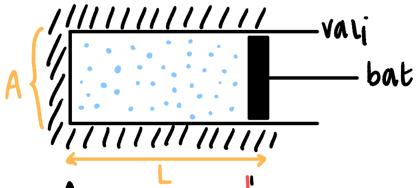
Enačba stanja

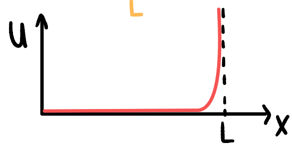
24.11.2020

↳ Zanima nas, kako jo bomo dobili iz faznega integrala, torej kako bomo iz njega tako kot $\bar{E}$ dobili še ostale količine, npr. tlak



Zanima nas, kaj se dogaja s tlakom, če premikamo bat. Bat za plin predstavlja nek potencial (U)

Potencial U deluje na vsako molekulo posebej



$$U_i(x_i, L) = \begin{cases} 0\ ; & x_i < L \\ \infty\ ; & x_i > L \end{cases} = U_i(x_i - L)$$

Koordinata i-te molekule

Opazimo, da potencial ni odv. od koordinate in parametra L posebej, temveč le od njune razlike

$$\text{Energija} = E_{kin.} + \underbrace{\sum_i U_i(x_i - L)}_{U}$$

→ Iz tega želimo izračunati silo bata na plin

$$E_{kin.} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$

→ Ni odvisna od lege bata

Ker Ekin. ni odvisna od L, bo odvod po L enak 0

$$\text{Sila bata na plin: } F_x = \sum_i F_{x_i} = \underbrace{-\sum_i \frac{\partial U_i}{\partial x_i}}_{} = +\sum_i \frac{\partial U_i}{\partial(-L)} = \frac{\partial}{\partial L}\sum_i U_i = \frac{\partial U}{\partial L} = \frac{\partial E}{\partial L}$$

sila bata na posamezno molekulo

Sila na posamezno molekulo plina, seštete po vseh molekulah v plinu = −gradient potenciala, ki ga bat predstavlja za plin

Tlak plina?

$$p = -\frac{\overline{F_x}}{A} = -\frac{1}{A}\cdot\overline{\frac{\partial E}{\partial L}} = -\overline{\frac{\partial E}{\partial V}} \quad (*)$$

$$\text{Fazni integral: } e^{-\beta F} = C\cdot\int e^{-\beta E}\, d\Gamma \quad \Big/ : e^{-\beta F}$$

$$1 = \underbrace{C\cdot\int e^{-\beta(E-F)}}_{\rho(E)}\, d\Gamma \quad \Big/ \frac{\partial}{\partial V}$$

$$0 = \underbrace{C\cdot\int -\left(\frac{\partial E}{\partial V}\right)\cdot e^{-\beta(E-F)}\, d\Gamma}_{= -\int \frac{\partial E}{\partial V}\rho(E)\, d\Gamma = -\overline{\frac{\partial E}{\partial V}}} + \underbrace{C\cdot\int \frac{\partial F}{\partial V}\cdot e^{-\beta(E-F)}\, d\Gamma}_{\frac{\partial F}{\partial V}\cdot \underbrace{C\cdot\int e^{-\beta(E-F)}\, d\Gamma}_{=1}}$$

$$\Rightarrow \left(\overline{\frac{\partial E}{\partial V}}\right)_\beta = \frac{\partial F}{\partial V} \to \text{Nesemo v } (*) \quad \Rightarrow \quad \boxed{p = -\left(\frac{\partial F}{\partial V}\right)_\beta}$$

