ŠTAT. FYZIKA A TERMODYNAMIKA

Balek, davinci.fmph.uniba.sk/~balek1; lit.: Tong (+Kittel, Reif...)

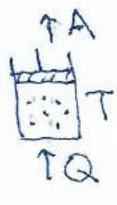
čo je termodynamika?

skúma tepelné deje ($\vartheta \acute{\varepsilon} \rho \mu \eta$ + $\delta \acute{\upsilon} \nu \alpha \mu \iota \varsigma$) = deje s účasťou tepla (Q), dôležitú úlohu v nich hrá teplota (T); štat. fyzika: ditto, ALE v inej mierke - $\begin{cases} \text{termodyn.: mierka látky} \\ \text{štat. fyzika: mierka at. a mol.} \end{cases}$

princípy: $\boxed{\text{1.+2. veta termodynamická}}$, $\begin{cases} \text{1. veta: z. zach. energie} \\ \text{2. veta: z. rastu entropie} \end{cases}$

$\begin{cases} (E = \text{konšt}), \text{ neex. PM 1. druhu} \\ (\dot{S} \geq 0), \text{ neex. PM 2. druhu} \end{cases}$ (ŠTR: princíp rel. + konšt. c); k 2. vete: viď Rumford (1798)

tepelné deje = vzáj. premeny tepla a práce (A) - Q, A sa vyjadrujú v J => sú to formy en.? $\begin{cases} \text{charakt. stavu (vn. en.) NIE} \\ \text{charakt. procesu (prenos. en.) ÁNO} \end{cases}$

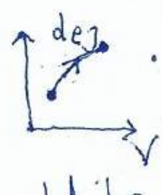


$\begin{cases} Q \leftrightarrow \text{neusporiad. pohyb} \\ A \leftrightarrow \text{usporiad. pohyb} \end{cases}$: Q → A? 2. veta: nie ÚPLNE, max. η: Carnotov cyklus (C. 1824) → tepel. stroje + df. T, S

stavy a deje

stav: $\begin{cases} \text{termodyn.: makrostavy (PLYN: } p, V, t = \text{empiric. teplota)} \\ \text{štat. fyzika: mikrostavy } (\vec{r}_i, \vec{v}_i = 6N \text{ veličín}, N \sim N_A = 6 \cdot 10^{23}) \end{cases}$

ľub. stav (rôzne p, t v rôznych V) $\xrightarrow[\text{podm.}]{\text{stále}}$ ROVNOVÁHA (jedno p, t v celom V) / stav. rovnica: $\boxed{f(p, V, t) = 0}$ => stav = bod na (p, V) diagrame; 0-tá veta termodyn.: rovnováha je tranzitívna (A, B sú v rovnováhe s C => A je v rovnováhe s B) → df. t

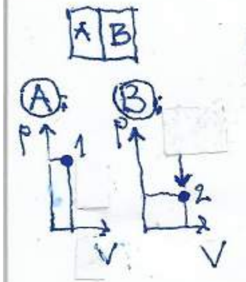


dej: $\begin{cases} \text{vratný - cez rovnováž. stavy = čiara na (p,V) diagrame (POMALÝ)} \\ \text{nevratný - cez nerovnováž. stavy (s disipáciou energie)} \end{cases}$

A (práca plynu)? $dA = F dx$, $\begin{cases} F = pS \\ x = \Delta h \end{cases}$: $dA = p\,S\,dh = p\,dV$,

$\boxed{A = \int_{V_A}^{V_B} p\,dV}$ (= ± plocha pod krivkou) / cyklický dej (B = A): $A =$

$= (\int_{I} - \int_{II}) \, p\,dV$ = ± plocha vnútri slučky



empirická teplota

spojenie A, B: prepážka $\begin{cases} \text{neprepúšťa } Q \text{ (adiabat.)}: A, B \text{ izolované} \\ \text{prepúšťa } Q \text{ (diatermál.)}: A, B \text{ v tepelnom kontakte} \end{cases}$

$\begin{cases} A: (p_1, V_1) \\ B: (p_2^{(0)}, V_2) \end{cases}$: kontakt + $p_1 = $ konšt.: $p_2^{(0)} \to p_2 \Rightarrow$ A je v rovnováhe s B: $F_{AB}(p_1, V_1, p_2, V_2) = 0$ / A, B sú v rovnováhe s C: $\begin{cases} F_{AC}(p_1 V_1 p_3 V_3) = 0 \Rightarrow p_3 = f_{AC}(p_1 V_1 V_3) \\ F_{BC}(p_2 V_2 p_3 V_3) = 0 \Rightarrow p_3 = f_{BC}(p_2 V_2 V_3) \end{cases}$, $f_{AC}(p_1 V_1 V_3) = f_{BC}(p_2 V_2 V_3)$ - toto sa musí dať zapísať ako $F_{AB}(p_1 V_1 p_2 V_2) = 0 \Rightarrow \begin{cases} f_{AC} = \Phi_C(\vartheta_A(p_1 V_1), V_3) \\ f_{BC} = \Phi_C(\vartheta_B(p_2 V_2), V_3) \end{cases}$ &

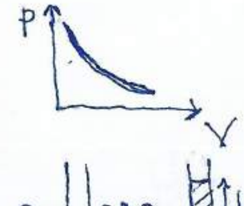
$\boxed{\vartheta_A(p_1 V_1) = \vartheta_B(p_2 V_2)} \to \boxed{t = \text{konšt.} \cdot \vartheta_{A,B}(p, V)}$ - ALE môže byť aj $\vartheta^2_{A,B}$...

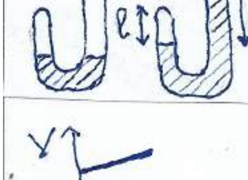
ideálny plyn

úplne stlačiteľný + bez priťahovania povrch. vrstvy, **mikroskop. opis: mol. neinteragujú medzi zrážkami**; lim. riedk. plynov pri $n \to 0$

deje v plynoch

posun. piesta („tlačiť"): ΔV, dodanie ΔQ („kúriť"): Δp al. Δt; id. plyn $\hat{=}$ riedky reál. plyn: (1) izotermický dej ($t = $ konšt): $\boxed{pV = \text{konšt}}$ (Boyle-Mariotte; B. 1662: trubica v tvare U + Hg: $l(h_0 + h) = $ konšt, $h_0 = 760$ mm); A?: $p = C/V$: $\boxed{A} = \int_{V_A}^{V_B} C/V \cdot dV = C \ln V \Big|_{V_A}^{V_B} = \boxed{C \ln(V_B/V_A)}$ - piest $\to \infty$: A je ∞-ná, (2) izobarický dej ($p = $ konšt): $\boxed{V = V_0(1 + \gamma t)}$, $\begin{cases} t = \text{teplota v } ^\circ C \\ \gamma = 1/273{,}15\,^\circ C \end{cases}$ (Gay-Lussac/Charles; G.-L. 1802: banku naplnil plynom s $t = 100\,^\circ C$ + ochladil na $0\,^\circ C$ + napustil do nej vodu $\to V/V_0 = 1{,}37$), (3) izochorický dej ($V = $ konšt): $\boxed{p = p_0(1 + \gamma t)}$ (Gay-Lussac; pred napustením vody: izochor. dej, $p_0' \overset{BM}{=} p V_0 / V \Rightarrow \boxed{p/p_0' = V/V_0}$)



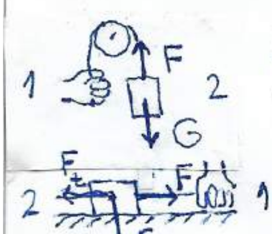


stavová rovnica

abs. teplota: $T = T_0 + t$, $T_0 = 273{,}15\,^\circ C$ / jedn.: $1\,K = 1\,^\circ C = \frac{1}{100} \cdot (t_{var} - t_{tuhn}) = \frac{1}{273{,}16} T_{troj}$: $V = V_0[1 + 1/T_0 \cdot (T - T_0)] = V_0 \cdot T/T_0$

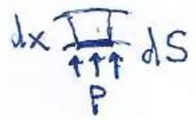
ZATIAĽ: df. T

$\Leftrightarrow \boxed{V/T = \text{konšt}}$; $\begin{cases} p_1 V_1 = p_2 V_1' \\ V_1'/T_1 = V_2/T_2 \end{cases}$: $p_1 V_1 = p_2 \cdot V_2/T_2 \cdot T_1 \Leftrightarrow$ $pV/T = $ konšt / konšt $= \mu R$, $R = 8{,}314\ J K^{-1}$, $\boxed{pV = \mu R T}$



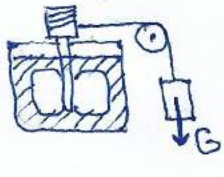
práca a teplo

práca: 1 koná p. na 2 $\left(\begin{cases}1: \text{„konateľ"}\\ 2: \text{„trpiteľ"}\end{cases}\right)$ = dodáva 2 en. mechanicky, A = dodaná en. $= Fs$ / 1 prijíma prácu od 2: $-Fs \to \vec{F}\cdot\Delta\vec{r}$;
plyn ako „konateľ": ① valcová nádoba: pdV, ② balón,...:



dtto $\left(dA = \oint p\, dS\, dx \overset{\text{Pascal}}{=} p\cdot\oint dS\, dx = p\, dV\right)$

teplo: 1 dodáva t. 2 = dodáva 2 en. nemech., zohrievaním, Q = dodaná en. (<0 ak 1 prijíma t. od 2) / mikroskop. opis: mol. 1 konajú prácu na mol. 2, „1 koná t. na 2"; kalorimetria: $Q = mc\Delta t$, c = merné t. $\to Q = \begin{cases} m_1c_1(t_1-t)\\ m_2c_2(t-t_2)\end{cases} \Leftrightarrow m_1c_1t_1 + m_2c_2t_2 = (m_1c_1+m_2c_2)t \to$ kalorikum ? NIE, plyn môžeme zahriať aj prácou; mech. ekvivalent tepla: Joule (1843) (Mager 42, 5): vrtuľka + závažie $\to \boxed{1\,\text{kcal}} \overset{\text{df}}{=}$ t. na zohriatie 1 l H_2O $= \boxed{4{,}186\,\text{kJ}}$

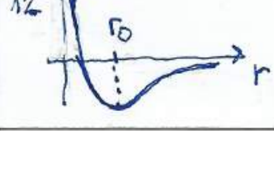


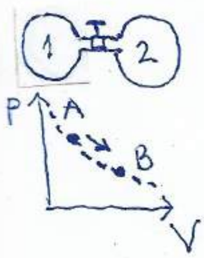
1. veta termodynamická

súhra Q, A (z exp.): $\begin{cases} Q = \text{t. dodané systému}\\ A' = \text{p. dodaná systému}\end{cases}$ (plyn: $A' = -A$, $A = \int p\,dV$): systém prejde z daného A do daného B: $\boxed{Q + A'\ \text{nezávisí od cesty}}$ (Q v J: dá sa sčítať s A'!) $\Rightarrow$ ex. fcia stavu systému U taká, že $\Delta U = Q + A'$ (df. až na konšt; Clausius 1850) / U = vn. en.: $U = E$, $\boxed{\Delta E = Q + A'}$; „mech." df. Q: z A do B sa vždy môžeme dostať iba dodaním/odobraním práce $\Rightarrow \Delta E = A'_0$, ① 1. veta: A'_0 nezávisí od cesty, ② df. Q: $\boxed{Q = A'_0 - A'}$; 1. veta v dif. tvare: $y(x)$: $dy \overset{\text{fyz.}}{=}$ infinitez. Δy (mat.: lin. časť Δy) - ALE dQ, dA' nie sú prírast. fcií $\to$ ozn. ich $\delta Q, \delta A'$ (T.: $đQ, đA'$; plyn: $\delta A = p\,dV$ / $df \overset{\text{CHYBA!}}{=} \partial_p f\, dp + \partial_V f\, dV$): $\boxed{dE = \delta Q + \delta A'}$

en. id. plynu

mikroskop. opis: $E \overset{\text{1-at.}}{=} \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_N^2 = N\cdot\frac{1}{2}m\overline{v^2}$ / kinetická teória: $\overline{v^2} \propto T \Rightarrow E \propto T$; reál. plyn: $+ V$





makroskop. opis: ① rozpín. do vákua (J. 1845): $\left\{\begin{array}{l}1: \text{stav } A\\ 2: \text{vákuum}\end{array}\right.$, otvor. kohútika → stav B: A' aj $Q = 0 \Rightarrow \Delta E = 0$ & $t_B \doteq t_A$ (id.: (=), reál. [väčšina] (<)) $\Rightarrow E = E(T)$, ② kalorimetria: $C_V =$ = konšt $\Rightarrow$ dtto; konšt ? 1 mol: $\boxed{E = \frac{1}{2} f RT}$, f = počet stupňov voľnosti mol. = $\left\{\begin{array}{l}3,\ \text{1-at. plyn}\\ 5,\ \text{2-at. plyn}\\ 6,\ \text{3-a viacat. plyn}\end{array}\right.$ (kalorimetric. rovnica);

stredná en. molekúl: 1 mol = množstvo látky ako v 12 g ^{12}C = N_A mol., $N_A = 6{,}022 \cdot 10^{23}$ (SI: $[N_A] = mol^{-1}$ + 2. rovnosť = df. molu) → Boltzmannova konšt. („plyn. konšt. v prepočte na 1 mol.“): $k = R/N_A \Rightarrow \boxed{\bar{\varepsilon} = E/N = \mu \cdot \frac{1}{2} f RT / (\mu N_A) = \frac{1}{2} f \cdot kT}$ / $k = 0{,}862 \cdot 10^{-4}$ eV K^{-1} (SI: df. K): stredná en. atómov H na povrchu Slnka ($T = 5778$ K) je $\bar{\varepsilon} = 0{,}747$ eV

adiabatický dej

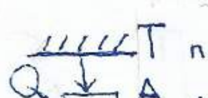
adiabatický = bez prenosu tepla (ἀ- = ne-, διά = cez, βαίνειν = ísť); merné teplá plynu (všetko pre 1 mol): $Q = C\Delta T$, C = = molárne merné teplo → ① V = konšt: $A = 0 \Rightarrow Q = \Delta E \overset{!}{=} C_V \Delta T \Rightarrow \boxed{C_V = \frac{1}{2} f R}$, ② p = konšt: $A = p\Delta V$, $pV = RT \Rightarrow A = \Delta(pV) = R\Delta T \Rightarrow Q = \Delta E + A = C_V \Delta T + R\Delta T \overset{!}{=} C_p \Delta T \Rightarrow \boxed{C_p = C_V + R}$ (Mayerov vzťah); tepelne izolovaný plyn: $\delta Q = dE + \delta A = C_V dT + p dV \overset{!}{=} 0$ /$\cdot R$: $C_V d(RT) + R \cdot p dV = C_V d(pV) + \% = C_V \cdot (dp \cdot V + p dV) + \% \overset{\text{Mayer}}{=} C_V dp \cdot V + C_p p dV = 0 \Rightarrow \boxed{\frac{dp}{dV} = -\varkappa \frac{p}{V}}$, $\varkappa$ (Poissonova konšt.) $= \frac{C_p}{C_V} \Rightarrow \int \frac{dp}{p} = -\varkappa \int \frac{dV}{V}$, $\ln p = -\varkappa \ln V + \underbrace{\text{konšt}}_{\ln C}$, $p = CV^{-\varkappa} \Leftrightarrow \boxed{pV^{\varkappa} = \text{konšt}}$ - $\varkappa > 1$: p↓ prudšie než pri T = konšt

rýchlosť zvuku

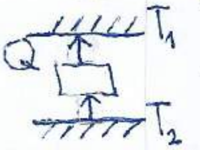
linearizované rovnice pre $\rho, \vec{v} \rightarrow v_{zv} = \sqrt{dp/d\rho}$; $\rho = mn = mN/V \Rightarrow$ adiabat. dej: $p \propto \rho^{\varkappa} \Rightarrow \frac{d \ln p}{d \ln \rho} = \frac{dp/p}{d\rho/\rho} = \varkappa \Rightarrow \boxed{v_{zv}^2 = \varkappa p/\rho}$; Newton: izoterm. dej $\Rightarrow v_{zv}^2 = p/\rho$ - $\forall\, \varkappa = \frac{f/2+1}{f/2} \overset{\text{2-at.}}{\doteq} 7/5$

