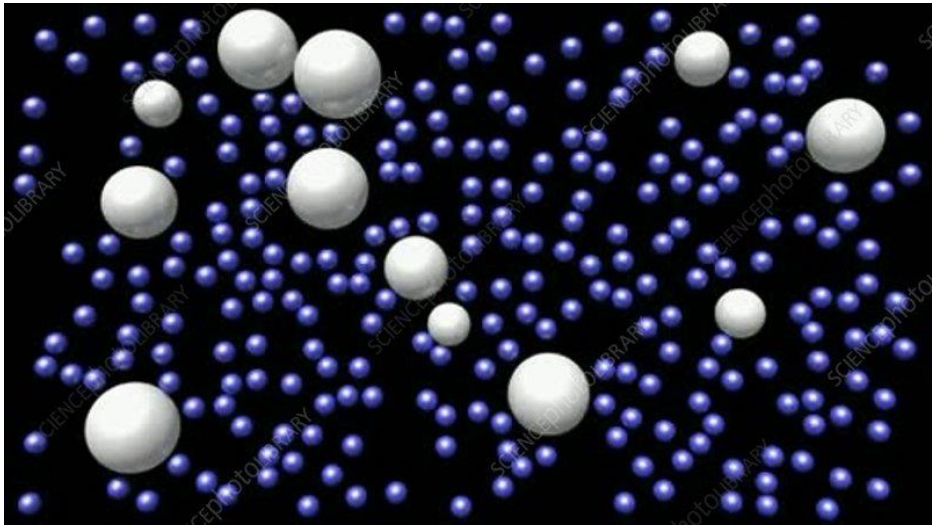
$$\frac{1}{2} M\overline{u}_z^2 = \frac{1}{2} RT$$

Princip ekviparticije energije

Translacijsko gibanje molekula može se rastaviti na tri komponente s istim srednjim sadržajem energije-posjeduje 3 stupnja slobode



Brownovo gibanje

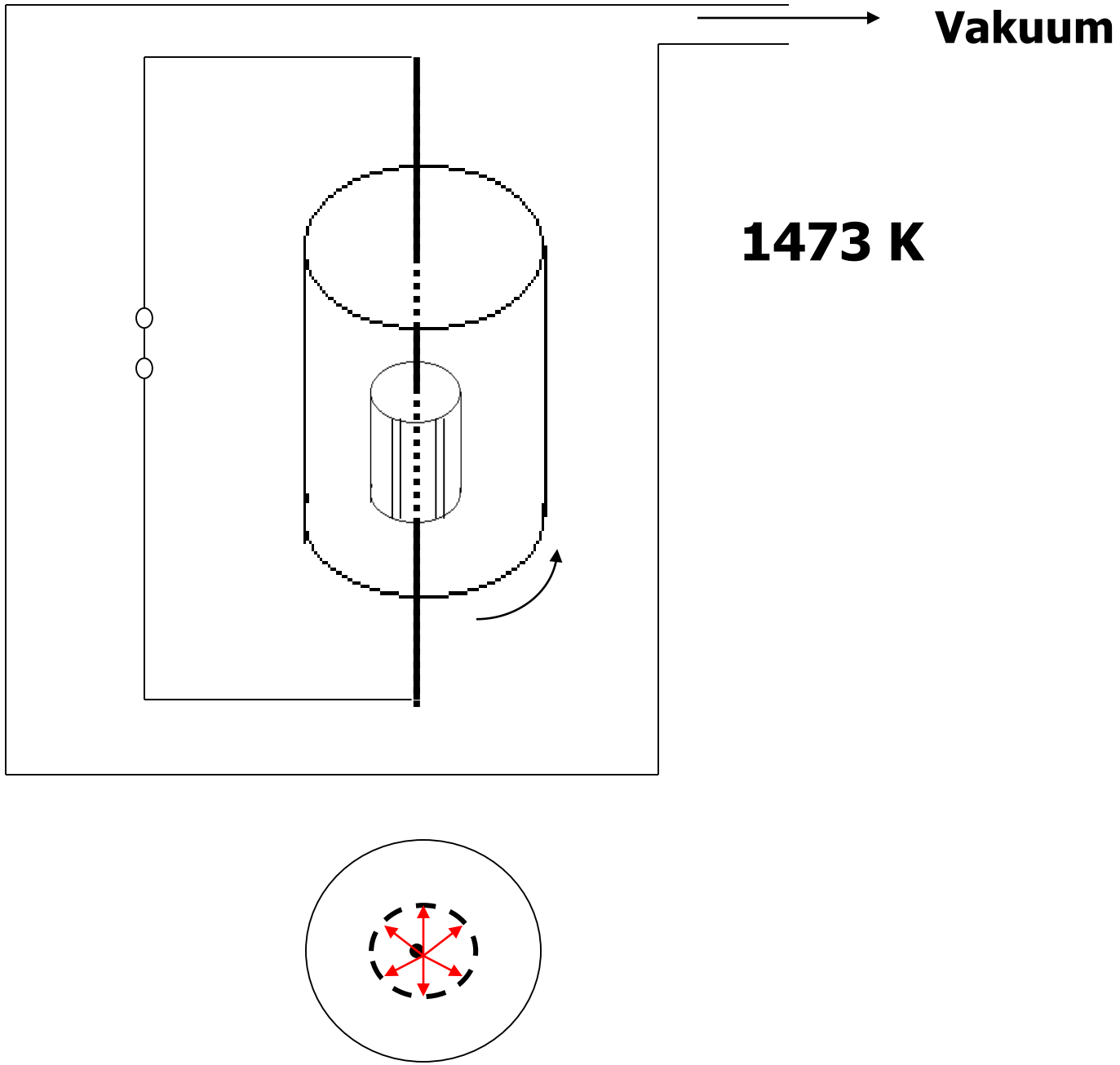


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https://www.sciencephoto.com/media/611608/view/brownian-motion-animation

1920.

O. Stern



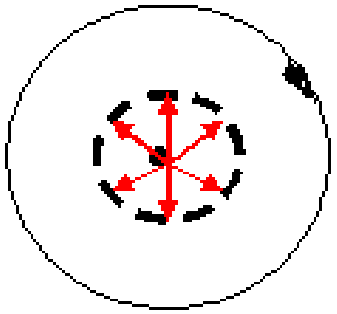
T=1473 K

u(exp)=550 m/s

$$\bar{u} = \sqrt{\frac{3RT}{M}}$$

$$\bar{u} = \sqrt{\frac{3 \cdot 8{,}314 \cdot 1473}{0{,}109}} = 586 m/s$$ **=2109,6 km/h**