Enačba stanja idealnega plina

$$E=\frac{p_{1x}^2}{2m}+\frac{p_{1y}^2}{2m}+\frac{p_{1z}^2}{2m}+\frac{p_{2x}^2}{2m}+\dots$$

$$e^{-\beta F}=C\cdot\int\exp\left[-\beta\sum_i\left(\frac{p_{ix}^2}{2m}+\frac{p_{iy}^2}{2m}+\frac{p_{iz}^2}{2m}\right)\right]\prod_{i=1}^{N}\underbrace{dx_i\,dy_i\,dz_i}_{V^N}\,dp_{ix}\,dp_{iy}\,dp_{iz}=C\,V^N\cdot\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N}$$

$$F=-\frac{1}{\beta}\cdot\left[\ln C+\underbrace{N\cdot\ln V}_{\text{za tlak je važen le ta člen}}+\frac{3N}{2}\cdot\ln\frac{2\pi m}{\beta}\right]$$

$N=\frac{\tilde{m}}{M}N_A$

$$p=-\left(\frac{\partial F}{\partial V}\right)_\beta=\frac{1}{\beta}\cdot N\cdot\frac{\partial}{\partial V}\ln V=\frac{N}{\beta V}=\frac{Nk_BT}{V}=\frac{\tilde{m}N_Ak_BT}{MV}$$

Virialna enačba stanja

↳ sile med delci

Enačba stanja idealnega plina: $p=\frac{N}{\beta V}$ ρ $/\cdot\beta/\rho$ $\Rightarrow\frac{\beta p}{\rho}=1$

Če nimamo idealnega plina, pričakujemo na desni odstopanje od 1, ki bo tem izrazitejše, čim gostejši bo plin

$$\frac{\beta p}{\rho}=\underbrace{1}_{\text{idealni plin}}+\underbrace{\sum_{i=2}^{\infty}B_i\rho^{i-1}}_{\text{odstopanje od idealnega plina zaradi sil med delci}}$$

Odstopanje lahko zapišemo kot razvoj po potencah gostote

Energija realnega plina:

$$E=E_{kin}+\sum_{i<j}\Phi_{ij}$$

Parski potencial med delcema i in j: $\Phi_{ij}=\Phi(|\vec{r}_i-\vec{r}_j|)$
(odvisen le od razdalje med delcema)

Fazni integral:

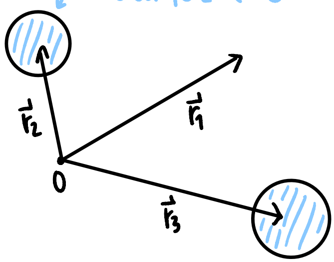
$$e^{-\beta F}=\underbrace{C\cdot\int\exp\left[-\beta\sum_{i=1}^{N}\frac{p_i^2}{2m}\right]\prod_{i=1}^{N}d\vec{p}_i}_{\text{integral po gibalnih količinah}\,=\,\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}}\;\underbrace{\int\exp\left[-\beta\sum_{i<j}\Phi_{ij}\right]\prod_{i=1}^{N}d\vec{r}_i}_{\text{konfiguracijski integral }Q_N}$$

$$Q_N=\int\exp[-\beta\Phi_{12}]\exp[-\beta\Phi_{13}]\cdot\ldots\cdot\exp[-\beta\Phi_{23}]\cdot\ldots\cdot d\vec{r}_1d\vec{r}_2\cdot\ldots\cdot d\vec{r}_N=$$

$$=\int[1-(1-e^{-\beta\Phi_{12}})][1-(1-e^{-\beta\Phi_{13}})]\cdot\ldots\cdot d\vec{r}_1d\vec{r}_2\cdot\ldots\cdot d\vec{r}_N$$

Upoštevamo, da so v dovolj redkem plinu interakcije med delci šibke, eksponente zapišemo malce drugače

Le tu je $[1-(1-e^{-\beta\Phi_{12}})]$ različen od 1.



Zdaj upoštevamo, da bo skoraj povsod v prostoru $\exp[-\beta\Phi_{12}]$ enak 1 oz. da bo torej $1-\exp[-\beta\Phi_{12}]$ enak 0.
Ko integriramo po $\vec r_1$ je koordinata delca 2 fiksna. Obstaja okolica delca 2, kjer je razdalja med delcema 1 in 2 tako majhna, da je $\Phi_{12}\neq 0$.