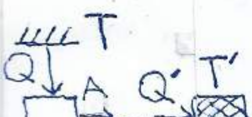
2. veta termodynamická

nie je možná ÚPLNÁ premena neusporiad. pohybu na usporiadaný; (Kelvin: 1851) nie je možný dej, kt. by mal jediný výsledok - konanie



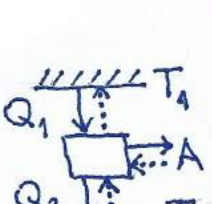
A na účet Q z rezervoára (Planck 1897; K.: „ochladením daného množstva látky pod teplotu najstudenšieho z okolitých telies"); (Clausius: 1850): nie je možný dej, kt. by mal jediný výsledok - prenos Q z chladnejšieho telesa na teplejšie; (Cl)





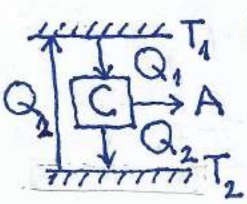
$\Rightarrow$ (K) ? non(K): rezervoár s $T \xrightarrow{Q}$ stroj $\xrightarrow{A}$ trenie $\xrightarrow{Q'}$ 3. teleso s T' / $T' > T$: non (Cl) čbtd

Carnotov cyklus

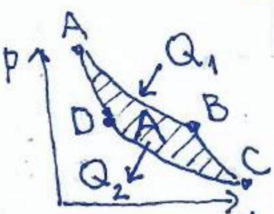


C. stroj: prijme Q_1 pri T_1 + odovzdá Q_2 (>0!) pri $T_2 < T_1$ + vykoná $A = Q_1 - Q_2$, $\forall$ VRATNÉ $\Rightarrow$ účinnosť: $\boxed{\eta} = A/Q_1 = \boxed{1 - Q_2/Q_1}$ /

C. chladnička = inverzný C. stroj (C. stroj pustený „dozadu v t");

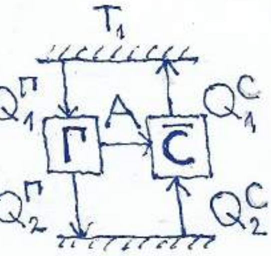


(K) $\Rightarrow$ (Cl) ? non (Cl): prenesieme Q_2 od T_2 k T_1, potom spustíme C. stroj $\Rightarrow$ A vykonáme iba na účet $\Delta Q = Q_1 - Q_2$, prijatého pri T_1 = non (K) čbtd



id. plyn: C. cyklus = postupnosť 4 dejov: $(p_A V_A) \xrightarrow{T_1} (p_B V_B) \xrightarrow{ad.} (p_C V_C) \xrightarrow{T_2} (p_D V_D)$, $\begin{cases} Q_1 = Q \text{ dodané na } AB \\ Q_2 = Q \text{ odovzdané na } CD \end{cases}$ (T = konšt: $Q = A \overset{1\,mol}{=} RT \ln(V_2/V_1) \Rightarrow \begin{cases} Q_1 \\ Q_2 \end{cases} \overset{1\,mol}{=} R \times \begin{cases} T_1 \ln(V_B/V_A) \\ T_2 \ln(V_C/V_D) \end{cases}$)

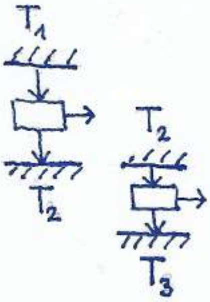
V: medzi všetkými strojmi Γ, kt. pracujú medzi danými dvomi teplotami T_1, T_2, sú C. stroje (s vratným dejom) najúčinnejšie, $\eta_\Gamma \leq \eta_C$, pričom = zaruč. platí ak $\Gamma = C$



D: majme Γ, C také, že práca, kt. vykonajú za 1 cyklus, je rovnaká, $A^\Gamma = A^C$ + spojme Γ s $\bar{C}$ (inv. strojom k C, C. chladničkou); (1) 1. veta: $\begin{cases} A^\Gamma = Q_1^\Gamma - Q_2^\Gamma \\ A^C = Q_1^C - Q_2^C \end{cases}$ $\Rightarrow$ aj celkové teplo, odobrané z rezervoára s T_1 a dodané do rezervoára s T_2, $\begin{cases} Q_{1tot} = Q_1^\Gamma - Q_1^C \\ Q_{2tot} = Q_2^\Gamma - Q_2^C \end{cases}$, je rovnaké, $Q_{1tot} = Q_{2tot}$, (2) 2. veta: $Q_{1tot} \geq 0$

$\Rightarrow Q_1^\Gamma \geq Q_1^C$, $\eta_\Gamma = A/Q_1^\Gamma \leq A/Q_1^C = \eta_C$ čbtd / ⊜? $\Gamma = C$: $\eta_\Gamma \leq \eta_C$ aj $\eta_C \leq \eta_\Gamma \Rightarrow \eta_\Gamma = \eta_C$ čbtd; iný postup: $Q_1^\Gamma = Q_1^C$; ALE čo ak sa A^C nedá „naladiť" na A^Γ? $A^C/A^\Gamma = p/q$ (Fermi): p cyklov Γ + q cyklov $\bar{C} \longrightarrow$ dtto čo predtým, ak prejdeme od A, Q_1, Q_2 k a, q_1, q_2 = celkovým $\boxed{A, Q_1, Q_2 \; (a^\Gamma = a^C \text{ atď.})}$

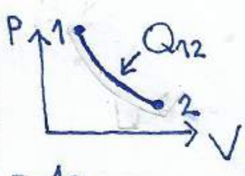
termodynamická teplota



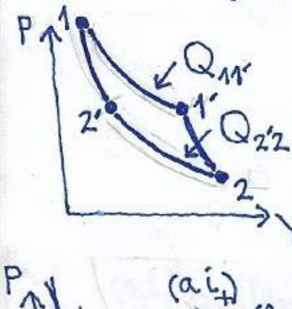
$\forall C$, stroj: to isté $Q_2/Q_1 = 1-\eta$ $\boxed{\Rightarrow Q_1/Q_2 = f(T_1, T_2)}$ / 2-stupňový stroj: dtto + $Q_2/Q_3 = f(T_2, T_3) \Rightarrow Q_1/Q_3 = f(T_1 T_2) f(T_2 T_3)$ - ALE $Q_1/Q_3 = f(T_1 T_3) \Rightarrow f(T_1 T_2) = \dfrac{f(T_1 T_3)}{f(T_2 T_3)} \overset{T_3 \text{ dané}}{=} \boxed{\dfrac{\varphi(T_1)}{\varphi(T_2)}} \rightarrow T \overset{df}{=} \varphi(T)$ (ľub. $\tilde{T}$ rastúce s T $\xrightarrow{exp.}$ $\varphi(\tilde{T})$ až na súčiniteľ $\xrightarrow{df}$ $T = \varphi(\tilde{T})$ také, aby 1 K vyšiel správne) $\Rightarrow Q_1/Q_2 = T_1/T_2$. $\boxed{\eta = 1 - T_2/T_1}$

id. plyn: $AB + CD$: $\begin{cases} Q_1 \\ Q_2 \end{cases} = R \times \begin{cases} T_1 \ln(V_B/V_A) \\ T_2 \ln(V_C/V_D) \end{cases}$ / $BC + DA$: $TV^{\varkappa_-} = $ konšt, $\varkappa_- = \varkappa - 1 \Rightarrow \begin{cases} T_B V_B^{\varkappa_-} = T_C V_C^{\varkappa_-} \\ T_A V_A^{\varkappa_-} = T_D V_D^{\varkappa_-} \end{cases} \Rightarrow V_B/V_A = V_C/V_D \Rightarrow Q_1/Q_2 = T_1/T_2$ - vyšlo!

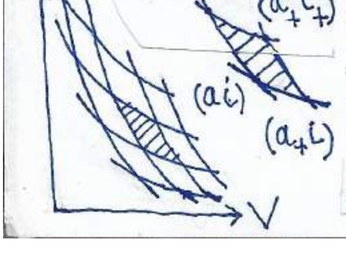
entropia

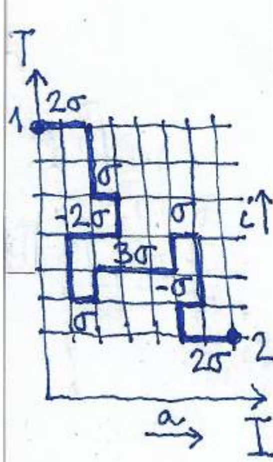


veličina „v premene" (ἐν - v, τρόπος - spôsob, zmena), miera neusporiadanosti systému; df. I: $I = \int_1^2 \delta Q/T$, $\int$ cez VRATNÝ dej: (1) 1,2 na tej istej izoterme: $I = Q_{12}/T$,

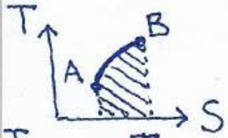


(2) 1,2 na rôznych izotermách: (i) prechod po vetvách C. cyklu: cesta I = $1 \xrightarrow{T_1} 1' \xrightarrow{ad} 2$: $I_1 = Q_{11'}/T_1$, cesta II = $1 \xrightarrow{ad} 2' \xrightarrow{T_2} 2$: $I_{II} = Q_{2'2}/T_2$ - ALE $Q_{11'} = Q_1$, $Q_{2'2} = -Q_{22'} = Q_2$ & $Q_1/Q_2 = T_1/T_2 \Rightarrow I_1 = I_{II}$; (ii) ľub. prechod: $\boxed{I \text{ nezávisí od cesty}}$ - D: zostrojíme mriežku z izoterm a adiabát; plaketa nad uzlom (a, i): $\Delta I_{hore} = \Delta I$ na hrane

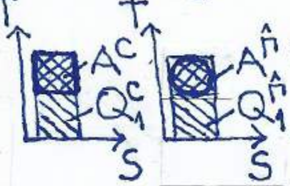




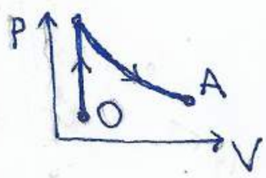
$(a\, i_+), (a_+ i_+) = Q_{i_+}/T_{i_+}$, $\Delta I_{dole} = \Delta I$ na hrane $(a i),(a_+ i) =$
$= Q_i/T_i$: C. cyklus $\to$ $\Delta I_{hore} = \Delta I_{dole}$ / ΔI na bokoch
$= 0 \Rightarrow \Delta I$ pri posune od adiabaty a k adiabate $a_\pm$ po ľub.
izoterme i $\overset{\text{voľba } \Delta a}{=} \pm\sigma$ & ΔI pri presune medzi izotermami $=$
$= 0 \Rightarrow I = n\sigma$, n = počet adiabát medzi 1 a 2 - nezávisí
od cesty čbtd; df. S: $I = \int_C \delta Q/T$ nezávisí od C ($I_{sluč} \equiv$
$I_a \equiv \oint \delta Q/T = 0$, $1/T$ = integrujúci súčiniteľ δQ): ex. fcia
stavu systému S taká, že $\boxed{\Delta S = I}$ (tiež df. až na konšt.);



prepis do dif. tvaru: $dS \overset{\text{vrat.}}{=} \delta Q/T \to$ prepis 1. vety: $\delta Q =$
$\overset{\text{vrat.}}{=} T dS$, $\delta A' = -\delta A = -p\,dV \Rightarrow \boxed{dE = T dS - p\,dV}$; (T,S)-diagram:



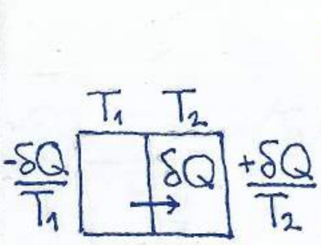
$Q \overset{\text{vrat.}}{=} \int_{S_A}^{S_B} T dS = \pm$ plocha pod krivkou / C. cyklus = □ : $A = Q_1$
$- Q_2$ = plocha □ $\Rightarrow \hat\Gamma$ = vratný stroj s $T_2 \le T \le T_1$: $\boxed{\eta_{\hat\Gamma} < \eta_C}$
id. plyn: $pV = RT$ & $E = C_V T \to S(\cancel{p}^{\,T}, V)$? $dS = 1/T \times$
$\times (dE + p\,dV) = C_V dT/T + R\,dV/V$ ($\begin{cases} \partial_T S = C_V/T \\ \partial_V S = R/V \end{cases}$:



$\partial_V \partial_T S$ aj $\partial_T \partial_V S = 0$ O.K.) $\Rightarrow \boxed{S = C_V \ln(T/T_0) + R \times \ln(V/V_0) + S_0}$ / 1-at. plyn: $\underline{S} = R\left[\frac{3}{2}\ln(T/T_0) + \ln(V/V_0) + \sigma_0\right] = \boxed{R \ln(\alpha T^{3/2} V)}$, konšt. α : z mikroskop. teórie;
podm. na T: $(\ldots) \gg 1 \Leftrightarrow T \gg T_{deg}$ ($T \lesssim T_{deg}$: kvantový
plyn); nezávislosť E od V : viď $dS = dE/T + R\,dV/V$,
$dE = \partial_T E\, dT + \partial_V E\, dV$; aditívnosť S : μ mol: $S \to \mu S$
(podm.: $E_{povrch} \ll E_{obj}$; intenzív.: p, T / extenzív.: V, S)

zákon rastu entropie

Q, A' pri nevrat. deji? disipácia en.: $\begin{cases} Q = Q_{vrat} - Q_t < \\ A' = A'_{vrat} + Q_t > \end{cases}$
$\begin{cases} < Q_{vrat} \\ > A_{vrat} \end{cases}$ / rozpín. do vákua: $\begin{cases} Q = 0, \ Q_{vrat} > 0 \\ A' = 0, \ A'_{vrat} < 0 \end{cases} \Rightarrow$ dtto



$\Rightarrow \boxed{dS = \delta Q_{vrat}/T \ge \delta Q/T}$, $\begin{cases} (=): \text{vrat. dej} \\ (>): \text{nevrat. dej} \end{cases} \Rightarrow \delta Q =$
$= 0$: $\boxed{dS \ge 0}$; 3. veta (Nernst): $\Delta S \to 0$ ($S \to S_0 = 0$ al.
~ 0) pri $T \to 0$ / max. rozšír. 2. vety: tepelná smrť vesmíru

čo je štatistická fyzika?

kinetická teória plynov (Maxwell, Boltzmann): opisuje rovnováhu plynu, viď $p \propto n\overline{v^2}$, aj prenosové javy - prenos tepla + viskozitu; vývoj mikrostavu - NIE $(\vec{r}_i, \vec{v}_i)$ ako fcie t, ale rozdeľovacia fcia $f(\vec{r}, \vec{v}, t)$; rovnica pre f (B. rovnica) $\Rightarrow$ ex. fcia $H(t)$ zostrojená z f taká, že $\dot{H} \leqq 0$ ($\rightarrow H \propto -S$; H-teoréma); štat. mechanika/fyzika (Gibbs): opisuje rovnováhu (IBA!) termodyn. systémov, metóda: ustrednenie cez štat. súbor (ansámbel); 1. krok (B. 1877): $S =$ konšt $\ln \Omega$, $\Omega =$ počet mikrostavov, viď $S = S_1 + S_2$ & $\Omega = \Omega_1 \Omega_2$ / konšt $= Nk$, viď $\Omega_{id} = \omega^N$, $\omega = \Omega$ 1 mol.