U idealnom plinu molekule (atomi) ne gibaju se istim brzinama





https://www.youtube.com/watch?v=d3g4W9cVHII

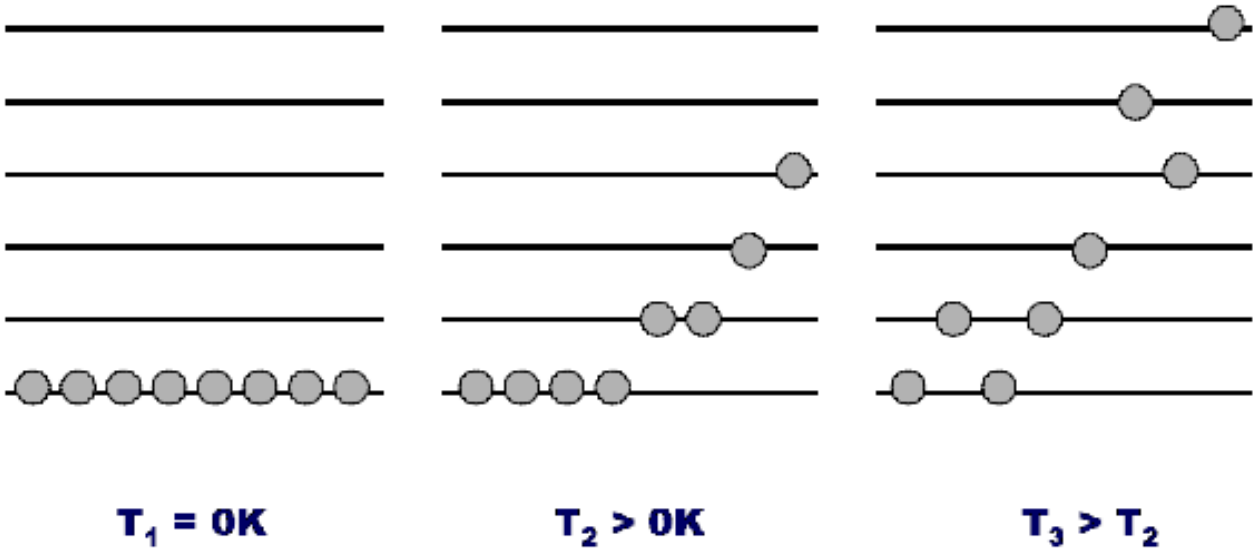
Boltzmann-ova raspodjela



(1844, Beč-1906)

-zakon statističke mehanike koji opisuje raspodjelu energije između molekula plina u termičkoj ravnoteži

-Molekule se raspodjeljuju po raspoloživim energijskim razinama



$$N_i = \frac{N \cdot e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

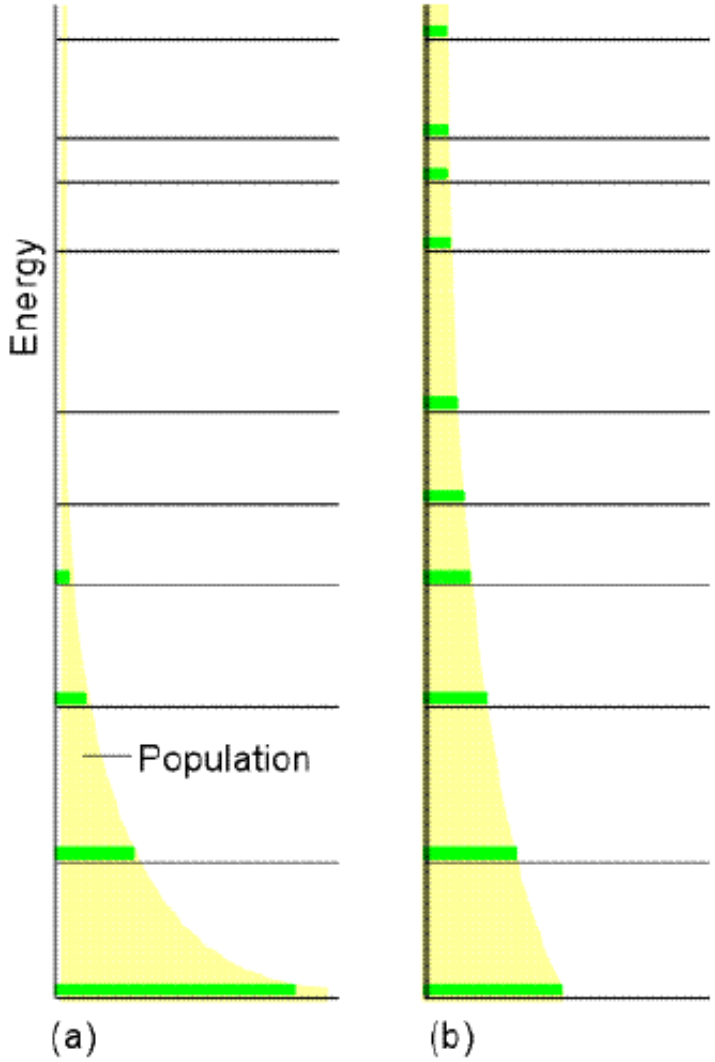
N_i-broj čestica u uzorku od N čestica koje imaju energiju E_i u uvjetima toplinske ravnoteže pri temperaturi T.

k=1,381 10^{-23} J/K

Omjer broja čestica u različitim energijskim stanjima

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT}$$

$$f(E) = Ae^{-(E_i/kT)}$$

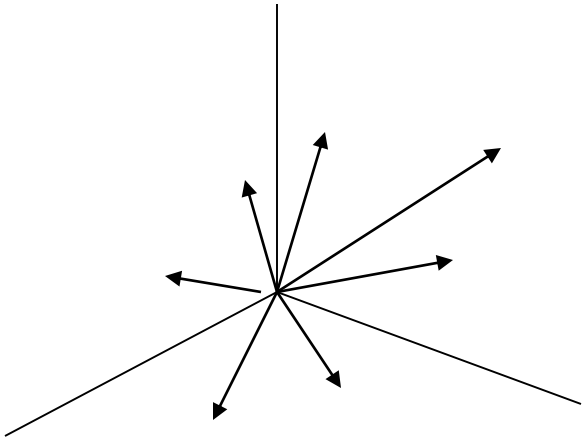


Niske T **Visoke T**

Vjerojatnost da će čestica imati energiju E eksponencijalno pada s energijom

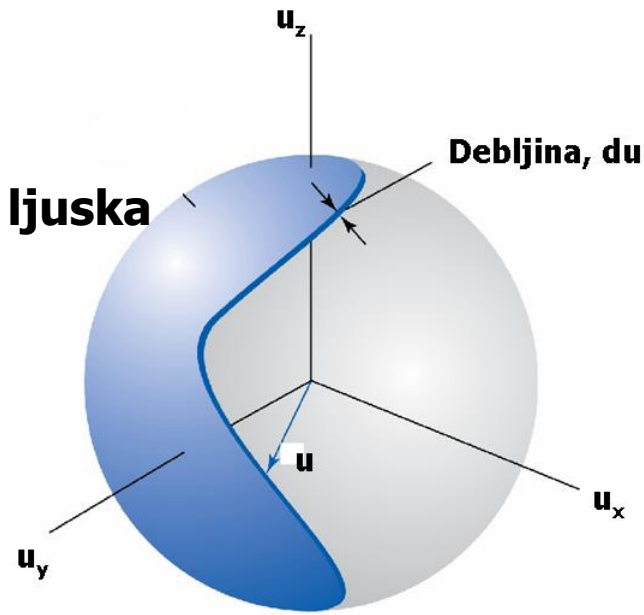
1859. J.C. Maxwell-izveo zakon raspodjela brzina