Če je plin dovolj redek so okolice 3,4,...,N-tega delca dovolj narazen. Produkt oklepajev v integralu lahko tedaj dovolj dobro aproksimiramo z najnižjim redom v produktu.

$$\Rightarrow Q_N \approx \int \left[1-(1-e^{-\beta\Phi_{12}})-(1-e^{-\beta\Phi_{13}})-(1-e^{-\beta\Phi_{14}})-\dots-(1-e^{-\beta\Phi_{23}})-\dots-\right] d\vec r_1 d\vec r_2\cdot\dots\cdot d\vec r_N =$$

$$= V^N - V^{N-2}\int(1-e^{-\beta\Phi_{12}})\,d\vec r_1 d\vec r_2 - \dots = V^N - V^{N-1}\underbrace{\int(1-e^{-\beta\Phi_{12}})\,d\vec r_{12}}_{2B_2} - V^{N-1}\int(1-e^{-\beta\Phi_{13}})\,d\vec r_{13} - \dots =$$

Prvi oklepaj je odvisen le od $\vec r_1, \vec r_2$, zato od integracije po $\vec r_3, \vec r_4, \dots, \vec r_N$ dobimo le to

$\Phi_{12}=\Phi(|\vec r_1-\vec r_2|)$ zato lahko uvedemo novo spr.: $\vec r_{12}=\vec r_1-\vec r_2$

Ker je Φ_{12} odv. le od r_{12} dobimo še en V

↳ = drugi virialni koeficient

$\vec r_{12}, \vec r_{13}, \dots$ so neme spremenljivke: ko pointegriramo, te spremenljivke ni več. Člena / in / sta zato enaka (in vsi ostali), zato lahko pišemo

$$Q_N\approx V^N - V^{N-1}\cdot \cancel{2}B_2\cdot\frac{N(N-1)}{\cancel{2}}$$ = število parov

Upoštevamo, da je delcev veliko $N\gg 1$, zato poenostavimo $N(N-1)\approx N^2$

$$Q_N\approx V^N - V^{N-1}\cdot B_2\cdot N^2$$

Izračunali smo torej:

$$e^{-\beta F}\approx C\cdot\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}\cdot\left[V^N-V^{N-1}B_2N^2\right] = C\cdot\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}\cdot V^N\left(1-\frac{N^2B_2}{V}\right)$$

Zdaj lahko izračunamo tlak:

Edina člena, ki bosta prispevala k p.

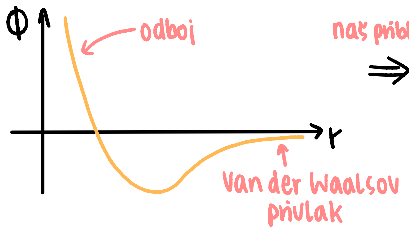
$$F=-\frac{1}{\beta}\left[\ln C + \frac{3N}{2}\ln\left(\frac{2\pi m}{\beta}\right) + N\cdot\ln V + \ln\left(1-\frac{N^2B_2}{V}\right)\right]$$
$$\approx -\frac{1}{\beta}\left[\dots+\dots+N\cdot\ln V - \frac{N^2B_2}{V}\right]$$

Upoštevamo, da smo v limiti, ko so delci dovolj narazen in ta člen razvijemo po Taylorju

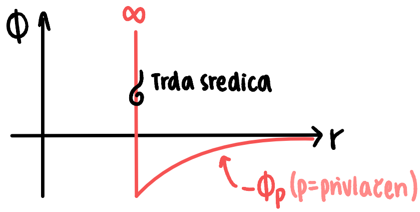
$$p=-\left(\frac{\partial F}{\partial V}\right)_\beta = \frac{1}{\beta}\left[\frac{N}{V}+\frac{N^2B_2}{V^2}\right] \Rightarrow \frac{\beta p}{\rho}=1+B_2\rho$$