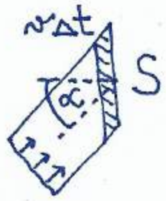
atómy

Demokritos: „dohodou horúce, dohodou studené, dohodou farba, v skutočnosti len atómy a prázdno" - princíp LEGA? Lucretius Carus: pri pohybe nadol malé vybočenia at., „aj my vybočujeme podobne v našich pohyboch, nie v určených časoch ani smere, ale len kam nás nesie naša myseľ"; at. v chémii: stechiometria (zisťovanie relatív. množstiev látok vstupujúcich do reakcií): ① zákon stálych zlučovacích pomerov (Proust):
$$\begin{cases} 1\,g\, H_2 + 7{,}94\,g\, O_2 = 8{,}94\,g\, H_2O \\ 5\,g\, H_2 + 39{,}68\,g\, O_2 = 44{,}68\,g\, H_2O \end{cases}$$
$\rightarrow 1/7{,}94 = 5/39{,}68$, ② zákon násobných zlučovacích pomerov (Dalton): $1\,g\, H_2 + 15{,}87\,g\, O_2 = 16{,}87\,g$ HO-OH (peroxidu H) $\rightarrow \frac{1/7{,}94}{1/15{,}87} = 2{,}00$; prvky z at.? $\begin{cases} \text{voda} = HO \\ \text{peroxid} = HO_2 \end{cases}$ & H: $A = 1 \Rightarrow$ O: $A \doteq 8$ ZLE, najmenšie jednotky = molekuly, ③ Avogadrov zákon: $V_1/V_2 = p/q$ (m_1/m_2: iba približne) $\rightarrow$ rovnaké V obs. rovnaký počet mol.; určenie N_A: Perrin (1909, NC 26): Brownov pohyb s λ, τ: $kT \sim \mu a \lambda^2/\tau$ $\rightarrow k = R/N_A \rightarrow N_A$

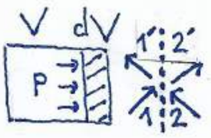
tlak ako dôsledok nárazov molekúl

izotropné rozdelenie mol.: $P = \frac{2}{3} n \bar{\varepsilon}$, $\bar{\varepsilon} = \frac{1}{2} m \overline{v^2}$ - D:

hustota počtu mol. s rýchlosťami z objemu $dV_{\vec v}$ okolo $\vec v = v\vec n$: $\delta n = n\,\overset{= dP}{\varrho(\underline{\underline{v}})\,dV_{\vec v}}$, ϱ = hustota pravdepodob. vo v-priestore $\longrightarrow \delta N$ = počet mol. s danými rýchlosťami, kt. dopadnú z ½-priestoru $x<0$ na plochu S v rovine (y,z) za čas

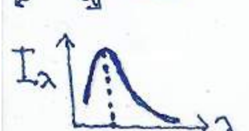


$\Delta t \overset{\alpha = \sphericalangle(\vec 1,\vec n)}{=} \delta n\, v\, \Delta t\, S\cos\alpha = \delta n\, v_x\, \Delta t\, S$ / $\Delta\vec p \equiv$ zmena $\vec p$ pri odraze mol. $= (-2mv_x, 0, 0) \Rightarrow \delta\vec F_{mol-S} = -\delta\vec F_{S-mol} = -\delta N \times \Delta\vec p/\Delta t = (\delta n\, v_x \cancel{\Delta t}\, S . 2mv_x, 0, 0)/\cancel{\Delta t} = (\delta n . 2mv_x^2, 0, 0) \times S \Rightarrow P = F_x/S = \int_{v_x>0} \delta n . 2mv_x^2 = \frac{1}{\cancel{2}}\int_{\forall v_x} n\varrho\, dV_{\vec v} . \cancel{2}mv_x^2 = nm\overline{v_x^2}$ /



$\overline{v^2} = \overline{v_x^2} + \underbrace{\overline{v_y^2}}_{\overline{v_x^2}} + \underbrace{\overline{v_z^2}}_{\overline{v_x^2}} = 3\overline{v_x^2} \Rightarrow P = \frac13 nm\overline{v^2}$ čbtd; Pascalov zákon: S vnútri plynu: dtto / mol. namiesto S: dtto

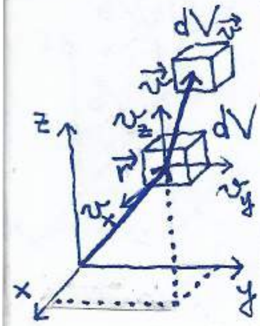
tlak žiarenia: ① Lebedev (1900): $P_1 < P_2 \to \vec M$ orient. hore, ② žiarenie ČT: teleso s teplotou T, kt. neprepúšťa žiarenie / dutinový žiarič → žiarenie s teplotou T - $\boxed{I}$ = intenzita $\propto$ $\propto \boxed{T^4}$ (Stefan-Boltzmann), $\boxed{\lambda_m}$ = vlnová dĺžka, na kt. pripadá maximum energie žiarenia $\propto \boxed{1/T}$ (Wien; spektrum: Planck 1900); tlak? $v = c$ & m = relativistická hmotnosť fotónu: $\begin{cases} E = mc^2 \\ p = mc \end{cases} \Rightarrow \boxed{P = n\frac{\bar\varepsilon_{celk}}{c^2}\underbrace{\overline{c_x^2}}_{\to c^2/3} = \frac13 n\bar\varepsilon_{celk} = \frac13 U}$, U = hustota



en. (nerelat. plyn: $P = \frac23 U_{kin} \ll U$) / závislosť od T? $\delta n = n \times \varrho(p)\, dV_{\vec p}$, $dV_{\vec p} = d\mathcal{V}_p . d\Omega/(4\pi)$, $\begin{cases} d\mathcal{V}_p = 4\pi p^2 dp \\ d\Omega = \sin\alpha\, d\alpha\, d\varphi \end{cases} \to \delta N$ = počet fotónov s danými hybnosťami, kt. dopadnú na plochu S za čas $\Delta t = \delta n\, c\, \Delta t\, S\cos\alpha$, $\delta I = \delta N\, \varepsilon_{celk}/(S\Delta t) = \delta n\, c\cos\alpha\cdot\varepsilon_{celk}$, $I = \int_{p_x>0} \delta n\, c\cos\alpha\cdot\varepsilon_{celk} = nc\int\varrho\,\varepsilon_{celk}\, d\mathcal{V}_p \times \int_{\alpha<\pi/2}\cos\alpha\, d\Omega/(4\pi) = nc\cdot\bar\varepsilon_{celk}\cdot\frac14 = \frac14 Uc$ & $I = \sigma T^4$, σ = SB konštanta $\Rightarrow \boxed{U = aT^4}$, $a = \frac4c\sigma$ = radiačná konštanta & $\boxed{P = \frac13 aT^4}$ (hv-y: $P_ž/P_\ell \propto M^2$, $M \lesssim 50 M_\odot \Rightarrow P_ž/P_\ell \lesssim 1$)

rozdeľovacia funkcia:

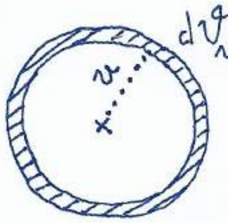
dN = počet mol. v dV, $dV_{\vec v} = f(\vec r, \vec v, t)\, dV\, dV_{\vec v}$ (f zadáva,



kol'ko je mol. s $\vec{r}_{mol} \doteq \vec{r}, \vec{v}_{mol} \doteq \vec{v}$); rovnováha: $f = f(v)$ $\Rightarrow \delta N$ = počet mol. z $V, dV_{\vec{v}} = f\, V\, dV_{\vec{v}}$ / df. ρ: $\delta N = V \times \delta n$, $\delta n = n \rho\, dV_{\vec{v}} \Rightarrow \boxed{f = n\rho}$ (normovanie f: $\int f\, dV dV_{\vec{v}} = \int n \rho V dV_{\vec{v}} = N \underbrace{\int \rho\, dV_{\vec{v}}}_{dP} = N$ O.K.)

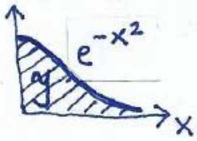
Maxwellovo rozdelenie

predp. 1: izotropia $\Leftrightarrow \rho = \varphi(v^2) = \varphi(v_x^2 + v_y^2 + v_z^2)$, predp. 2: nezávislost' $v_x, v_y, v_z \Leftrightarrow \rho = \psi_1(v_x)\psi_2(v_y)\psi_3(v_z)$, $\psi_i \overset{p1}{\doteq} \psi$ / $e^{a(v_x^2+v_y^2+v_z^2)} = e^{a v_x^2} e^{a v_y^2} e^{a v_z^2} \to \rho = C e^{-\alpha v^2}$, $\ominus$: aby sa ρ dalo normovat'; ① $\alpha \overset{?}{:}$ $\overline{v^2} = \int \rho v^2 dV_{\vec{v}}$,

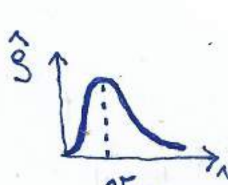


$\int \rho\, dV_{\vec{v}} = 1 \Rightarrow \overline{v^2} = \int \rho v^2 dV_{\vec{v}} / \int \rho\, dV_{\vec{v}}$ & $dV_{\vec{v}} \hat{=} d\vartheta_v = 4\pi v^2 dv \Rightarrow \overline{v^2} = \int_0^\infty \rho v^4 dv / \int_0^\infty \rho v^2 dv = I_4 / I_2$, $I_n = \int_0^\infty e^{-\alpha v^2} v^n dv$; $I_0 = \int_0^\infty e^{-\alpha v^2} dv = \alpha^{-1/2} \mathcal{J}$, $\mathcal{J} = \int_0^\infty e^{-x^2} dx$ (Gauss):

$I_2 = -\partial_\alpha I_0 = \frac{1}{2}\alpha^{-3/2}\mathcal{J}$, $I_4 = -\partial_\alpha I_2 = \frac{3}{4}\alpha^{-5/2}\mathcal{J} \Rightarrow \overline{v^2} = \frac{3}{2}\alpha^{-1}$ / $pV = \mu RT$, $R = N_A k$: $pV = NkT \Rightarrow p = nkT$ & $p = \frac{1}{3} n \times m \overline{v^2} \Rightarrow \overline{v^2} = \frac{3}{m} kT$, $\alpha^{-1} = \frac{2}{m} kT$, $\boxed{\rho = C e^{-\frac{m v^2}{2kT}}}$ $(\Leftrightarrow \rho = C e^{-\frac{\varepsilon}{kT}})$; ② $C \overset{?}{:}$ $\int \rho\, dV_{\vec{v}} = \int C e^{-\alpha v^2} d^3 v = C\left(\int_{-\infty}^{\infty} e^{-\alpha u^2} du\right)^3$

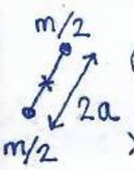


$= C(2I_0)^3 \overset{!}{=} 1$ / $\mathcal{J} = \frac{1}{2}\sqrt{\pi}$, vid' $\int e^{-r^2} dx\, dy$: $2I_0 = \alpha^{-1/2} \cdot 2\mathcal{J} = (2/m \cdot kT)^{1/2} \cdot \sqrt{\pi} \Rightarrow \boxed{C = (2I_0)^{-3} = \left[m/(2\pi kT)\right]^{3/2}}$; rýchlost' mol.: $\boxed{v_{s.kv.} = \sqrt{\overline{v^2}} = \sqrt{\tfrac{3}{2}}\,\alpha^{-1/2}}$ / $v_m \overset{?}{:}$ $dP = \rho\, dV_{\vec{v}} \hat{=} \rho\, d\vartheta_v = C e^{-\alpha v^2} \cdot 4\pi v^2 dv = \hat{\rho}\, dv$, $\hat{\rho} \propto e^{-\alpha v^2} v^2$: $\partial_{v^2} \hat{\rho} \propto e^{-\alpha v^2} \times (-\alpha v^2 + 1) \overset{!}{=} 0 \to \boxed{v_m = \alpha^{-1/2}}$ $(= 0.82\, v_{s.kv.})$

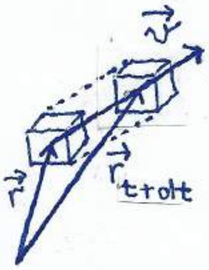


ekvipartičná teoréma

1-at. plyn: $\boxed{\overline{\varepsilon} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT}$, vid' p_{kin} + stav. rovnica;
2-at. plyn: $\varepsilon = \varepsilon_0 + \varepsilon_1$, $\begin{cases} \varepsilon_0 = \frac{1}{2} m v^2 \\ \varepsilon_1 = \frac{1}{2} I \Omega^2 \end{cases}$, $I = m a^2$ & $\Omega^2 = \Omega_X^2 + \Omega_Y^2 \to dP = dP_0\, dP_1$, $dP_0 = C_0 e^{-\varepsilon_0/(kT)} d^3 v$ & $dP_1 = C_1 e^{-\varepsilon_1/(kT)} d^2\Omega$ (podl'a analógie s dP_0 / zo štat. mechaniky)

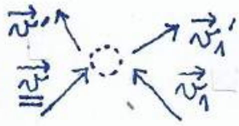


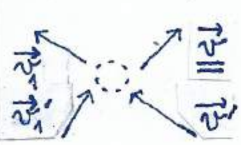
⇒ $\bar{\varepsilon}_0 = \frac{3}{2}kT$ & $\bar{\varepsilon}_1 = kT$ ($z\ \overline{\Omega^2} = \int e^{-\alpha_1\Omega^2}\Omega^2 d^2\Omega / \int e^{-\alpha_1\Omega^2} \times d^2\Omega$, $\alpha_1^{-1} = \frac{2}{I}kT$) ⇒ $\boxed{\bar{\varepsilon} = \frac{5}{2}kT}$ / 3- a viacat. plyn: analog.; kmity: $f \to f + 2f_{kmit}$ (od x, p) - ALE sú „zamrznuté"



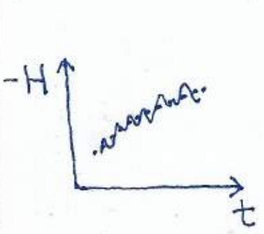
Boltzmannova rovnica

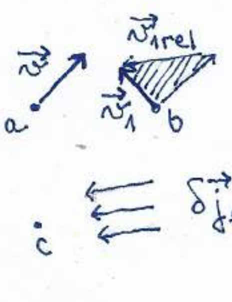
bez zrážok: $\delta N_{t+dt} = \delta N_t \Rightarrow f(\vec{r}_{t+dt}, \vec{v}, t+dt) = f(\vec{r}, \vec{v}, t)$, ľ. str. $= f(\vec{r},\vec{v},t) + \nabla f(\ )\cdot \underbrace{d\vec{r}}_{\vec{v}dt} + \partial_t f(\ )\,dt \Rightarrow \boxed{\partial_t f + \vec{v}\cdot\nabla f = 0}$ (plyn v grav. poli: $+\vec{g}\cdot\nabla_{\vec{v}} f$); pridanie zrážok: $\boxed{\partial_t f + \vec{v}\cdot\nabla f = (\partial_t f)_{coll}}$, $\boxed{(\partial_t f)_{coll}}$ = zrážkový člen (LL X: St f, St = Stoß) $= \boxed{\int (f'f_1' - f f_1)\, v_{rel}\, d\sigma\, dV_{\vec{v}_1}}$, $\left\{\begin{matrix} f = f(\vec{r},\vec{v},t) \\ f_1 = f(\vec{r},\vec{v}_1,t)\end{matrix}\right.$, $\left\{\begin{matrix} f' = f(\vec{r},\vec{v}',t) \\ f_1' = f(\vec{r},\vec{v}_1',t)\end{matrix}\right.$





→ rovnováha: $f_0 f_{01} = f_0' f_{01}' \Rightarrow f_0 \propto e^{-\beta\varepsilon}$ / p_{kin} + stav. rovnica ⇒ $\beta^{-1} = kT$; H-teoréma: $H = \int f(\ln f - 1)\, dV \times dV_{\vec{v}}$ ($-H_0 \leftrightarrow S$ v kánonickom súbore): Boltzmann. rovnica ⇒ $\boxed{\dot{H} \leq 0}$; PROBLÉM: ako môže nevratnosť na na makroskop. úrovni vzniknúť z vratnej dynamiky na mikroskop. úrovni? (Newtonova mechanika: presná T-sym., QM: ε-ové narušenie pri K-ónoch) ① $\vec{v}_i \to -\vec{v}_i$: opačný vývoj po zač. stav / približne $-\vec{v}_i$: opačný vývoj počas Δt, viď veta o fluktuáciach (B.: NIE, mal molekulárny chaos), ② vesmír: $S_0 \sim 0$ / $S_{g0} \sim 0$, S_{e0} blízka k maximu (Penrose)