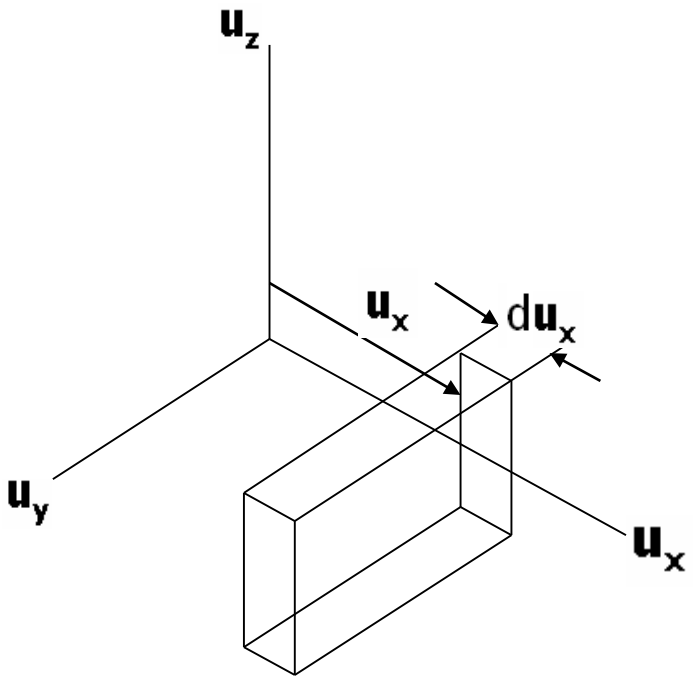


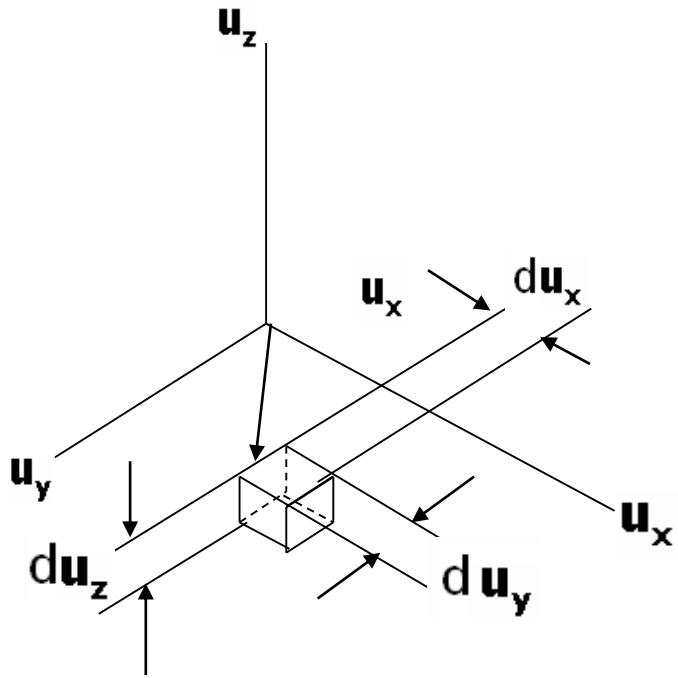


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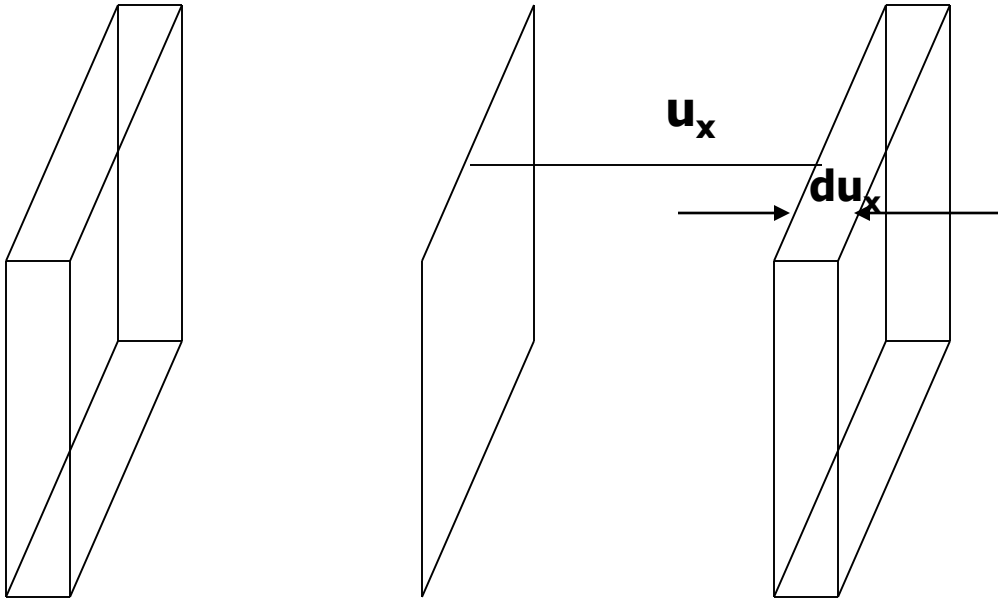
- Sve čestice istovremeno kreću iz ishodišta i gibaju se u svim smjerovima
- Ovisno o njihovoj brzini (odnosno energiji) stići će na određene udaljenosti od ishodišta


u_z
Debljina, du
ljuska
u
u_x
u_y


u_z
u_x
du_x
u_y
u_x

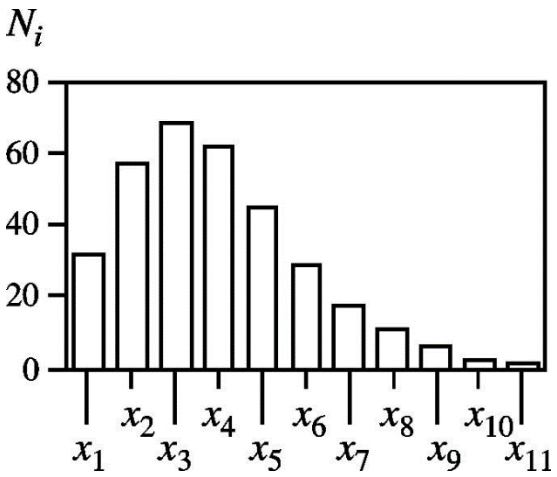

u_z
u_x
du_x
u_y
u_x
du_z
du_y

Razmatrajmo gibanje (translacijsko) čestica samo uzduž jedne osi (npr.x)