Drugi virialni koeficient

Tipična odvisnost meddelčnega potenciala v plinih:



naš približek $\Rightarrow$



$$B_2=\frac{1}{2}\int(1-e^{-\beta\Phi})\,d\vec{r}=\frac{1}{2}\int(1-e^{-\beta\Phi})\underbrace{4\pi r^2 dr}=2\pi\int_0^{\sigma}1r^2dr-2\pi\int_{\sigma}^{\infty}(\cancel{1}-(\cancel{1}-\beta\Phi_p))r^2dr=$$

privzeli, da je Φ odvisen le od r, da nismo integrirali po kotih

$\beta\Phi_p \ll 1$ (razvili eksponent po Taylorju)

$$=2\pi\frac{\sigma^3}{3}-2\pi\int_{\sigma}^{\infty}\beta\Phi_p r^2dr=2\pi\cdot\frac{\sigma^3}{3}-\beta\cdot\alpha$$

To zdaj nesemo v naš rezultat za tlak

$$\Rightarrow p=\frac{N}{\beta V}+\frac{1}{\beta}\frac{N^2}{V^2}B_2=\frac{N}{\beta V}+\frac{1}{\beta}\frac{N^2}{V^2}\left(\frac{2\pi}{3}\sigma^3-\beta\alpha\right)=\frac{N}{\beta V}+\frac{1}{\beta}\frac{N^2}{V^2}\cdot\frac{2\pi}{3}\sigma^3-\frac{N^2\alpha}{V^2}$$

→ Količine, ki so za nas interesantne

$$p=\frac{Nk_BT}{V}+\frac{N^2k_BT}{V^2}\cdot\frac{2\pi}{3}\sigma^3-\frac{N^2\alpha}{V^2}$$

Spomnimo se, kako izgleda Van der Waalsova enačba stanja:

$$\left(p+\frac{a}{V_M^2}\right)(V_M-b)=RT$$

Razvijemo

$$p+\frac{a}{V_M^2}=\frac{RT}{V_M-b}=\frac{RT}{V_M\left(1-\frac{b}{V_M}\right)}\approx\frac{RT}{V_M}\left(1+\frac{b}{V_M}\right)=\frac{RT}{V_M}+\frac{RTb}{V_M^2}$$

$$p=\frac{RT}{V_M}+\frac{RTb}{V_M^2}+\frac{a}{V_M^2}$$

$a \rightarrow$ povezan s privlačnimi interakcijami med delci: $a=N^2\alpha$ integral privlačnega repa potenciala po prostoru

$b \rightarrow$ povezan s σ, torej z lastno prostornino molekul

Entropija

1.12.2020

Do zdaj smo ugotovili: $\beta = 1/k_BT$, $\bar{E}$ ustreza U, $e^{-\beta F} = C \cdot \int e^{-\beta E} d\Gamma$

$$\bar{E} = \frac{d(\beta F)}{d\beta} = \left(\frac{\partial(\beta F)}{\partial \beta}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\beta = -\left(\frac{\partial(\beta F)}{\partial(\beta V)}\right)_\beta$$

ker je β = konst.

Totalni diferencial $d(\beta F)$:

$$d(\beta F) = \bar{E} d\beta - p\, d(\beta V) = \bar{E} d\beta - p \beta dV \quad (1)$$

Energijski zakon: $dU = dQ - p dV \rightarrow d\bar{E} = dQ - p dV \quad /\cdot\beta$

$\bar{E}$ ustreza

$$\beta d\bar{E} = \beta dQ - p\beta dV \quad (2)$$

(1) − (2): $d(\beta F) - \beta d\bar{E} = \bar{E} d\beta - \beta dQ$

$$\Rightarrow -\beta dQ = d(\beta F) - \underbrace{\beta d\bar{E} - \bar{E} d\beta}_{\text{Totalni dif.}} = d(\beta F) - d(\beta \bar{E}) = d(\beta(F - \bar{E})) \quad /\cdot(-k_B)$$