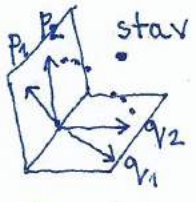




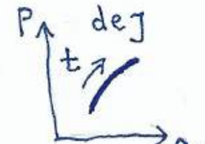
zostrojenie $(\partial_t f)_{coll}$: ① $(\partial_t f)_{coll,-}$ = úbytok f za 1s pri zrážkach $\vec{v},\vec{v}_1 \to \vec{v}',\vec{v}_1'$: rozptyl mol. b s rýchlosťou $\vec{v}_1$ na mol. a s rýchlosťou $\vec{v}$ ⟺ rozptyl fiktívnej častice f s hmotnosťou m/2 a rýchlosťou $\vec{v}_{1rel} = \vec{v}_1 - \vec{v}$ ($= -\vec{v}_{rel}$, $\vec{v}_{rel} = \vec{v} - \vec{v}_1$) na pevnom centre c: $\delta\vec{j}_f$ = prúd častíc f $= \delta n_1 \vec{v}_{1rel}$, $\delta n_1 = f_1\, dV_{\vec{v}_1} \Rightarrow \delta P_-$ = príspevok mol. b k pravdepodobnosti rozptylu mol. a za 1s $= \int \delta j_f\, d\sigma = \left(\int f_1 v_{rel}\, d\sigma\right) dV_{\vec{v}_1}$, $d\sigma$ = infinitezimál. úč. prierez ⇒ $(\partial_t f)_{coll,-} = f P_- = f \int\int f_1 v_{rel} \times d\sigma\, dV_{\vec{v}_1}$, ② $(\partial_t f)_{coll,+}$ = prírastok f za 1s pri zrážkach

$\vec{v}', \vec{v}_1' \to \vec{v}, \vec{v}_1$: analog., s využitím $dV_{\vec{v}'} dV_{\vec{v}_1'} = dV_{\vec{v}} dV_{\vec{v}_1}$

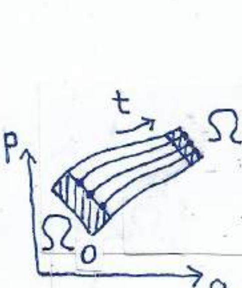
<u>mikrostavy</u>



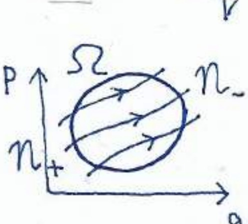
klasická (nekvantová) fyzika: $\begin{cases} q_i = \text{zovšeob. súradnice} \\ p_i = \text{zovšeob. hybnosti} \end{cases}$, $i = 1, \dots f$ (1-at. plyn: $(\vec{r}_a, \vec{p}_a = m\vec{v}_a)$, EM pole: $(\vec{B}_{\vec{r}}, \vec{E}_{\vec{r}})$): $2f$ hodnôt (q_i, p_i) = bod vo <u>fázovom priestore</u>; vývoj mikrostavu: $H(q, p, t) \equiv$ Hamiltonián : $\begin{cases} \dot{q}_i = \partial_{p_i} H \\ \dot{p}_i = -\partial_{q_i} H \end{cases}$ (<u>Hamilt. rovnice</u>) + $(q_{i0}, p_{i0}) \to (q_i(t), p_i(t))$ = krivka vo fázovom priestore – pr.: častica v poli konzervatívnych síl: $H = E = T + U = \frac{1}{2m}\vec{p}^2 + U$: $\begin{cases} \dot{\vec{r}} = \nabla_{\vec{p}} H = \frac{1}{m}\vec{p} \\ \dot{\vec{p}} = -\nabla H = -\nabla U = \vec{F} \end{cases}$; <u>uzavretý systém</u>: H nezávisí explicitne od $t \Rightarrow \dot{H} = \underbrace{\partial_{q_i} H}_{-\dot{p}_i} \dot{q}_i + \underbrace{\partial_{p_i} H}_{\dot{q}_i} \times \dot{p}_i = 0 \Leftrightarrow \boxed{H = E}$ (en.; Einsteinovo sumačné pravidlo: $u_i v_i = u_1 v_1 + \dots + u_f v_f = \sum_{i=1}^{f} u_i v_i$)

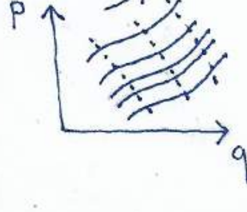


<u>Liouvillova veta</u>



majme súbor systémov $\mathcal{S} = \{\sigma_I, I = 1, \dots N_{\mathcal{S}}\}$ s dráhami $(q_i^I(t), p_i^I(t))$: dráhy sa nepretínajú $\Rightarrow N$ = počet σ_I v objeme $\Omega(t)$, kt. sa prenáša pozdĺž dráh = konšt $\Leftrightarrow f$ = rozdeľovacia fcia $\sigma_I = dN/d\Omega$, $d\Omega = dq\,dp \equiv \prod_{i=1}^{f} dq_i\,dp_i$: $\boxed{\partial_t f + \partial_{q_i}(f \dot{q}_i) + \partial_{p_i}(f \dot{p}_i) = 0}$ $\left(/ \int d\Omega(\dots)\right.$: $\partial_t N + n = 0$, n = čistý počet σ_I, kt. vyjdú z Ω za 1 s = počet vychádzajúcich σ_I – počet vchádzajúcich σ_I): $\boxed{\dot{f}} = \underbrace{\partial_{q_i} f\, \dot{q}_i}_{\partial_{q_i}(f\dot{q}_i) - \dots} + \underbrace{\partial_{p_i} f\, \dot{p}_i}_{\partial_{p_i}(f\dot{p}_i) - \dots} + \partial_t f = -f(\partial_{q_i} \underbrace{\dot{q}_i}_{\partial_{p_i} H} + \partial_{p_i} \underbrace{\dot{p}_i}_{-\partial_{q_i} H}) = \boxed{0}$, hustota $\sigma_I = \underbrace{\text{konšt pozdĺž dráh}}_{\Leftrightarrow \Omega(t) = \text{konšt}}$; <u>uzavreté systémy</u>: dráhy σ_I = <u>prúdnice</u> (čiary dotyčnicové k rýchlostiam), L. veta: hustota prúdnic = konšt pozdĺž prúdnic





<u>štatistické súbory</u>

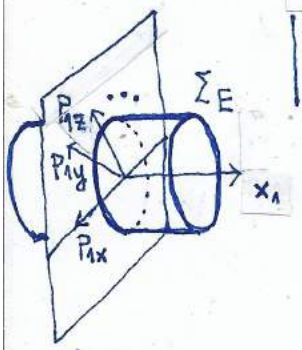
majme systém σ s dráhou $(q_i(t), p_i(t))$ + sledujme ho po čas $T \gg$

$\gg \tau$ (relaxačný čas): dráha prejde veľakrát cez $\forall$ objem $\Delta\Omega$, kt. je systému dostupný (systém je ergodický) $\Rightarrow \Delta t =$ = čas, kt. σ strávi v $\Delta\Omega$, má konečnú $\lim \Delta t/T$; ΔP (pravdepodobnosť výskytu σ v $\Delta\Omega$) $= \lim \Delta t/T \to \rho$ (hustota pravdepodobnosti nájsť σ v stave (q,p)) $= dP/d\Omega \leftrightarrow f \overset{t_0}{=} N_\gamma \rho$ - ρ = tiež rozdeľ. fcia (f: rozdelenie systémov, ρ: rozdelenie pravdepodobnosti) / f pri $t > t_0$? uzavretý systém: f stále $= N_\gamma \rho$, viď MKS; stredné hodnoty: $A(q,p) \to \bar{A}$ (štatistická stredná hodnota A) $= \int A\rho \times d\Omega$ - ALE $\rho\, d\Omega = dP = dt/T \Rightarrow \boxed{\bar{A} = 1/T \cdot \int_0^T A\, dt}$ (časová stredná hodnota); fluktuácie A? N = počet mol.: $\bar{A} = N\bar{a}$ & $\sigma_A = \Delta A_{s.kv.} = \sqrt{N}\,\sigma_a$, $\sigma_a = \Delta a_{s.kv.} \sim \bar{a}$ (binom.: $\bar{\nu} = Np$, $\sigma_\nu = \sqrt{Npq}$) $\Rightarrow \boxed{\delta_A}$ (relatívna odchýlka) $\sim \boxed{1/\sqrt{N}}$; súbory (Gibbs 1902): mikrokánonický (MKS, dané V, N, E) - kánonický (KS, dané V, N) - grandkánonický (GKS, dané V)

mikrokánonický súbor

idealizácia (systémy sú úplne tepelne izolované) - slúži na zostrojenie KS a GKS + dáva názornú predstavu o súvise s makroskopickou teóriou a o rozdeleniach pre ideálne plyny;

|| df.: mikrokánonický súbor = súbor systémov s en. E, kt. sú $\forall$ rovnako pravdepodobné, $\rho = \begin{cases} \text{konšt, ak } H = E \\ 0 \text{ inde} \end{cases}$ /

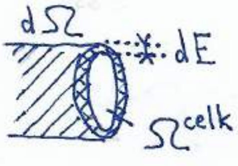


$H = E \leftrightarrow$ nadplocha $\Sigma_E \Rightarrow \rho =$ konšt na Σ_E & 0 mimo Σ_E - PREČO? ① σ v rovnováhe: mikrostavy sú max. neusporiadané $\Rightarrow$ sú rovnocenné / σ prechádza do rovnováhy: mikrostavy nie sú rovnocenné (pr.: $\forall$ mol. v jednej 1/2 nádoby) - majú $\Delta P \sim 0$, ALE zaberajú zanedbateľný objem $\Delta\Omega \Rightarrow$ môžeme aj pre ne vziať ρ = konšt;

rovnováha

také ρ súhlasí s Liouvill. vetou ($f(t_0)$ = konšt & $\dot{f} = 0$;

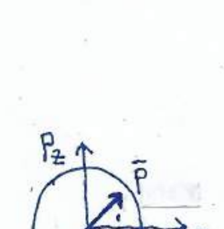
$f(t) = $ konšt), ② také ρ súhlasí aj so štat. nezávislosťou podsystémov ($\rho = \prod \rho_a$ & $\ln \rho_a = -\alpha_a - \beta E_a$, viď KS: $\ln \rho = -\alpha - \beta E$; LLV: E = jediný aditívny $\int$ pohybu pre stojaci systém => ρ_a, ρ musia mať daný tvar) - toto je len motivácia, df. MKS je v skutočnosti postulát (Tong: „najnaivnejší možný prístup", často: rovnomernosť = súčasť ergodičnosti);



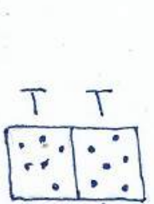
konšt? $\int \rho \, d\Omega = 1$: ① $H = E$ presne: $\boxed{\rho = C\delta(H-E)}$ (konšt $= C\delta(0) = \infty$!) & $\int C\,\delta(H-E)\underbrace{d\Omega}_{\omega\, dE} = C\omega(E) \doteq 1$, $\omega = d\Omega^{celk}/dE$ = hustota stavov => $\boxed{C = 1/\omega(E)}$. ② H rozmazané po ΔE: $\boxed{\rho = C\,\vartheta_{\Delta E}}$, $\vartheta_{\Delta E} = \vartheta(E - E_{min})\,\vartheta(E_{max} - E)$ & $\int C\,\vartheta_{\Delta E}\, d\Omega = C\Omega \doteq 1$, Ω = objem vo fázovom priestore pripadajúci na en. ΔE ($= \omega(E)\Delta E$) => $\boxed{C = 1/\Omega}$

Boltzmannova df. entropie

uzavretý systém s en. z ΔE: $\boxed{S = k\ln\Omega}$ - predbežná df., pod ln nemôže byť rozmerová veličina => Ω treba vydeliť objemom bunky Ω_b; id. plyn (ODHAD): $\forall$mol. $\to V, V_p$ $\leftrightarrow \varepsilon \lesssim \bar\varepsilon = \frac{3}{2}kT$ => $V_p \sim \frac{4\pi}{3}\bar p^3$, $\bar p = (2m\bar\varepsilon)^{1/2} = (3m \times kT)^{1/2}$ & $\Omega \sim \Omega_1^N$, $\Omega_1 = V V_p \sim V \cdot \frac{4\pi}{3}(3mkT)^{3/2}$: $\boxed{S \sim Nk\ln[V\cdot\frac{4\pi}{3}(3mkT)^{3/2}]}$ / termodynamika (1 mól): $S = R\ln(\alpha T^{3/2} V)$ O.K.



Gibbsov paradox



problém s S_{id}: $\frac{1}{2}$ mólu plynu v $\frac{1}{2}V$ vľavo + $\frac{1}{2}$ mólu plynu v $\frac{1}{2}V$ vpravo + prepážka prepúšťajúca Q (=> plyny majú rovnakú T), ① vytiahneme prepážku: $\Delta S = R\ln(\alpha T^{3/2} \times V) - 2\cdot\frac{R}{2}\ln(\alpha T^{3/2}\frac{V}{2}) = R\ln 2$, ② zasunieme prepážku: $S\downarrow$ na S_0 (vzorky 1, 2 sú premiešané, ALE sú makroskop. nerozlíšiteľné); riešenie: $\begin{cases} \Gamma_1 = \text{počet stavov mol.} \ (= \Omega_1/\Omega_{1b}) \\ \Gamma = \text{počet stavov plynu} \ (= \Omega/\Omega_b) \end{cases}$; neidentické častice: $\Gamma \sim \Gamma_1^N$ / identické častice, viď QM:

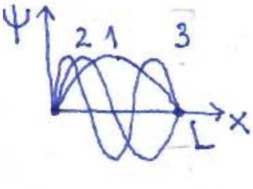
$\Gamma \sim \frac{1}{N!}\Gamma_1^N$ (permutácie 1-čast. stavov nedajú nový stav!) STAČÍ

& $N! = \sqrt{2\pi N}\,\underbrace{(N/e)^N}$ (Stirling), $(\sqrt{2\pi N})^{1/N} = \underbrace{(2\pi)^{1/(2N)}}_{\to 1} \times$

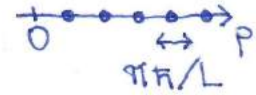
$\times \underbrace{e^{\ln N/(2N)}}_{\to 1} \doteq 1 \Rightarrow \Gamma \sim \left(\frac{e\Gamma_1}{N}\right)^N$, $\boxed{S_\Gamma = k\ln\Gamma \sim Nk\ln\frac{e\Gamma_1}{N}}$ /

$\Omega_1 \sim C(mkT)^{3/2}V$: $\boxed{\frac{e\Gamma_1}{N} = C\,\frac{(mkT)^{3/2}}{\Omega_{1b}\,n}}$ $\to S_\Gamma$ aditívna

kvantové stavy



elektrón na úsečke: $\Psi_n \propto \sin\frac{2\pi x}{\lambda_n}$, $\lambda_n = 2L, L, \frac{2}{3}L \ldots = \frac{2L}{n}$
$\to \boxed{p_n = \frac{2\pi\hbar}{\lambda_n} = \frac{\pi\hbar}{L}\,n}$ $\left(\varepsilon_n = \frac{\pi^2\hbar^2}{2mL^2}\,n^2\right)$: $p>0$ + bunky s dĺžkou $\Delta p_0 = \pi\hbar/L$ – ALE $\sin\frac{p_n x}{\hbar} \leftrightarrow p = \pm p_n \to p$ ľub.