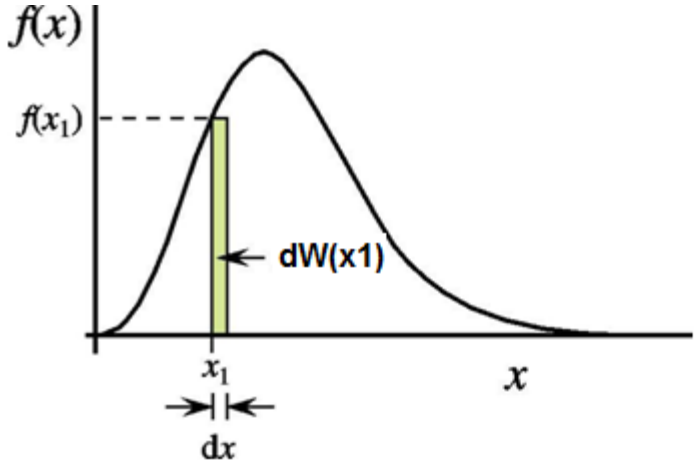


Za plin koji sadrži N čestica, broj čestica koje imaju brzinu u smjeru osi x između u_x i u_x+du_x je $N\, f(u_x)\, du_x$





$$W(x_i) = \frac{N_i}{N}$$



$$dW(x_i) = \frac{dN_i}{N} = f(x)dx$$

Vjerojatnost da komponenta brzine leži u intervalu između u_x i $u_x + du_x$:

$$dW_x = \frac{dN_x}{N} = f(u_x)du_x$$

Raspodjela komponente brzine paralelne s osi x

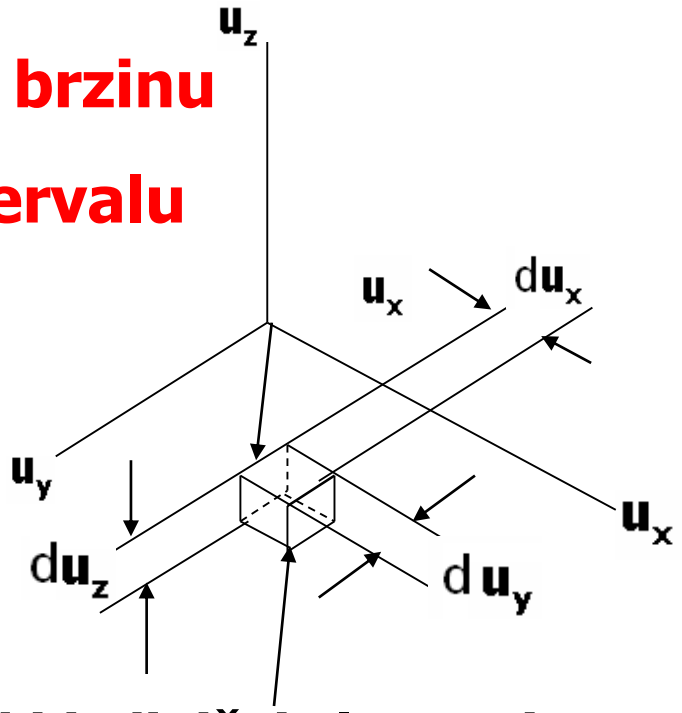
Vjerojatnost da molekula ima brzinu

s komponentama brzine u intervalu

u_x do u_x+du_x,

u_y do u_y+du_y,

u_z do u_z+du_z,



(trodimenzijski jedinični element)

$$dW = dW_x \cdot dW_y \cdot dW_z =$$

$$= f(u_x)du_x \cdot f(u_y)du_y \cdot f(u_z)du_z =$$

$$= F(u_x, u_y, u_z)du_x \cdot du_y \cdot du_z$$

$$f(E) = Ae^{-(E_i/kT)}$$

- Udio molekula s komponentama brzine u_x, u_y, u_z proporcionalan je eksponencijalnoj funkciji njihove kinetičke energije:

$$E_{kin} = \frac{1}{2}m \cdot u_x^2 + \frac{1}{2}m \cdot u_y^2 + \frac{1}{2}m \cdot u_z^2$$

Prema tome, možemo pisati

$$F(u_x, u_y, u_z) = f(u_x) \cdot f(u_y) \cdot f(u_z) = Ae^{-\frac{E}{kT}} =$$

$$= Ae^{-\left(\frac{1}{2}mu_x^2 + \frac{1}{2}mu_y^2 + \frac{1}{2}mu_z^2\right)/kT} = Ae^{-mu_x^2/2kT} e^{-mu_y^2/2kT} e^{-mu_z^2/2kT}$$

Budući su svi smjerovi “ravnopravni”

$$f(u_x) = A^{1/3} e^{-mu_x^2/2kT}$$

$$f(u_y) = A^{1/3} e^{-mu_y^2/2kT}$$

$$f(u_z) = A^{1/3} e^{-mu_z^2/2kT}$$

Kako odrediti konstantu A?

Čestica plina mora imati neku brzinu u intervalu

$$-\infty < u_x < +\infty$$

Ukupna vjerojatnost da su brzine u tom području =1

$$\int_{-\infty}^{+\infty} f(u_x)du_x = 1$$

$$A^{1/3}\int_{-\infty}^{+\infty} e^{-mu_x^2/2kT}\,du_x = 1$$

$$A^{1/3} = \frac{1}{\int_{-\infty}^{+\infty} e^{-mu_x{}^2/2kT}\,du_x}$$

$$I_n = \int_0^{+\infty} x^n e^{-ax^2}$$

$$n = 0$$

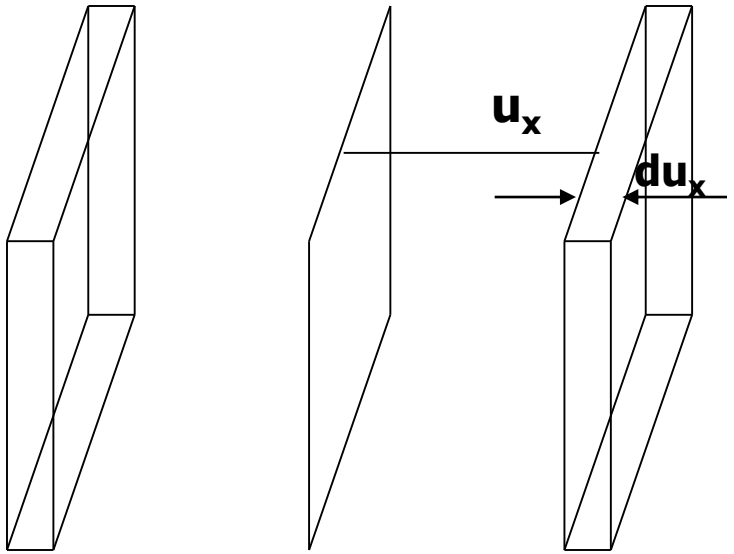
$$a = \frac{m}{2kT}$$

n	0	1	2
I_n	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$	$\frac{1}{2a}$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{\frac{1}{2}}$

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

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

$$A = \left(\frac{m}{2kT\pi}\right)^{3/2}$$



$$dW_x = \frac{dN_x}{N} = f(u_x)du_x = \sqrt{\frac{m}{2kT\pi}} \cdot e^{-\frac{mu_x^2}{2kT}} \cdot du_x$$

$$\frac{dW_x}{du_x} = \frac{\frac{dN_x}{N}}{du_x} = f(u_x) = \sqrt{\frac{m}{2kT\pi}} \cdot e^{-\frac{mu_x^2}{2kT}}$$