$-\beta dQ = -\frac{1}{k_BT} \cdot TdS$

$1/k_BT$

$$\Rightarrow dS = \frac{dQ}{T} = \cancel{k_B} \cdot \frac{d(\bar{E} - F)}{\cancel{k_B}T} = \frac{d(\bar{E} - F)}{T} \Rightarrow S = \frac{\bar{E} - F}{T} \text{ oz. } F = \bar{E} - TS = U - TS$$

prosta energija

Ugotovili smo torej:

(*) $S = k_B \cdot \beta \cdot (\overline{E - F})$

$\bar{F} = F$, ker smo F dobili z integriranjem po faznem prostoru, je neka konstanta, na katero nadaljne povprečevanje ne vpliva

Kanonična porazdelitev: $\rho(E) = C \cdot e^{-\beta(E - F)} \quad /:C, \ln, \cdot(-1)$

$$\Rightarrow -\ln \frac{\rho(E)}{C} = \beta(E - F) \quad \text{(To lahko zdaj vstavimo v (*))}$$

Računanje povprečij: $\bar{Y} = \int Y \rho \, d\Gamma$

$$\Rightarrow \boxed{S = -k_B \int \rho \cdot \ln \rho/C \cdot d\Gamma} \quad \text{Gibbsova formula za entropijo}$$

BOLTZMANOVA FORMULA

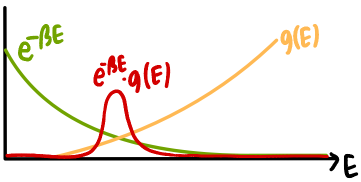
Pogledati moramo primerjavo med kanonično in mikrokanonično porazdelitvijo

$$1 = \int \rho \, d\Gamma = C \cdot \int e^{-\beta(E - F)} \underbrace{d\Gamma}_{= g(E)dE}$$

$\rho(E)$

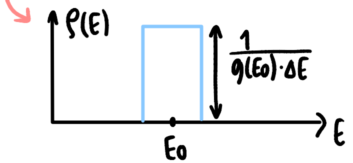
gostota stanj: $g(E) = \frac{d\Gamma}{dE}$

$$\Rightarrow 1 = C \cdot \int \underbrace{e^{-\beta(E - F)}}_{\text{eksponentno pada z } E} \underbrace{g(E)}_{\text{narašča z } E} dE$$



Mikrokanonična porazdelitev:

$$\rho(E)=\begin{cases}\frac{1}{g(E_0)\cdot\Delta E} & ;\ E_0-\frac{\Delta E}{2}<E<E_0+\frac{\Delta E}{2}\\ 0 & ;\ \text{sicer}\end{cases}$$



$$1=\int\rho\, d\Gamma=\int\rho\, g(E)\, dE$$

To vstavimo v Gibbsovo formulo:

$$S=-k_B\cdot\int\rho\cdot\ln\frac{\rho}{C}\,d\Gamma=-k_B\cdot\int\frac{1}{g(E_0)\cdot\Delta E}\cdot\ln\frac{1}{g(E_0)\cdot\Delta E\cdot C}\,g(E_0)\cdot dE=$$

$$=-k_B\cdot\frac{1}{\cancel{g}(E_0)\cdot\Delta E}\ln\frac{1}{\underbrace{g(E_0)\Delta E}_{=\Delta\Gamma}\cdot C}\cdot\cancel{g}(E_0)\cdot\Delta E=k_B\cdot\ln(C\cdot\Delta\Gamma)$$