+ bunky s dĺžkou $\Delta p = 2\pi\hbar/L$ (formálne: periodické okrajové podmienky); elektrón v kocke: stojaté vlny:

$\vec{p}(n_x,n_y,n_z) = \frac{\pi\hbar}{L}(n_x,n_y,n_z)$, $n_{x,y,z} > 0 \to$ bunky s $\Delta V_{p0} = (\pi\hbar)^3/V$ / postupné vlny: $\vec{p} = \frac{2\pi\hbar}{L}(n_x,n_y,n_z)$, $n_{x,y,z}$ ľub. $\to$ bunky s $\Delta V_p = (2\pi\hbar)^3/V \leftrightarrow$ bunky vo fáz. priestore s $\boxed{\Omega_{1b}} = V\Delta V_p = \boxed{(2\pi\hbar)^3}$; hustota stavov:

w_1 = hustota stavov 1 mol. id. plynu $= d\Omega_1^{celk}/d\varepsilon$, $\Omega_1^{celk}(\varepsilon)$ = objem v 1-časticovom fázovom priestore pripadajúci na mol. s en. $<\varepsilon$ $= V\,V_p(\varepsilon_p < \varepsilon) = V\cdot\frac{4\pi}{3}p^3$, $p = (2m\varepsilon)^{1/2}$

$\Rightarrow w_1 = V\cdot 4\pi\underbrace{p^2\,dp/d\varepsilon}_{p\cdot\frac{1}{2}d(p^2)/d\varepsilon = mp} = V\cdot 4\pi m(2m\varepsilon)^{1/2}$ / QM stavy:

$w_{1\Gamma} = d\Gamma_1^{celk}/d\varepsilon$, $\Gamma_1^{celk}(\varepsilon)$ = počet stavov s en. $<\varepsilon = \Omega_1^{celk}/\Omega_{1b}$

$\Rightarrow \boxed{w_{1\Gamma} = \frac{V\cdot 4\pi m(2m\varepsilon)^{1/2}}{(2\pi\hbar)^3}}$; analog. $w_\Gamma \propto E^{3N/2-1}$

entropia ako logaritmus počtu stavov

Sackur-Tetrode 1912

S v teórii s diskrétnymi stavmi: $\boxed{S = k\ln\Gamma}$, $\Gamma = \frac{\Omega}{\Omega_b}$, $\Omega_b = (2\pi\hbar)^f$; id. plyn: $\boxed{S = Nk\ln\left[C\frac{(mkT)^{3/2}}{(2\pi\hbar)^3 n}\right]}$

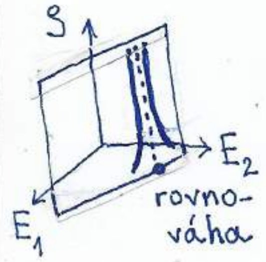
– odhad: $C = 4\pi\sqrt{3}\,e$, presný výpočet: $\boxed{C = (2\pi)^{3/2}e^{5/2}}$

$\to T_{deg}$ elektrónov v kovoch? $\varepsilon = kT_{deg}$: $p = (2m_e\varepsilon)^{1/2} \sim$

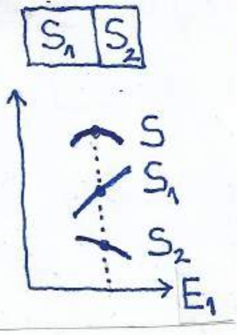
$\sim h n_e^{1/3} = h \nu_{val}^{1/3}/a$, Fe: $\begin{cases} a = 0.3\,\text{nm} \\ \nu_{val} = 8 \end{cases} \to \varepsilon \sim 60\,\text{eV}\ (\varepsilon_F = 11\,\text{eV})$

zákon rastu entropie v MKS

majme uzavretý systém σ s podsystémami σ_a + sledujme ho počas $T \gg \tau_a$, ale $\ll \tau$; ρ = rozdelenie pravdepodobnosti medzi stavy vo fáz. priestore: $\rho \overset{MKS}{=} \text{konšt}\ \delta(E-E_0) \to dP = \rho \times d\Gamma$ / prechod $\sigma \to \sum \sigma_a$: $d\Gamma = \prod d\Gamma_a$, $d\Gamma_a = \omega(E_a)dE_a = \Gamma_a/\Delta E_a \cdot dE_a$, $\Gamma_a = e^{\frac{1}{k}S_a} \Rightarrow \boxed{dP = \text{konšt}\ \delta(E-E_0) \times e^{\frac{1}{k}S} \prod dE_a/\Delta E_a}$; ΔE_a sa môžu meniť s E_a, ale to má zanedbateľný efekt v porovnaní so zmenami Γ_a $\Rightarrow \prod \Delta E_a \sim \text{konšt}$ a E_0 sa prerozdeľuje tak, aby S rástla



teplota v MKS



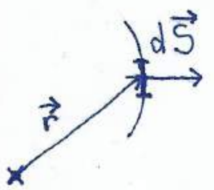
majme uzavretý systém σ zložený z podsystémov σ_1, σ_2 v tepelnom kontakte; $S = S_1(E_1) + S_2(E_2)$, $E_1 + E_2 = E$: S má max.: $\frac{dS}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} = 0 \Rightarrow \frac{dS}{dE} \overset{df}{=} \frac{1}{T}$: $\boxed{T_1 = T_2}$; T = teplota? id. plyn: ① $T(E)$? $\Omega_1 = V V_p \propto \bar{p}^3 = (2m\bar{\varepsilon})^{3/2}$, $\bar{\varepsilon} = \frac{3}{2}kT$? - NIE, $\bar{\varepsilon} = E/N \Rightarrow S = Nk \ln\left(\text{konšt} \times \frac{V E^{3/2}}{N^{5/2}}\right) = Nk\left(\ldots + \frac{3}{2}\ln E\right) \Rightarrow T^{-1} = Nk \times \frac{3}{2}E^{-1} \Leftrightarrow \boxed{NkT = \frac{2}{3}E}$, ② $P(E)$? kin. teória plynov: $\boxed{P = F_{mol\text{-}S}/S = \text{POČTY} = \frac{2}{3}E/V}$ / QM: $\vec{p}_{(n_x,n_y,n_z)} \overset{\text{period. o.p.}}{=} 2\pi\hbar/L \times (n_x,n_y,n_z) \Rightarrow \varepsilon_{(n_x,n_y,n_z)} = \frac{1}{2m}\vec{p}^{\,2}_{(n_x,n_y,n_z)} = \frac{1}{2m}4\pi^2\hbar^2/L^2 \cdot (n_x^2 + n_y^2 + n_z^2)$ & $1/L^2 = 1/V^{2/3} \Rightarrow P_{(n_x,n_y,n_z)} = -\partial_V \varepsilon_{(n_x,n_y,n_z)} = \frac{2}{3} \times \varepsilon_{(n_x,n_y,n_z)}/V$, P = dtto O.K. ($PV = \frac{2}{3}E \overset{①}{=} NkT$); id. plyn = pracovná látka v C. stroji $\to T$ = termodyn. teplota

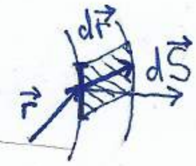
$T_1 > T_2$: $\dot{S} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\dot{E}_1 > 0 \Rightarrow \dot{E}_1 < 0$, $\dot{E}_2 > 0$ O.K.

adiabatický dej - všeob. prípad

majme tepelne izolovaný systém = systém, kt. interaguje s okolím jediným spôsobom - že podmienky, v kt. sa nachádza, sa menia, $\lambda = V, \vec{E}$ al. $\vec{B}, \ldots$ = fcia t; λ = makroskop. prvok:

dynamiky, nemá vplyv na počet mikrostavov (id. plyn: $V\downarrow$: $\varepsilon_{(n_x,n_y,n_z)}\uparrow$ ako $V^{-2/3}$ [všetky $\varepsilon\uparrow$ rovnako!] $\Rightarrow E\uparrow$, ALE Γ ostane) $\Rightarrow$ aj pri zmenách λ platí zákon rastu S; adiabatické deje (v užšom zmysle) = deje s pomalou zmenou λ: ① $S(\lambda)$: $\dot{S}=0$ pri $\dot{\lambda}=0$ & $\dot{S}$ nemôže byť <0 pri $\dot{\lambda}\neq 0 \Rightarrow \dot{S}=A\dot{\lambda}^2$ $\Leftrightarrow dS/d\lambda = A\dot{\lambda} \Rightarrow \boxed{\dot{\lambda}\to 0:\ S=\text{konšt}}$, adiabatické deje sú vratné, ② $E(\lambda)$: $E=H(q,p,\lambda)$, $\dot{H}=\underbrace{\partial_{q_i}H}_{-\dot{p}_i}\dot{q}_i+\underbrace{\partial_{p_i}H}_{\dot{q}_i}\dot{p}_i+\partial_t H=\partial_t H=\partial_\lambda H\,\dot{\lambda}$: $\dot{E}=\overline{\dot{H}}=\overline{\partial_\lambda H}\,\dot{\lambda}$ – ALE $E=E(S,\lambda)$ & S pri adiabat. deji = konšt $\Rightarrow \dot{E}=(\partial_\lambda E)_S\dot{\lambda} \Rightarrow \boxed{(\partial_\lambda E)_S=\overline{\partial_\lambda H}}$



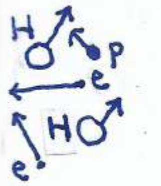


tlak v MKS

sila pôsobiaca na element plochy $d\vec{S}$: $\vec{F}=-\nabla_{\vec{r}}H(q,p,\vec{r})$, $\vec{r}$ = polohový vektor $d\vec{S} \Rightarrow \overline{\vec{F}}=-\overline{\nabla_{\vec{r}}H}=-(\nabla_{\vec{r}}E)_S\overset{\text{plyn}}{=}-(\partial_V E)_S \times$ $\times\nabla_{\vec{r}}V=-(\partial_V E)_S\,d\vec{S} \Rightarrow \boxed{p=-(\partial_V E)_S}$ / df. T: $T^{-1}=(\partial_E S)_V$ $\Leftrightarrow T=(\partial_S E)_V \Rightarrow \boxed{dE=TdS-pdV}$ (1. veta termodyn. v MKS); mechanická rovnováha: $S=S_1(E_1,V_1)+S_2(E_2,V_2)$, $V_1+V_2=V$: $\partial_{V_1}S=\partial_{V_1}S_1-\partial_{V_2}S_2=0$ & $dS=1/T\cdot(dE+$ $+pdV) \Rightarrow p_1/T_1=p_2/T_2$ – ALE $T_1=T_2 \Rightarrow \boxed{p_1=p_2}$ (dosahuje sa makroskopickým pohybom $\Rightarrow$ nastáva skôr než $T_1=T_2$)

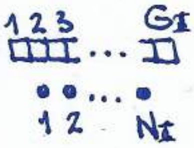
chemický potenciál

E (formálne) = aj fcia N: $dE=TdS-pdV+\mu dN$; id. plyn: $\mu(n,T)$? $\mu=-T(\partial_N S)_{E,V}$ & $S=Nk\ln\left[C\frac{(mkT)^{3/2}}{(2\pi\hbar)^3 n}\right]$, $C=(2\pi)^{3/2}e^{5/2}$: $S=Nk(\ln\mathcal{F}+\frac{5}{2})$, $\mathcal{F}=\frac{(2\pi mkT)^{3/2}}{(2\pi\hbar)^3 n}$ / $\mathcal{F}=\frac{(2\pi m\cdot 2/3\cdot E/N)^{3/2}}{(2\pi\hbar)^3 N/V}=\text{konšt}\,\frac{VE^{3/2}}{N^{5/2}}$: $\ln\mathcal{F}=\ldots-\frac{5}{2}\ln N$ $\Rightarrow \boxed{\mu=-T\left[k(\ln\mathcal{F}+\frac{5}{2})+Nk\underbrace{\partial_N(-\frac{5}{2}\ln N)}_{-5/2\cdot N^{-1}}\right]=-kT\ln\mathcal{F}}$ – nedeg. plyn: $T\gg T_{deg} \Leftrightarrow \mathcal{F}\gg 1 \Rightarrow \mu<0$ & $|\mu|\gg kT$



chemická rovnováha: $H \rightleftarrows p + e$ - $S = S_H(N_H) + S_p(N_p) + S_e(N_e)$, $\begin{cases} N_H + N_p = N \\ N_e = N_p \end{cases}$: $\partial_{N_p} S = -\partial_{N_H} S_H + \partial_{N_p} S_p + \partial_{N_e} S_e = 1/T \cdot (\mu_H - \mu_p - \mu_e) = 0 \Rightarrow \boxed{\mu_H = \mu_p + \mu_e} \to x = n_p/n$ (stupeň ionizácie) ako fcia n, T (Sahova rovnica)

Maxwellovo-Boltzmannovo rozdelenie

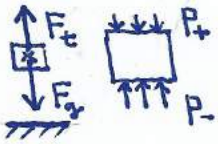


id. plyn (klasický): max. S pri daných $N, E \to \bar{n}_i$ = stredný počet v stave s en. ε_i ako fcia ε_i; S pri zadaných N_I: en. $\varepsilon \leftrightarrow$ vrstva = súbor 1-čast. stavov s en. rozmazanými okolo ε: $\boxed{G_I}$ = počet 1-čast. stavov („priehradiek") v I-tej vrstve, N_I = počet mol. („guľôčok") v I-tej vrstve $\Rightarrow$ mol. sú identické + $N_I \ll G_I$: Γ_I = počet N-čast. stavov v I-tej vrstve $= \frac{1}{N_I!} G_I^{N_I} \doteq \left(\frac{eG_I}{N_I}\right)^{N_I}$ / $S = k \ln \Gamma$, $\Gamma = \prod \Gamma_I$: $S = k \sum \ln \Gamma_I = \sum N_I k \ln \frac{eG_I}{N_I}$; variácia S: $\mathcal{S} = S - aN - bE$, $\begin{cases} N = \sum N_I \\ E = \sum N_I \varepsilon_i \end{cases}$, $\begin{cases} a \\ b \end{cases}$ = Lagrangeove multiplikátory: S má max. pri daných $N, E \Leftrightarrow \delta \mathcal{S} = 0$; $\bar{n}_i = N_I / G_I$, $\begin{cases} a \\ b \end{cases} = k \times \begin{cases} \alpha \\ \beta \end{cases}$: $\mathcal{S} = \sum G_I \times \bar{n}_i k [\ln(e/\bar{n}_i) - \alpha - \beta \varepsilon_i]$ & $\delta \mathcal{S} = 0 \Leftrightarrow \partial_{\bar{n}_i} \mathcal{S} = 0$ pre $\forall i$; $[x \ln(e/x)]' = \underbrace{\ln(e/x)}_{1 - \ln x} - x \underbrace{(\ln x)'}_{x^{-1}} = -\ln x \Rightarrow$ ľ. str. $= G_I k (-\ln \bar{n}_i - \alpha - \beta \varepsilon_i) \Rightarrow \boxed{\bar{n}_i = e^{-\alpha - \beta \varepsilon_i}}$ & $S = \sum \underbrace{G_I \bar{n}_i}_{N_I} \cdot k \underbrace{\ln(e . e^{\alpha + \beta \varepsilon_i})}_{\alpha + 1 + \beta \varepsilon_i} = k[(\alpha + 1) N + \beta E]$; výpočet α, β:

$\sum G_I \to \int \frac{V d\mathcal{V}_p}{(2\pi\hbar)^3} = \int \omega_1 \times d\varepsilon$ (častice s $s > 0$: $V d\mathcal{V}_p \times g$, g = počet polarizácií = $2s + 1$ ak $m_0 \neq 0$ / 2 ak m_0 aj $q = 0, s > 0$): $\begin{cases} N \propto e^{-\alpha} \beta^{-3/2} \\ E = N \cdot \frac{3}{2} \beta^{-1} \end{cases}$ $\Rightarrow \begin{cases} \alpha = -\mu/(kT) \\ \beta = 1/(kT) \end{cases} \Rightarrow \boxed{\bar{n}_i = e^{(\mu - \varepsilon_i)/(kT)}}$ & $S = k\left[\left(-\frac{\mu}{kT} + 1\right) N + \underbrace{\frac{1}{kT} \cdot E}_{3/2 \cdot N}\right] = Nk\left(-\frac{\mu}{kT} + \frac{5}{2}\right)$ O.K. $\left(-\frac{\mu}{kT} = \ln \mathcal{F}\right)$

barometrický vzorec: $\varepsilon \overset{1\text{-at.}}{=} \frac{1}{2} m v^2 + u$, GP Zeme: $u = mgz$;