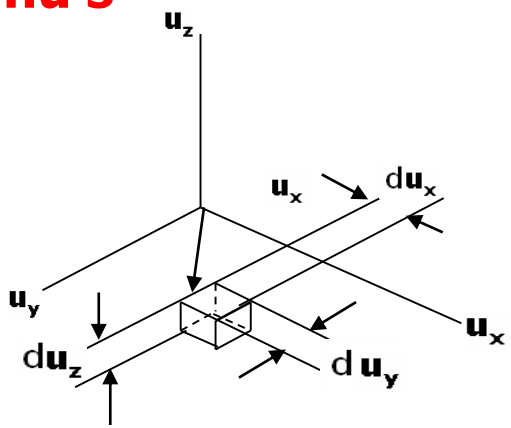
Raspodjela komponenata brzine koje su paralelne s nekom osi po volji

Vjerojatnost da molekula ima brzinu s komponentama brzine u intervalu

u_x do u_x+du_x,

u_y do u_y+du_y,

u_z do u_z+du_z,



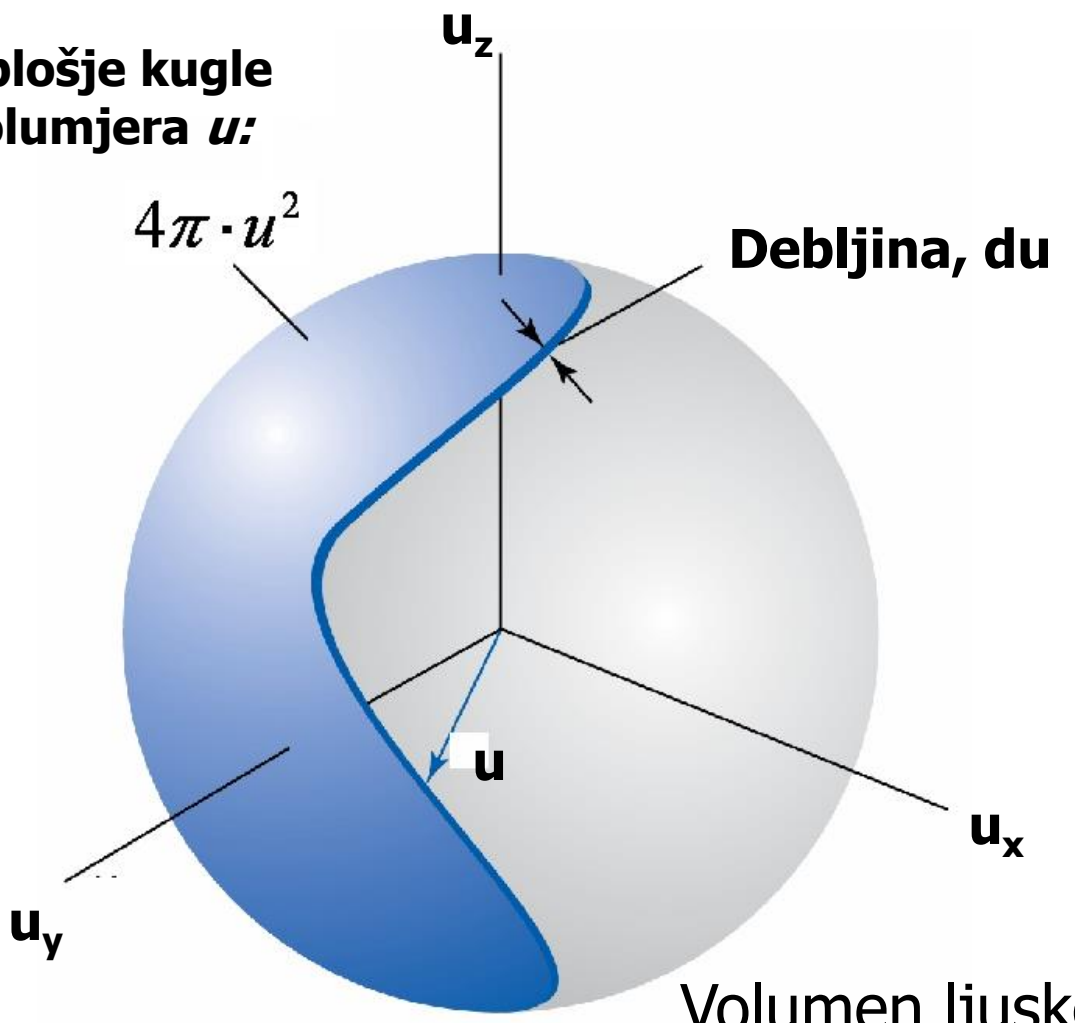
$$dW = \frac{dN}{N} = dW_x \cdot dW_y \cdot dW_z =$$

$$= \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{m(u_x^2+u_y^2+u_z^2)}{2kT}} du_x \cdot du_y \cdot du_z =$$

$$= \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mu^2}{2kT}} du_x \cdot du_y \cdot du_z$$

? Vjerojatnost da će se čestice jednakih brzina naći u ljusci (jednako udaljeno od ishodišta)

Oplošje kugle polumjera *u:*

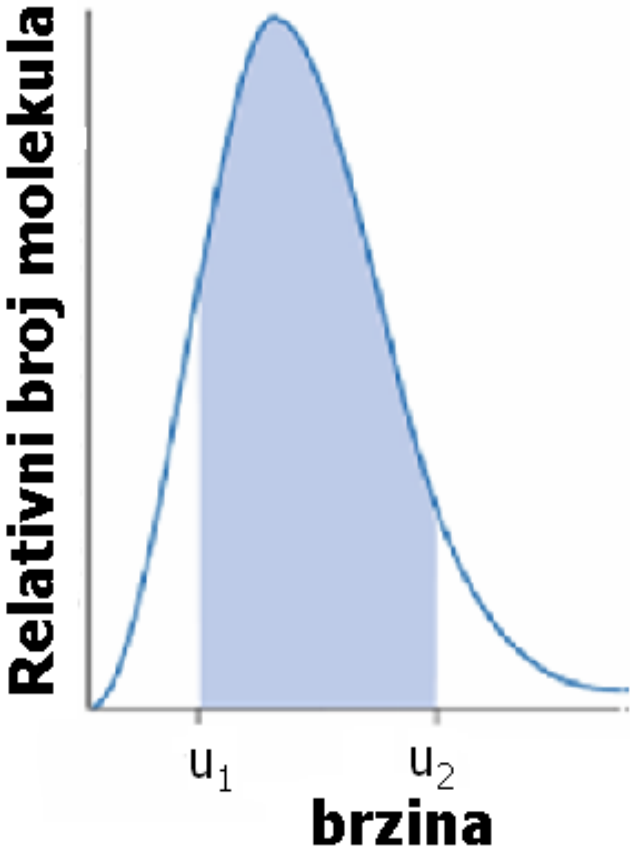


Volumen ljuske: $4\pi \cdot u^2 \cdot du$

$$dW = \frac{dN}{N} = 4\pi\left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mu^2}{2kT}} \cdot u^2 \cdot du$$

$$\frac{dW}{du} = \frac{dN/N}{du} = F(u) = 4\pi\left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mu^2}{2kT}} \cdot u^2$$