$\Rightarrow$ $\boxed{S=k_B\cdot\ln(C\cdot\Delta\Gamma)}$ **Boltzmanova formula za entropijo** → Nanaša se na entropijo kot funkcijo energije, saj je parameter mikrokanonične porazdelitve en. E_0

To beremo kot $S(E)=k_B\cdot\ln(C\cdot\underbrace{\Delta\Gamma(E)}_{\text{=velikost faznega prostora pri energiji, ki jo obravnavamo}})$

Zgled: Entropija idealnega plina

$$e^{-\beta F}=C\cdot V^N\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

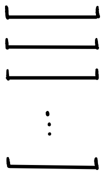
$$F=-k_BT\cdot\ln(CV^N)-k_BT\cdot\ln(2\pi m k_BT)^{\frac{3N}{2}}=-k_BT\cdot\ln C-Nk_BT\cdot\ln V-\frac{3N}{2}k_BT\cdot\ln(2\pi m k_BT)$$

$$\bar{E}=\frac{3Nk_BT}{2}$$

$$S=\frac{\bar{E}-F}{T}=\frac{3Nk_B}{2}+k_B\cdot\ln C+Nk_B\ln V+\frac{3Nk_B}{2}\cdot\ln T+\frac{3Nk_B}{2}\cdot\ln(2\pi m k_B)=$$

$$=\underbrace{Nk_B}_{\frac{\tilde{m}}{M}\underbrace{N_Ak_B}_{R}}\ln V+\underbrace{\frac{3Nk_B}{2}}_{N=\frac{\tilde{m}}{M}N_A,\ c_v=\frac{3k_B}{2}\cdot N}\ln T+\text{konst.}=\underbrace{\tilde{m}\frac{R}{M}\cdot\ln V+\tilde{m}c_v\cdot\ln T}_{\text{Enaka kot pri TD}}+\text{konst.}$$

OD BOLTZMANOVE FORMULE H GIBBSOVI



j, N_j število delcev v stanju j

stanje sistema

Celotno stanje sistema podamo z vektorjem $\{N_1, N_2, \dots, N_j, \dots\}$ ki opisuje zasedenost posameznih stanj sistema

$$S = k_B \cdot \ln(C \cdot \Delta\Gamma)$$

Multinomski simbol – pove nam št. načinov, na katere lahko razporedimo delce v sistemu:

$$\Delta\Gamma = \frac{N!}{N_1!N_2!N_3! \cdot \ldots \cdot (N-N_1-N_2-\ldots)!} = \frac{N!}{N_1! \cdot N_2! \cdot \ldots \cdot N_K!}$$

Za izračun bomo uporabili Stirlingovo formulo: $\ln N! \approx N \cdot \ln N - N$

$$\Rightarrow S = k_B \cdot [\ln N! - \ln N_1! - \ln N_2! - \ldots] = k_B [\overset{N_1+N_2+\ldots}{N} \cdot \ln N - \cancel{N} - N_1 \cdot \ln N_1 + \cancel{N_1} - N_2 \cdot \ln N_2 + \cancel{N_2} - \ldots] =$$

$$= k_B [N_1 \ln N + N_2 \cdot \ln N + N_3 \cdot \ln N + \ldots - N_1 \cdot \ln N_1 - N_2 \cdot \ln N_2 - N_3 \cdot \ln N_3 - \ldots] =$$

$$= -N \cdot k_B \left[\frac{N_1}{N} \cdot \ln \frac{N_1}{N} + \frac{N_2}{N} \cdot \ln \frac{N_2}{N} + \frac{N_3}{N} \cdot \ln \frac{N_3}{N} + \ldots\right]$$

$$P_3 = \frac{N_3}{N}$$

$$= -N \cdot k_B \cdot \sum_{j=1}^{K} P_K \cdot \ln P_K$$

Gibbs: $S = -k_B \int \rho \cdot \ln \frac{\rho}{C} \, d\Gamma$

Vidimo: Dobili smo diskretno verzijo Gibbsove formule