$\Delta N_I = \Delta G_I \nu_i,\ \nu_i \equiv \overline{n}_i:\ dN = \nu\, dG,\ dG = \frac{dV\,dV_{\vec p}}{(2\pi\hbar)^3} =$
$= \frac{m^3}{(2\pi\hbar)^3}\, dV\,dV_{\vec v} \Rightarrow dN = f\,dV\,dV_{\vec v},\ f = \frac{m^3 \nu}{(2\pi\hbar)^3}$, ① $\int dV$:
$dN = f_{\vec v}\, dV_{\vec v},\ f_{\vec v} = \int f\,dV \propto \int e^{-\varepsilon/(kT)}\,dV \propto e^{-mv^2/(2kT)}$
$\Rightarrow \varrho = f_{\vec v}/N \propto$ dtto O.K., ② $\int dV_{\vec v}$: $dN = \overset{n}{\cancel{f_{\vec r}}}\, dV$,
$\boxed{n = \int f\,dV_{\vec v} \propto \int e^{-\varepsilon/(kT)}\, dV_{\vec v} \propto e^{-mgz/(kT)}}$ (→ výškomer); overenie: $F_g = -mg = -\varrho \Delta V \cdot g,\ F_t = (p_- - p_+)S =$

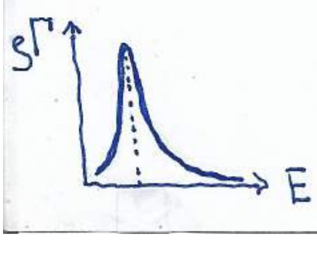


$= -\frac{dp}{dz}\Delta z\, S = -\frac{dp}{dz}\Delta V \Rightarrow \frac{dp}{dz} = -\varrho g \;/\; \begin{cases} p = nkT \\ \varrho = nm \end{cases} : \frac{dn}{dz} =$
$= -\frac{mg}{kT} n \Rightarrow$ dtto

<u>kánonický súbor</u>

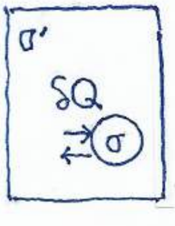
MKS: systémy s <u>danou en. E</u>, majú aj dobre df. (jednu) teplotu T, kt. vieme zrátať z fcie $S(E,V,N)$ (Tong: „dnes je možno B.-ova genialita lepšie [než v jeho df. S] zachytená v prekvapujúcej rovnici pre teplotu, $1/T = \partial_E S$") / KS: systémy v kontakte s rezervoárom $\Rightarrow$ majú <u>danú teplotu T</u> + ich en. fluktuuje okolo $\bar E$ (nemá 1 dobre df. hodnotu) - ALE fluktuácie sú malé, s disperziou $\sigma_E/\bar E \sim 1/\sqrt{N} \Rightarrow$ v dobrom priblížení majú <u>tiež</u> danú en. E; <u>Boltzmannovo rozdelenie</u> (LLV: Gibbsovo rozdelenie, B. rozdelenie = rozdelenie N_{id} v ε, $\nu \propto e^{-\varepsilon/(kT)}$): $\boxed{\varrho \propto e^{-E/(kT)}}$ - <u>nepostuluje sa</u>, vyjde z mikrokánonického rozdelenia, viď ďalej. ① súboj E s S (= súboj snáh systému znížiť E a zvýšiť S):

$E\uparrow: \varrho\downarrow \Rightarrow E = E_0$? NIE, lebo $\Gamma = e^{\frac{1}{k}S}\uparrow$; $E \lessgtr \bar E$: $dP = \varrho\, d\Gamma =$
$= \varrho\Gamma/\Delta E \cdot dE \begin{cases} \uparrow \text{ (dominuje } S) \\ \downarrow \text{ (dominuje } E) \end{cases} \Rightarrow \bar E \leftrightarrow \max.\ dP$ (id.
plyn: $\varrho\Gamma \propto e^{-E/(kT)}\, e^{N \ln(\text{konšt}\, E^{3/2})} \propto E^{3/2 \cdot N}\, e^{-E/(kT)} \Rightarrow$



$(\varrho\Gamma)' \propto [\frac{3}{2}N E^{3/2.N-1} - E^{3/2.N}/(kT)]\, e^{-E/(kT)} \doteq 0 : E = \frac{3}{2}\cdot NkT$ O.K.). ② konzistentnosť ϱ s $\dot{f} = 0$; systém, kt. bol v t_0 v mikrostave P_0 s $E \gtrless \bar{E}$, si na $\Sigma_{\bar{E}}$ prinesie $f\Delta\Gamma \ll (f\Delta\Gamma)_0 \Rightarrow$ neovplyvní f_0

odvodenie ϱ_{KS} z ϱ_{MKS}



majme uzavretý systém σ_+ zložený z uvaž. systému σ + rezervoáru σ' ; pravdep., že σ_+ sa nachádza v $d\Gamma_+$: $dP_+ = \varrho_+ d\Gamma_+ \propto \delta(E+E'-E_0)\, d\Gamma\, d\Gamma' \Rightarrow$ pravdep., že σ sa nachádza v $d\Gamma$: $dP = \int_{\Gamma'} dP_+ \propto \left(\int \delta(E+E'-E_0)\, d\Gamma'\right) d\Gamma$ / $d\Gamma'$ (viď zákon rastu S) $= \Gamma'/\Delta E' \cdot dE'$: $\varrho \propto \int\delta(\ )\, d\Gamma' = \Gamma'(E_0-E)\cdot 1/\Delta E' = e^{\frac{1}{k}S'(E_0-E)}/\Delta E'$ & $S'(E_0-E) = S'(E_0) - \partial_{E'}S'(E_0)\cdot E$, $\partial_{E'}S'(E_0) = T'^{-1}(E_0) \doteq T'^{-1}(E')$ & $T(E) = T'(E') = T$: $\varrho \propto e^{-\frac{1}{k}T^{-1}E}/\Delta E' \propto e^{-E/(kT)}$ O.K.

ideálny plyn ako KS

$\forall$ molekula = systém v kontakte s rezervoárom zlož. z ostatných molekúl $\Rightarrow \varrho_1$ aj $\nu = N\varrho_1 \propto e^{-\varepsilon/(kT)}$ O.K.; S v KS: $S \doteq k\ln\Gamma_{\bar{E}}$, $\int\varrho\, d\Gamma \doteq \varrho_{\bar{E}}\Gamma_{\bar{E}} = 1$: $\Gamma_{\bar{E}} = 1/\varrho_{\bar{E}}$, $S = -k\ln\varrho_{\bar{E}}$ / $\varrho = e^{-a-\beta E}$, $\beta = 1/(kT)$: $\ln\varrho_{\bar{E}} = -a-\beta\bar{E} = -(\overline{a+\beta E}) = \overline{\ln\varrho} \Rightarrow \boxed{S = -k\overline{\ln\varrho} = -k\int\varrho\ln\varrho\, d\Gamma} \rightarrow$ id. plyn: $S_1 = -k\int\varrho_1\ln\varrho_1\, d\Gamma_1$, $d\Gamma_1 \equiv dG = g\frac{dV\, dV_{\vec{p}}}{(2\pi\hbar)^3}$: $S = NS_1$?: NIE, identičnosť častíc: $S = NS_{1mod}$, $\varrho_1 = 1/\Gamma_1 \xrightarrow{\ln} \varrho_{1mod} = 1/\Gamma_{1mod}$, $\Gamma_{1mod} = \Gamma_1/(N!)^{1/N} = e\Gamma_1/N \Rightarrow \boxed{S = -Nk\cdot\int\varrho_1 \underbrace{\ln\varrho_{1mod}}_{-\ln\Gamma_{1mod}}\, d\Gamma_1 = k\int N\varrho_1\ln(e\underbrace{\Gamma_1}_{1/\varrho_1}/N)\, d\Gamma_1 = k\int\nu\ln(e/\nu)\cdot dG}$, $\nu = N\varrho_1$ - to je dtto ako v MKS ($S = k\sum G_i\bar{n}_i\ln(e/\bar{n}_i)$) aj v kin. teórii ($S = -kH$, $H = \int f(\ln \underset{(2\pi\hbar)^3 m^3\cdot}{\wedge} f - 1)\, dV\, dV_{\vec{v}}$)

termodynamické potenciály

$E(S,V)$: (S,V) = premenné v $dE \overset{vrat.}{=} TdS - pdV$, prirodzené premenné E → t.p. = fcie, ktorých prirodzené premenné sú kombinácie T, S, p, V: ① $E(S,V)$ = en., ② $F(T,V)$ = voľná en. (Tong: dostupná, NIE zadarmo): $TdS = d(TS) - SdT$ ⇒ $d(E-TS) = -SdT - pdV$ → $\boxed{F = E - TS}$ (Legendrova transformácia); význam F: $dE = \delta Q + \delta A'$, $\delta Q \le \delta Q_{vrat} = TdS$: $\delta A = -\delta A' = -(dE - \delta Q) \le -(dE - TdS) \overset{T=konšt}{=} -dF$ ⟺ $\boxed{(\delta A_{max})_T = -dF}$ & $dF \overset{T=konšt}{\le} \delta A' \overset{V=konšt}{=} 0$ ⇒ $\boxed{F \text{ má min. pri } T,V = \text{konšt}}$ (viď súboj E s S), ③ $H(S,p)$ = entalpia: $d(E+pV) = TdS + Vdp$ → $\boxed{H = E + pV}$ - použ. v chémii, ④ $G(T,p)$ = t.p. v užšom zmysle, Gibbsova voľná en.: $d(E-TS+pV) = -SdT + Vdp$ → $\boxed{G = E - TS + pV}$; G extenz. + T,p intenz.: $G = Nf(T,p)$ / t.p. (formálne) aj fcie N: $d(\text{t.p.})$ = predch. výraz + μdN ⇒ $\mu = (\partial_N G)_{T,p} = f$, $\boxed{G = N\mu}$

voľná energia v KS

$\alpha = -\mu/(kT)$ → $a = -F/(kT)$

$S = -k\overline{\ln\rho}$, $\rho = A e^{-E/(kT)}$: $S = -k\ln A + \bar{E}/T$ ⇒ $F = \bar{E} - TS = kT\ln A$ / $\int \rho\, d\Gamma = 1$, $d\Gamma = d\Gamma_0/N!$, $d\Gamma_0 = d\Omega/(2\pi\hbar)^{3N}$: ľ. str. $= \int A e^{-E/(kT)} d\Gamma = AZ$, $Z = \int e^{-\beta E} d\Gamma$, $\beta = 1/(kT)$ (štatistická suma; QM: $Z = \sum e^{-\beta E_n} = \mathrm{Tr}(e^{-\beta \hat{H}})$) ⇒ $A = Z^{-1}$, $\boxed{F = -kT\ln Z}$ → opis termodyn. systémov (aj molekúl id. plynu!) v KS: $Z(T,V) \to F(T,V) \to \begin{cases} p = -\partial_V F \\ S = -\partial_T F \end{cases}$; id. plyn: $d\Gamma = d\Gamma_0/N!$, $d\Gamma_0 = \prod d\Gamma_a$ ⇒ $Z = Z_0/N!$, $Z_0 = \int e^{-\beta E} \times d\Gamma_0 = \int e^{-\beta\sum\varepsilon_a} \prod d\Gamma_a = \int \prod e^{-\beta\varepsilon_a} d\Gamma_a = \left(\int e^{-\beta\varepsilon} d\Gamma_1\right)^N$ (viď

$\int_{\square} f(x)f(y)\,dx\,dy = \int_0^a f(x)\left[\int_0^a f(y)\,dy\right]dx = \left(\int_0^a f(x)\,dx\right)^2$) & $1/N! = (e/N)^N$ ⇒ $\boxed{Z = z^N}$, $\boxed{z = e/N \cdot z_0}$, $\boxed{z_0 = \int e^{-\beta\varepsilon} d\Gamma_1 = \int_0^\infty e^{-\beta\varepsilon}\omega_1 d\varepsilon =}$

$= \text{POČTY} = \boxed{\frac{V.(2\pi m k T)^{3/2}}{(2\pi\hbar)^3}} \Leftrightarrow z = e\mathcal{F},\ \mathcal{F} = \frac{(2\pi m k T)^{3/2}}{(2\pi\hbar)^3 n}$

$\Rightarrow \boxed{F = -kT\ln z^N = -NkT\ln(e\mathcal{F})}$, ① $p = -\partial_V F = NkT \times \partial_V \underbrace{\ln(e\mathcal{F})}_{\dots+\ln V} = NkT/V$ O.K., ② $S = -\partial_T F = Nk[\ln(e\mathcal{F}) + T\partial_T \underbrace{\ln(e\mathcal{F})}_{\dots + 3/2\cdot\ln T}] = Nk[\ln(e\mathcal{F}) + \frac{3}{2}] = Nk\ln(e^{5/2}\mathcal{F})$, ③ $dF = -S \times dT - p\,dV + \mu\,dN$: $\mu = \partial_N F = -kT[\ln(e\mathcal{F}) + N\partial_N \underbrace{\ln(e\mathcal{F})}_{\dots - \ln N}] = -kT[\ln(e\mathcal{F}) - 1] = -kT\ln\mathcal{F}$

grandkánonický súbor

σ v kontakte s rezervoárom v danom V: vymieňa si Q aj N → $\varrho_N \propto \int \delta(E_N + E' - E_0)\underbrace{d\Gamma'}_{\Gamma'/\Delta E'.dE'} = \Gamma'/\Delta E' = e^{\frac{1}{k}S'}/\Delta E'$, $S' = S'(E_0 - E_N, N_0 - N) = S'_0 - \underbrace{\partial_{E'}S'_0}_{1/T} E_N - \underbrace{\partial_{N'}S'_0}_{-\mu/T} N = S'_0 + (\mu N - E_N)/T$

$\Rightarrow \boxed{\varrho_N = \tilde{A}\, e^{(\mu N - E_N)/(kT)}}$ / $\sum_N \int \varrho_N\, d\Gamma_N = 1$: $\tilde{A} = \tilde{Z}^{-1}$, $\boxed{\tilde{Z} = \sum_N \int e^{\beta(\mu N - E_N)}\, d\Gamma_N}$; veľký (Landavov) potenciál: $dF = \dots + \mu\,dN$, $\mu\,dN = d(\mu N) - N\,d\mu \to (T, V, \mu)$: $\boxed{\Omega = F - \mu N}$ ($F = G - pV$, $G = \mu N$: $\Omega = -pV$!) / $S \doteq k\ln\Gamma(\bar{E}, \bar{N}) = -k\ln\varrho_{\bar{N}}(\bar{E}) = -k\overline{\ln\varrho_N(E)} = -k\ln\tilde{A} - (\mu\bar{N} - \bar{E})/T \Rightarrow \boxed{\Omega = kT\ln\tilde{A} = -kT \times \ln\tilde{Z}}$; id. plyn: σ = súbor mol. v stave i vo vrstve I, n_i = počet mol. v súbore: $\varrho_{n_i} = \tilde{A}_i\, e^{n_i(\mu - \varepsilon_i)/(kT)}$ / mol. sú v stavoch rozmiestnené „nariedko": $\varrho_0 = \tilde{A}_i \doteq 1$, $\varrho_1 \doteq e^{(\mu - \varepsilon_i)/(kT)} \ll 1$, $\varrho_2 \doteq \varrho_1^2 \ll \varrho_1$ atď. $\Rightarrow \bar{n}_i = \sum \varrho_{n_i} n_i \doteq \varrho_1$ O.K.

kvantové plyny

$\left\{\begin{array}{l}\text{bozóny: ident. častice} + n_i \text{ ľub. (Bose-Einstein)} \\ \text{fermióny: ident. častice} + n_i = 0 \text{ al. } 1 \text{ (Fermi-Dirac)}\end{array}\right.$: max. S /

$\tilde{Z}_i = \tilde{A}_i^{-1} \to \boxed{\bar{n}_i = \frac{1}{e^{(\varepsilon_i - \mu)/(kT)} \mp 1}}$ (klasický plyn: $\mu < 0$ & $|\mu| \gg kT \Rightarrow Q_i = e^{(\varepsilon_i - \mu)/(kT)} \gg 1$, $\bar{n}_i = Q_i^{-1}$ O.K.)