MAXWELL-BOLTZMANN-OVA RASPODJELA BRZINA

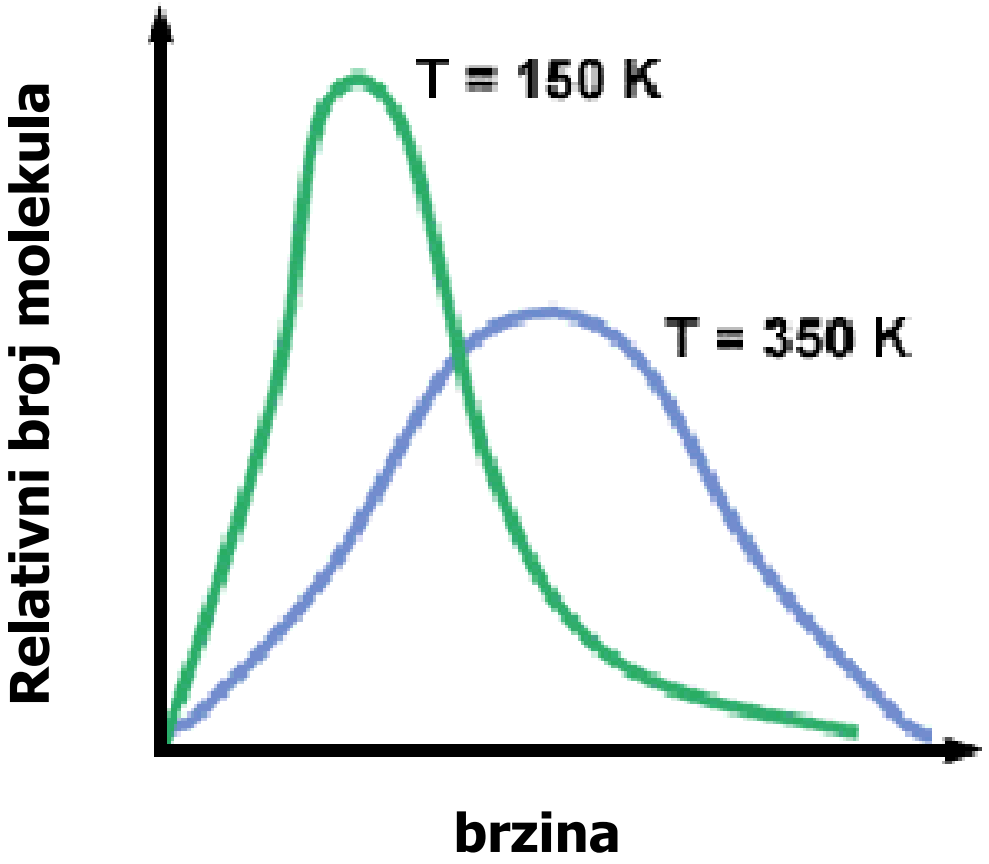


Udio molekula koje imaju brzine u intervalu

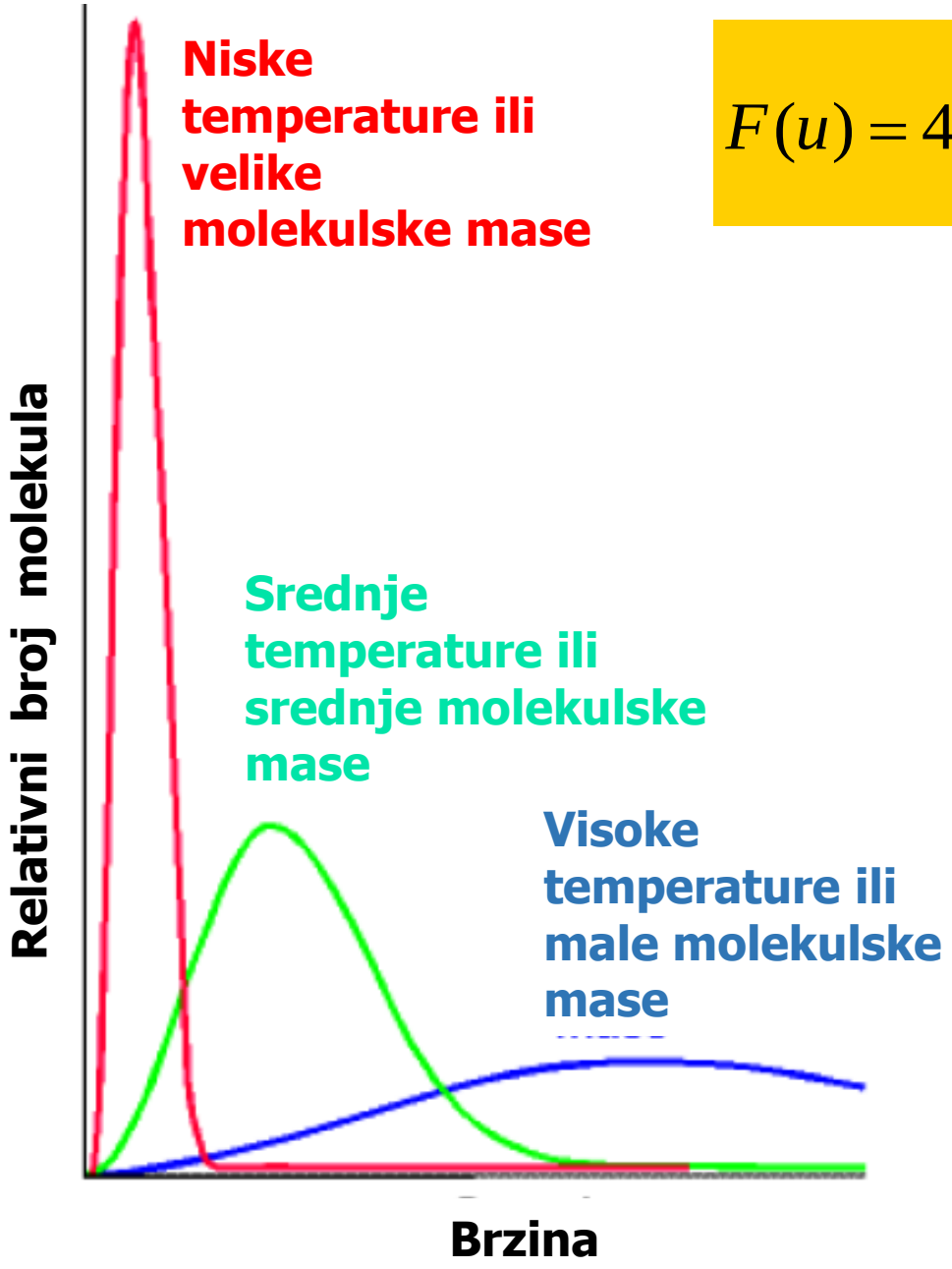
u_1 do u_2

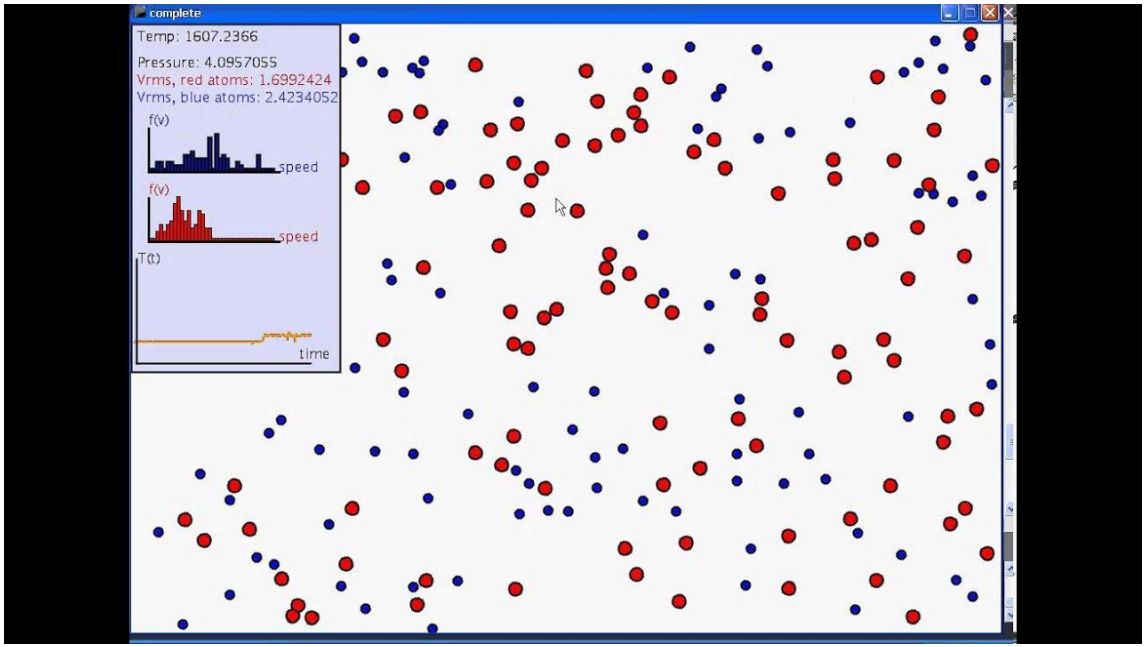
jednak je integralu

$$\int_{u_1}^{u_2} F(u)du$$


T = 150 K
T = 350 K
Relativni broj molekula
brzina

$$F(u) = 4\pi\left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mu^2}{2kT}} \cdot u^2$$





https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.youtube.com%2Fwatch%3Fv%3DYgGik5q1JSA&psig=AOvVaw1o3P1noLYa8R8UpCbykqv9&ust=1633765761088000&source=images&cd=vfe&ved=0CAsQjRxqFwoTCKjVsPCpuvMCFQAAAAAdAAAAABAD

1.Najvjerojatnija brzina

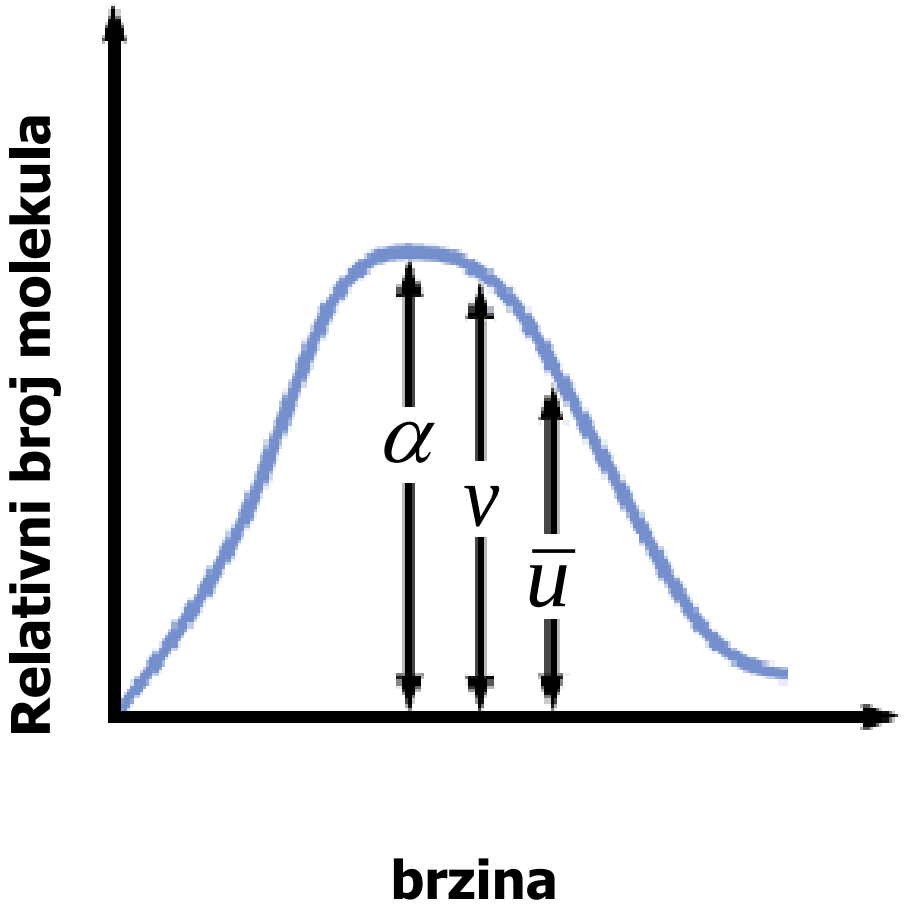
$$\alpha = \sqrt{\frac{2kT}{m}} \equiv \sqrt{\frac{2RT}{M}}$$

2.Statistički prosjek

$$\sqrt{\overline{u}^2} = \sqrt{\frac{1}{N}\int_0^\infty u^2 dN} = \sqrt{\frac{3kT}{m}} \equiv \sqrt{\frac{3RT}{M}}$$

3.Aritmetički prosjek brzina

$$v = \frac{1}{N}\int_0^\infty u dN = \sqrt{\frac{8kT}{\pi m}} \equiv \sqrt{\frac{8RT}{\pi M}}$$



$$\bar{u} : v : \alpha = 1{,}00 : 0{,}92 : 0{,}82$$

Broj sudara jedne čestice (s ostalim molekulama) u jedinici vremena

$$z_1 = \sqrt{2}\pi \cdot d^2 \frac{N}{V} \cdot v$$

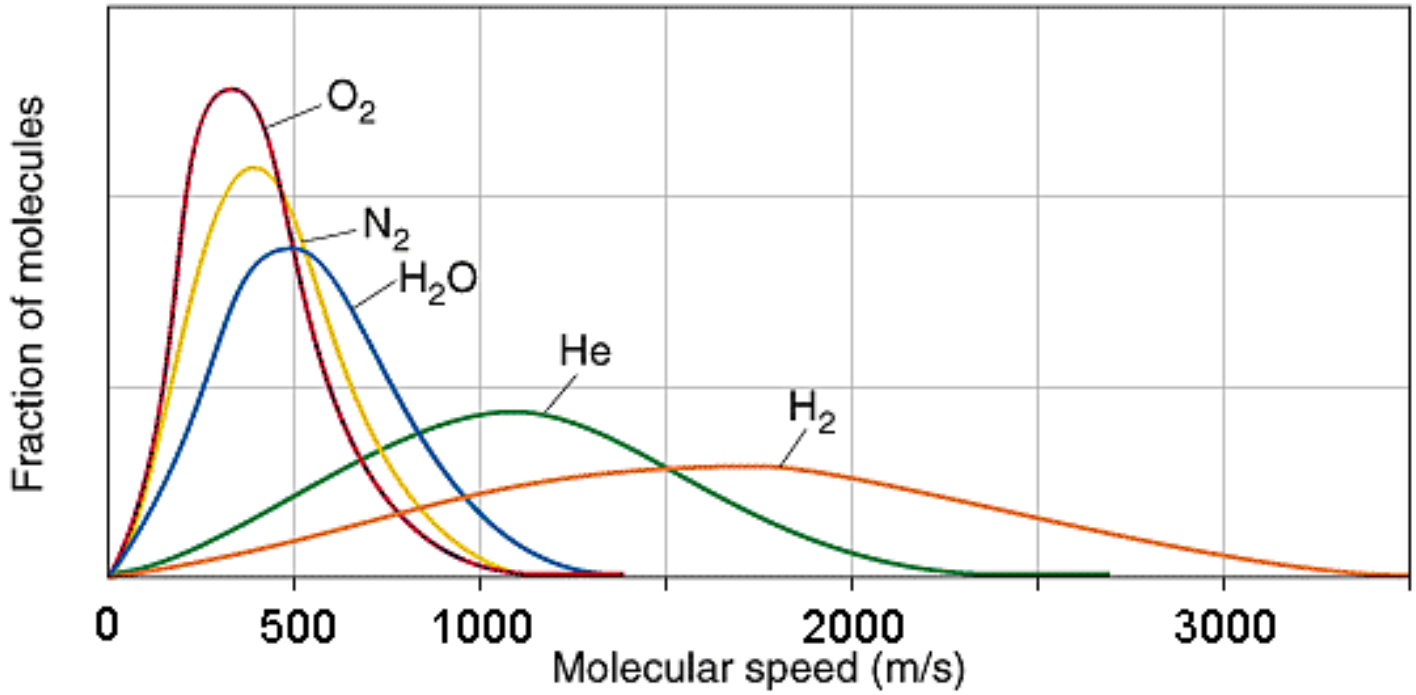
Brojčana gustoća

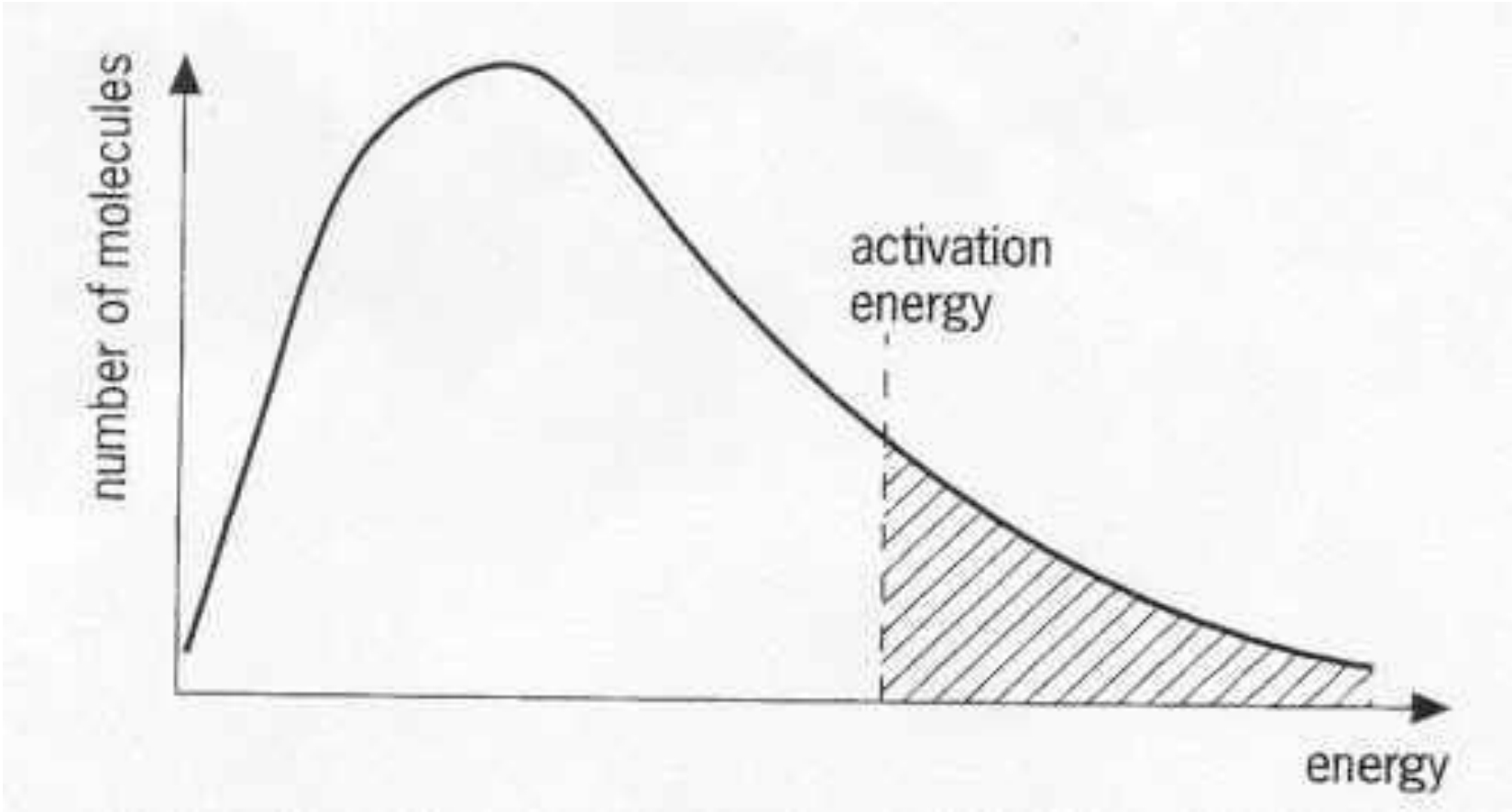
Aritmetički prosjek

d **efektivni promjer molekule**

Srednji slobodni put-put koji prijeđe molekula između dva sudara

$$l = \frac{1}{\frac{N}{V}\sqrt{2}\pi \cdot d^2}$$


Fraction of molecules
O_2
N_2
H_2O
He
H_2
0
500
1000
2000
3000
Molecular speed (m/s)


number of molecules
activation
energy
energy