odvodenie z max. S : ① FD rozdelenie (v $\forall$ priečinku je max. 1 guľôčka): $\Gamma_I = \binom{G_I}{N_I} = \frac{G_I!}{(G_I-N_I)!\,N_I!} = \frac{(G_I/e)^{G_I}}{[(G_I-N_I)/e]^{G_I-N_I}} \times \frac{1}{(N_I/e)^{N_I}} = \frac{1}{(1-\bar n_i)^{G_I-N_I}\,\bar n_i^{N_I}} \Rightarrow S = k\sum \ln\Gamma_I = -k\sum G_I[(1-\bar n_i)\times \ln(1-\bar n_i)+\bar n_i\ln\bar n_i] \Rightarrow \partial_{\bar n_i}\mathcal{S} = \partial_{\bar n_i}(S-aN-bE) = kG_I\,\partial_{\bar n_i}[-(1-\bar n_i)\times \ln(1-\bar n_i)-\bar n_i\ln\bar n_i-\bar n_i(\alpha+\beta\varepsilon_i)]$ / $(x\ln x)' = \ln x+1$: $\partial_{\bar n_i}\mathcal{S} = k\times G_I[\underbrace{\ln(1-\bar n_i)-\ln\bar n_i}_{\ln(\bar n_i^{-1}-1)}-(\alpha+\beta\varepsilon_i)] \stackrel{!}{=} 0$: $\ln(\bar n_i^{-1}-1) = \underbrace{\alpha}_{-\beta\mu}+\beta\varepsilon_i = \beta\times(\varepsilon_i-\mu)$, $\beta = 1/(kT) \Rightarrow \bar n_i = [e^{\beta(\varepsilon_i-\mu)}+1]^{-1}$ O.K., ② BE rozdelenie (v priečinkoch je ľub. počet guľôčok): N_I guľôčok + G_I-1 stien

$\underbrace{\bullet|\bullet\bullet\bullet||\bullet\bullet\dots}_{G_I+N_I-1}$

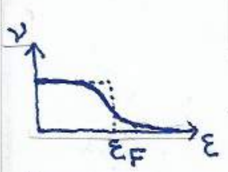
$\rightarrow \Gamma_I = \binom{G_I+N_I-\cancel{1}}{N_I} = \frac{(G_I+N_I)!}{G_I!\,N_I!} = \frac{[(G_I+N_I)/e]^{G_I+N_I}}{(G_I/e)^{G_I}(N_I/e)^{N_I}} = \frac{(1+\bar n_i)^{G_I+N_I}}{\bar n_i^{N_I}} \Rightarrow S = k\sum G_I[(1+\bar n_i)\ln(1+\bar n_i)-\bar n_i\ln\bar n_i]$

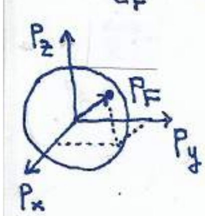
$\Rightarrow \partial_{\bar n_i}\mathcal{S} = kG_I\,\partial_{\bar n_i}[(1+\bar n_i)\ln(1+\bar n_i)-\bar n_i\ln\bar n_i-\bar n_i(\alpha+\beta\varepsilon_i)] = kG_I\times[\underbrace{\ln(1+\bar n_i)-\ln\bar n_i}_{\ln(\bar n_i^{-1}+1)}-(\alpha+\beta\varepsilon_i)] \stackrel{!}{=} 0$: $\bar n_i$ = dtto s $\ominus$ O.K.

odvodenie zo $\tilde Z_i$: $\tilde Z_i = \sum e^{\beta(\mu n_i - E_i)} = \sum q_i^{n_i}$, $q_i = e^{\beta(\mu-\varepsilon_i)}$ $\rightarrow$ ① FD rozdelenie ($n_i = 0,1$): $\tilde Z_i = 1+q_i \Rightarrow \bar n_i = \sum \varrho_{n_i} n_i = \tilde Z_i^{-1}\sum n_i q_i^{n_i} = \frac{q_i}{1+q_i} = \frac{1}{q_i^{-1}+1}$ O.K., ② BE rozdelenie ($n_i = 0, 1, \dots$): $\tilde Z_i = \frac{1}{1-q_i} \Rightarrow \bar n_i = \tilde Z_i^{-1} q_i\partial_{q_i}\tilde Z_i = (1-q_i)q_i\frac{1}{(1-q_i)^2} = q_i\times\frac{1}{1-q_i} = \frac{1}{q_i^{-1}-1}$ O.K.

Fermiho plyn

$T=0$: $\mu \equiv \varepsilon_F$ (Fermiho en.) >0, $e^{\beta(\varepsilon_i-\varepsilon_F)} = \begin{cases} 0, \text{ ak } \varepsilon_i<\varepsilon_F \\ \infty, \text{ ak } \varepsilon_i>\varepsilon_F \end{cases}$ $\Rightarrow \bar n_i = \begin{cases} 1, \text{ ak } \varepsilon_i<\varepsilon_F \\ 0, \text{ ak } \varepsilon_i>\varepsilon_F \end{cases}$ / $T \ll \varepsilon_F/k$: $\bar n_i \downarrow$ z 1 na 0 v intervale $\Delta\varepsilon \sim kT$ okolo ε_F ; stavová rovnica : $T=0$: $N = g(\varepsilon<\varepsilon_F) = g\,\frac{V V_p(p<p_F)}{(2\pi\hbar)^3}$, p_F (Fermiho hybnosť) $\leftrightarrow \varepsilon_F$ / $V_p(p<p_F) = \frac{4\pi}{3}p_F^3$ & $g_e = 2$: $n = \frac{8\pi/3.\ p_F^3}{(2\pi\hbar)^3} = \frac{p_F^3}{3\pi^2\hbar^3} \Rightarrow \boxed{p_F = (3\pi^2)^{1/3}\hbar n^{1/3}}$ -



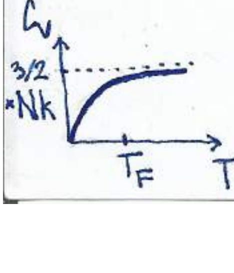


$p_F \leftrightarrow \lambda = 2\pi\hbar/p_F$ (de Broglieho vln. dĺžka) $\doteq a = n^{-1/3}$ (hrana kocky, kt. pripadá na 1 elektrón), ① nerelat. plyn: $\varepsilon = \frac{1}{2m} \cdot p^2 \Rightarrow \boxed{\underbrace{\varepsilon_F}_{\equiv T_F} = \frac{1}{2m}(3\pi^2)^{2/3}\hbar^2 n^{2/3}}$ $\left(\mathcal{F} = 2 \cdot \frac{(2\pi m kT)^{3/2}}{(2\pi\hbar)^3\, n} = \frac{3}{4}\sqrt{\pi}\left(\frac{kT}{\varepsilon_F}\right)^{3/2} \to T_{deg} = \varepsilon_F/k\right)$; tlak: $E = \int\limits_{\varepsilon<\varepsilon_F} \varepsilon\, dG = \int\limits_{p<p_F} \frac{p^2}{2m}\, g\, \frac{V\, d\mathcal{V}_p}{(2\pi\hbar)^3}$, $d\mathcal{V}_p = 4\pi p^2 dp \Rightarrow E = \frac{1}{2m} \underbrace{\int_0^{p_F} p^4 dp}_{1/5 \cdot p_F^5} \Big/ \underbrace{\int_0^{p_F} p^2 dp}_{1/3 \cdot p_F^3} \cdot N = \frac{3}{5} N \varepsilon_F$ $(\bar{\varepsilon} = \frac{3}{5} \cdot \varepsilon_F)$, $\boxed{P = \frac{2}{3}E/V = \frac{2}{3}\cdot\frac{3}{5}N\varepsilon_F/V = \frac{2}{5}n\varepsilon_F = \frac{(3\pi^2)^{2/3}}{5m}\hbar^2 n^{5/3}}$;

② relat. plyn: $v \to c$: $\begin{cases} \varepsilon \doteq mc^2 \\ p \doteq mc \end{cases}$, $m \equiv m_{rel} = m_0/\sqrt{1-v^2/c^2}$ $\Rightarrow \varepsilon \doteq pc \to p_{Fc} \overset{(3\pi^2)^{1/3}}{=} m_0 c$ $(a_c = 2\pi\hbar/(m_0 c) \doteq \overset{1,25}{2,5} \cdot 10^{-3}\,\text{nm} \leftrightarrow m$ zápalkovej škatuľky $= 26\,\text{t})$: $\boxed{\varepsilon_F = (3\pi^2)^{1/3}\hbar c n^{1/3}} \Rightarrow E = c \times \underbrace{\int_0^{p_F} p^3 dp}_{1/4 \cdot p_F^4} \Big/ \underbrace{\int_0^{p_F} p^2 dp}_{1/3 \cdot p_F^3} \cdot N = \frac{3}{4}N\varepsilon_F$, $\boxed{P = \frac{1}{3}E/V = \frac{1}{4}(3\pi^2)^{1/3}\hbar c n^{4/3}}$;

coulomb. interakcia: $\varepsilon_C = \frac{e^2/(4\pi\varepsilon_0)}{a_e} = \underset{1/137}{\alpha}\frac{\hbar c}{a_e} \overset{Fe}{\doteq} 40\,\text{eV} \gtrsim \varepsilon_F = 11\,\text{eV}$ - ALE $\varepsilon_C/\varepsilon_F \propto a_e \downarrow$ ak $n_e \uparrow$ (!); tepelná kapacita: $E = \int_0^\infty \frac{C\varepsilon^{3/2}d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = \int_{-\mu}^\infty \frac{C(\mu+\Delta\varepsilon)^{3/2}}{e^{\beta\Delta\varepsilon}+1}d\Delta\varepsilon$, $\int_{-\mu}^\infty = \int_{-\mu}^0 + \int_0^\infty$, 1. int. $= \int_0^\mu \frac{C(\mu-\Delta\varepsilon)^{3/2}}{e^{\beta\Delta\varepsilon}+1}d\Delta\varepsilon = \int_0^\mu \left(1 - \frac{1}{e^{\beta\Delta\varepsilon}+1}\right)C(\mu-\Delta\varepsilon)^{3/2}d\Delta\varepsilon = \int_0^\mu C\varepsilon^{3/2}d\varepsilon - \int_0^{\cancel{\mu}\,\infty} \frac{C(\mu-\Delta\varepsilon)^{3/2}}{e^{\beta\Delta\varepsilon}+1}d\Delta\varepsilon \Rightarrow E = E_\mu + \int_0^\infty \frac{C[(\mu+\Delta\varepsilon)^{3/2} - (\mu-\Delta\varepsilon)^{3/2}]}{e^{\beta\Delta\varepsilon}+1}d\Delta\varepsilon$, $E_\mu = E_0(\varepsilon_F \to \mu)$ /

$[\ldots] = \mu^{3/2}(\cancel{1} + \frac{3}{2}\Delta\varepsilon/\mu) - \mu^{3/2}(\cancel{1} - \frac{3}{2}\Delta\varepsilon/\mu) = 3\mu^{1/2}\Delta\varepsilon$: $\Delta E = 3\mu^{1/2} \times C\beta^{-2}\underbrace{\int_0^\infty \frac{x\,dx}{e^x+1}}_{\pi^2/12} = \frac{\pi^2}{4}\mu^{1/2}C(kT)^2$ & $E_\mu = \frac{2}{5}C\mu^{5/2}$: $\Delta E = \frac{5\pi^2}{8} \times E_\mu(kT/\mu)^2 \doteq \frac{5\pi^2}{8}E_0(kT/\varepsilon_F)^2 = \frac{3\pi^2}{8}N\varepsilon_F^{-1}(kT)^2 \propto n^{-2/3}T^2$ - ALE my potrebujeme $\Delta E_0 = E - E_0$; postup: dtto s $N \to \Delta\mu \to \Delta E_0 = \frac{\pi^2}{4}N\varepsilon_F^{-1}(kT)^2$, $\boxed{C_V = \partial_T E = \frac{\pi^2}{2}Nk \cdot kT/\varepsilon_F}$



kompaktné hviezdy

$\begin{cases} F_g \sim \varkappa M/R^2 \cdot \rho S R \\ F_t \sim pS \end{cases} : p \sim \varkappa M/\underset{[M/(\frac{4\pi}{3}\rho)]^{1/3}}{R} \cdot \rho \sim \varkappa M^{2/3} \rho^{4/3}$ - na väčšie

ρ (kompaktnejšiu hviezdu) treba väčšie p ; BT: $p \sim n_e \times$

$\times \varepsilon_{Fe}$, $n_e = Z n_{nucl} = Z/A \cdot n_N \doteq \frac{1}{2} \cdot \rho/m_p \Rightarrow \varepsilon_{Fe} \sim 2\varkappa M \times$

$\times m_p/R = r_g/R \cdot m_p c^2$, r_g (grav. polomer) $= 2\varkappa M/c^2$

($r_{g\odot} = 3\,\mathrm{km}$) => hranica medzi nerelat. a relat. Fermiho

plynom: $\varepsilon_{Fe} = m_e c^2 \Rightarrow R \sim r_g \cdot m_p/m_e \doteq 2 \cdot 10^3 r_g \leftrightarrow$

$M_\odot$ vnútri R_Z ; NH: F. plyn neutrónov, $\varepsilon_{Fn} = m_n c^2$:

$R \sim r_g$, $M_\odot$ vnútri 10 km (BT aj NH: $p = C\rho^{4/3} \to M_{max} \sim (C/\varkappa)^{3/2}$)

Boseho-Einsteinova kondenzácia

$T \downarrow$ k T_c: $\mu < 0$ & $|\mu| \downarrow$ k 0, ① $T = T_c$: $\begin{cases} N \\ E_c \end{cases} = \int_0^\infty \frac{C}{e^{\beta_c \varepsilon} - 1} \times$

$\times \begin{cases} \varepsilon^{1/2} \\ \varepsilon^{3/2} \end{cases} d\varepsilon = C \times \begin{cases} I_{1/2}(kT_c)^{3/2} \\ I_{3/2}(kT_c)^{5/2} \end{cases}$, $I_n = \int_0^\infty \frac{x^n dx}{e^x - 1} \to T_c = 0.69 \times$

$\times T_F$, $E_c = 0{,}77\, NkT_c$, ② $T < T_c$: $\begin{cases} N_{\varepsilon > 0} \\ E \end{cases} = \int_0^\infty \frac{C}{e^{\beta\varepsilon} - 1} \times \begin{cases} \varepsilon^{1/2} \\ \varepsilon^{3/2} \end{cases} \times$

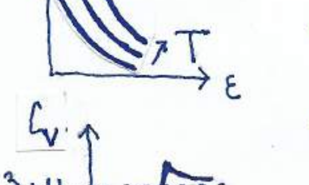
$\times d\varepsilon = \begin{cases} N(T/T_c)^{3/2} \\ E_c(T/T_c)^{5/2} \end{cases}$. $C_V = \partial_T E = \frac{5}{2} E_c T^{3/2}/T_c^{5/2} = \boxed{1{,}925 \times Nk(T/T_c)^{3/2}}$

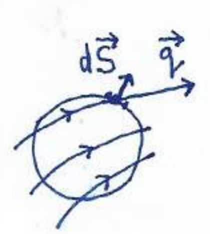
prenosové javy

prenos $\begin{cases} \varepsilon = \text{vedenie tepla} \to \varkappa \text{ (koef. vedenia tepla)} \\ \vec{p} = \text{vn. trenie} \to \eta \text{ (viskozita)} \\ \text{častíc} = \text{difúzia} \to D \text{ (koef. difúzie)} \end{cases}$, id. plyn:

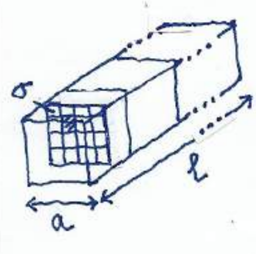
mech. prenosu = zrážky molekúl → kvalitatívny opis: prenos ε, $\vec{p}$ al. samých seba „v batohu" / teória: Boltzmann. rovnica;

vedenie tepla: majme plyn s teplotami T_A, $T_B < T_A$ pri $x = 0, L$ + uvažujme úsek medzi x_1 a $x_2 = x_1 + \ell$, ℓ = stredná voľná dráha mol.: q = prúd en. $\sim j_1 \varepsilon_1 - j_2 \varepsilon_2$, j = prúd častíc $= nv$, $v \sim \bar{v} = (3kT/m)^{1/2}$ ($v = \langle v_x \rangle_{\alpha < \pi/2}$, $\alpha = \sphericalangle$(os $x, \vec{v}$)) & $j_1 = j_2 = j$: $q \sim j(\varepsilon_1 - \varepsilon_2) = -nv\varepsilon' \ell$ / $\varepsilon = \frac{3}{2} kT$:





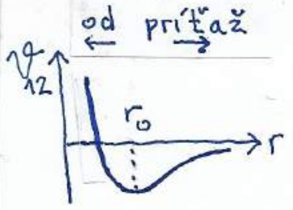
$\boxed{q = -\varkappa T'}$, $\boxed{\varkappa \sim k n l v}$ → rovnica vedenia tepla: $\begin{cases} w = \\ \vec{q} = \end{cases}$ $\begin{cases} = \text{hustota en.} \\ = \text{tok en.} \end{cases}$: $\partial_t w + \nabla\cdot\vec q = 0$ (viď $\dot E = -\oint \vec q\cdot d\vec S \overset{\text{Gauss}}{=} -\int \nabla\cdot\vec q \,\times$ $\times\, dV$) / $\begin{cases} w = 3/2 . nkT \\ \vec q = -\varkappa\nabla T \end{cases}$: $\boxed{\partial_t T = \alpha\Delta T}$, [$\alpha$ = koef. teplotnej vodivosti („difuzivity") $= \frac{\varkappa}{3/2 . nkT} \sim \boxed{lv}$]; prechod od l k σ: a =

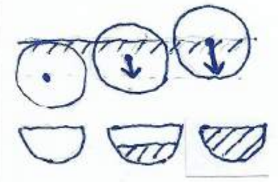


= stredná vzdialenosť medzi mol.: $l = N_{terč}\, a$, $N_{terč}$ = počet terčíkov s plochou σ pripadajúci na plochu $a^2 = a^2/\sigma$ => $\boxed{l = a^3/\sigma = 1/(n\sigma)}$, $\boxed{\varkappa \sim kv/\sigma}$; výpočet $\varkappa$ z Boltzmann. rovnice: $\dot f = (\partial_t f)_{coll}$, $\begin{cases} \dot f = \partial_t f + \vec v\cdot\nabla f \\ (\partial_t f)_{coll} = \int (f'f_1' - ff_1)\, v_{rel}\, d\sigma\, dV_{\vec v_1} \end{cases}$ & $\vec q = \int f \vec v \varepsilon\, dV_{\vec v}$ => $f = f_0(1+u)$, $|u| \ll 1$: $\dot f \doteq \vec v\cdot\nabla f_0$ = POČTY = $-f_0/T . (5/2 - \beta\varepsilon)\, \vec v\cdot\nabla T$, $(\partial_t f)_{coll} = \int f_0 f_{10} (u' + u_1' - u - u_1)\, v_{rel}\, d\sigma \,\times$ $\times\, dV_{\vec v_1}$ → $\mathcal U(\vec r, \vec v)$: $u \overset{\text{izotropia}}{=} \mathcal U\, \vec v\cdot\nabla T$ & $\vec q = \int f_0 u \vec v \varepsilon\, dV_{\vec v} \overset{\text{izotropia}}{=} -\varkappa\nabla T$, $\varkappa = -\frac13 \int \mathcal U v^2 \varepsilon\, dV_{\vec v}$; viskozita: majme vrstvy 1,2 s rýchlosťami V_1, V_2 + uvažujme priečny úsek s dĺžkou l: σ = napätie medzi 1 a 2 / prúd hybnosti od 1 k 2 $= df_{2\to 1}/dS \sim j_2 p_2 - j_1 p_1 = j(p_2 - p_1) = nv . m(V_2 - V_1) = +mnv\,\partial_y V\, l$ => $\boxed{\sigma = +\eta\,\partial_y V}$, $\boxed{\eta \sim mnlv = mv/\sigma}$ (kinematická viskozita: $\nu = \eta/\varrho \sim lv$ - dtto ako α!) → viskózny člen v Navierovej-Stokesovej rovnici: σ_{ij} od $\nabla\vec V$ $= +\eta(\partial_i V_j + \partial_j V_i - \frac23 \nabla\cdot V \delta_{ij})$ => $f_{v,i} = \partial_j \sigma_{ij} = \eta(\Delta V_i + \frac13 \partial_i \nabla\cdot\vec V)$ (nestlač. kvapalina: $\nabla\cdot\vec V = 0$ => $\vec f_v = \eta\Delta\vec V$); difúzia: majme nehomogénny plyn + uvažujme úsek s dĺžkou l v smere klesania n: J = čistý prúd častíc $\sim j_1 - j_2 \overset{T=\text{konšt}}{=} (n_1 - n_2) v = -n' l v$ → rovnica difúzie: $\boxed{\partial_t n = D\Delta n}$, $D \sim lv$ (opäť ako α)

Van der Waalsova rovnica

id. plyn: $pV = RT$ / reálny plyn: ① $V \to V - b$, $b = N_A b_1$, $b_1 =$



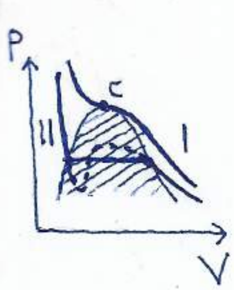


$= V_{1\,mol.}$ - započítava f_{od} na malých vzdial., kt. zvyšuje tlak $(p \propto 1/(V-b) > 1/V)$, ② $p \to p + a/V^2$, $a = N_A^2 a_1 \Rightarrow \delta p = a_1 \times$
$\times n^2$ - započítava $f_{prítaž}$ na veľkých vzdial., kt. znižuje tlak $(p = p_{id} - \delta p < p_{id}$; r_d = dosah $f_{prítaž}$: vo vrstve s hrúbkou r_d je $f_{prítaž}$ čiastočne nevykompenzovaná $\Rightarrow$ plyn vnútri priťahuje povrchovú vrstvu k sebe / $f_{celk} = \sum_a \sum_{b(a)} f_{b\to a} \sim N_a \bar{N}_b \times$
$\times f \propto n^2$ O.K.) $\to$ $\boxed{(p + a/V^2)(V-b) = RT}$; odvoď. a-člena zo Z: $Z = \int e^{-\beta E}\, d\Gamma$, $E = E_{kin} + \vartheta$, $\vartheta = \sum_{i<j} \vartheta_{ij}$,

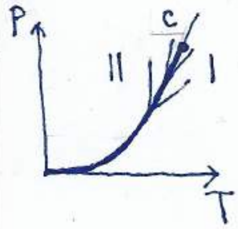
$\vartheta_{ij} = \vartheta_{12}(|\vec{r}_i - \vec{r}_j|)$ & $d\Gamma = \frac{1}{N!}\, d\Gamma_0 = \frac{1}{N!} \prod \frac{dV_i\, dV_{p_i}}{(2\pi\hbar)^3} \left[\times \frac{V^N}{V^N}\right] =$
$= d\Gamma_{id} \prod \frac{dV_i}{V}$: $Z = \int e^{-\beta(E_{kin} + \vartheta)}\, d\Gamma_{id} \prod \frac{dV_i}{V} = Z_{id} Z_\vartheta$, $Z_\vartheta =$
$= \int e^{-\beta\vartheta} \prod \frac{dV_i}{V}$; poruch. metóda: $e^{-\beta\vartheta} \doteq 1 - \beta\vartheta = 1 - \beta \sum_{i<j} \vartheta_{ij}$
$\Rightarrow Z_\vartheta \doteq \int \prod \frac{dV_i}{V} - \beta \sum_{i<j} \int \vartheta_{ij} \prod \frac{dV_k}{V} = 1 - \binom{N}{2} \beta I$, $I = \int \vartheta_{12}(r) \times$
$\times \frac{dV_1\, dV_2}{V^2}$ & $\begin{cases} \vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \\ \vec{r} = \vec{r}_2 - \vec{r}_1 \end{cases}$: $J = \frac{\partial(\vec{R}, \vec{r})}{\partial(\vec{r}_1, \vec{r}_2)} = \begin{pmatrix} J_x & & 0 \\ & J_y & \\ 0 & & J_z \end{pmatrix}$, $J_i =$
$= \frac{\partial(X_i, x_i)}{\partial(x_{1i}, x_{2i})} = \begin{pmatrix} \frac{1}{2} & -1 \\ \frac{1}{2} & 1 \end{pmatrix} \Rightarrow |J| = |J_x||J_y||J_z| = 1 \Rightarrow I = \int \vartheta_{12}(r) \times$
$\times \frac{dV\, dV_{\vec{R}}}{V^2} = \int \vartheta_{12} \frac{dV}{V} = V^{-1} \mathcal{Y}$, $\mathcal{Y} = \int \vartheta_{12}\, dV = \int_0^\infty \vartheta_{12} \cdot 4\pi r^2\, dr \Rightarrow Z_\vartheta =$
$\doteq 1 - \frac{1}{2} N^2 V^{-1} \beta \mathcal{Y}$, $\ln Z = \ln Z_{id} + \ln Z_\vartheta \doteq \ln Z_{id} - \frac{1}{2} N^2 V^{-1} \times$
$\times \beta \mathcal{Y}$ / $F = E - TS$: $dF = -S\,dT - p\,dV \Rightarrow p = -\partial_V F$ & $F =$
$= -kT \ln Z$: $p = +kT\, \partial_V \ln Z = p_{id} + \cancel{kT} \cdot \frac{1}{2} n^2 \cancel{\beta} \mathcal{Y} = p_{id} - a_1 n^2$,
$\boxed{a_1 = -\frac{1}{2} \mathcal{Y}}$

fázové prechody

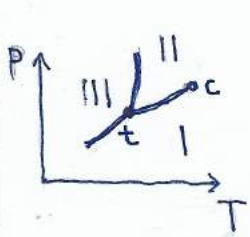
plyn $\rightleftarrows$ kvapalina: $\begin{cases} a = 3 p_c V_c^2 \\ b = \frac{1}{3} V_c \end{cases}$: $p_c(\tilde{p} + 3/\tilde{V}^2) \cdot V_c(\tilde{V} - \frac{1}{3}) =$
$= R T_c \tilde{T}$, $\begin{cases} \tilde{p} = p/p_c \\ \tilde{V} = V/V_c \end{cases}$, $\tilde{T} = T/T_c \Rightarrow T_c \doteq \frac{8}{3} \frac{p_c V_c}{R}$ („aby to



pekne vyšlo": $\boxed{(\tilde{p}+3/\tilde{V}^2)(\tilde{V}-1/3)=8/3.\tilde{T}}$ $\longrightarrow$ $(\tilde{p},\tilde{V})$-diagram = zvlnené hyperboly, $\tilde{T}=1$: $\begin{cases}\tilde{p}(1)=1\\ \tilde{p}'(1) \text{ aj } \tilde{p}''(1)=0\end{cases}$ - kritický bod (c), nad ním: iba plyn ≡ fáza I / $\tilde{T}<1$: $\tilde{p}'=0$ vo $\tilde{V}_\pm \gtrless 1 \Rightarrow \tilde{p}$ prekmitne medzi $\tilde{p}_-$ a $\tilde{p}_+ > \tilde{p}_-$ ZLE; OPRAVA: $\tilde{p} \to \tilde{p}_0$ také, že plocha pod ním je rovnaká (Maxwellovo pravidlo; $\begin{cases}1 \text{ pozdĺž } \tilde{p} \text{ s } \tilde{V}\downarrow\text{-čím}\\ 2 \text{ pozdĺž } \tilde{p}_0 \text{ s } \tilde{V}\uparrow\text{-čím}\end{cases}$; $T_1=T_2 \Rightarrow Q_1 \overset{\text{vrat.}}{=} Q_2$, $A \overset{\text{vrat.}}{=} 0$) $\leftrightarrow$ rovnováha fáz, vpravo plyn, vľavo kvapalina ≡ fáza II; krivka rovnováhy fáz: $\forall\, \tilde{T}<1$: $\tilde{p}_0(\tilde{T})$, $\tilde{T}\uparrow$: $\tilde{p}_0\uparrow$ & $\tilde{T}\sim 0$: $\boxed{\tilde{p}_0 \propto e^{-27/8.\tilde{T}^{-1}}}$ / $\tilde{p}(\tilde{T})$ pri $\tilde{V}$= konšt: V-čka s vrcholmi na $\tilde{p}_0$; Clausiova-Clapeyronova rovnica: rovnováha fáz: $\mu_I=\mu_{II}$, $\mu=\mu(p,T) \to d/dT$: $\partial_T\mu_I + \partial_p\mu_I\, dp/dT$ = dtto s μ_{II} / $\mu=G_1$: $d\mu = s\,dT - v\,dp$, $\begin{cases}s=S_1\\ v=V_1\end{cases} \Rightarrow \begin{cases}\partial_T\mu = s\\ \partial_p\mu=-v\end{cases} \Rightarrow \Delta s - \Delta v.\, dp/dT = 0$, $dp/dT = \boxed{\Delta s/\Delta v}$ & q ≡ latentné teplo $\overset{\text{na 1 mol}}{=}$ $T\Delta s$ ($\mu = \varepsilon - Ts + pv = h - Ts$: $\Delta\mu = \boxed{\Delta h} - q = 0 \Rightarrow q = \Delta h$)

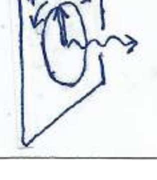


$\Rightarrow \boxed{dp/dT = q/(T\Delta v)}$; plyn-kvapalina ďaleko od c: $v_I \gg v_{II}$ & $pv_I = kT$: $dp/dT \doteq q/(Tv_I) = q/k.\, p/T^2 \Rightarrow q \doteq$ konšt: $p \doteq p_0\, e^{q/k.(T_0^{-1}-T^{-1})}$; trojný bod (t): aj tuhá látka ≡ fáza III $\to$ 3 krivky rovnováhy fáz, t = bod, v kt. sa stretnú



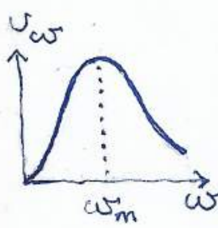
Žiarenie čierneho telesa

majme nádobu s teplotou T + EM žiarenie, kt. je s ňou v rovnováhe $\Rightarrow$ má tiež teplotu T: žiarenie = plyn fotónov $\to u$ ≡ hustota en. + u_ω ≡ spektrálna hustota en. (dutinový žiarič: I ≡ intenzita = $\frac{1}{4}uc$, I_ω ≡ spektrálna intenzita = $\frac{1}{4}u_\omega c$ / $\omega = kc$, $k=2\pi/\lambda$: $d\omega = -2\pi c.\, d\lambda/\lambda^2 \Rightarrow I_\lambda = I_\omega \times 2\pi c/\lambda^2$); módy EM poľa: ① voľné pole: $\forall \vec{k} = k\vec{n} \to \vec{E} = \mathrm{Re}(\vec{\mathcal{E}}_0 e^{-i\omega t + i\vec{k}.\vec{r}})$, $\vec{\mathcal{E}}_0 \perp \vec{k}$ (rovinná monochromatická vlna; $\vec{\mathcal{E}}_0 = (\sum E_{0\lambda}\vec{e}_\lambda)e^{i\psi}$, $\begin{cases}\vec{e}_\lambda \text{ reálne}, \vec{e}_\lambda\cdot\vec{e}_{\lambda'} = \delta_{\lambda\lambda'} \text{ - lin. polarizácia}\\ \vec{e}_\pm = 1/\sqrt{2}.(\vec{e}_1 \pm i\vec{e}_2) \text{ - kruh. polarizácia}\end{cases}$);



(2) pole v nádobe: kocka s hranou L + periodické o.p.: $\vec{k}_{(n_x,n_y,n_z)} = 2\pi/L \cdot (n_x, n_y, n_z)$ (nulové o.p.: π/L + $n_i > 0$; $\vec{E}_\parallel = 0$ + Gauss. zákon: $\vec{e}_{(n_x,n_y,n_z)} = (e_x c_x s_y s_z,\ e_y s_x c_y s_z,\ e_z s_x s_y c_z)$) → $\boxed{d\Gamma_{mód} = 2\frac{d\mathcal{V}_k}{(2\pi/L)^3} = 2\frac{V\,d\mathcal{V}_k}{(2\pi)^3} = \frac{1}{\pi^2} V k^2 dk = \frac{1}{\pi^2 c^3} V\omega^2 d\omega}$ ($\begin{cases}\varepsilon = \hbar\omega\\ p = \hbar k\end{cases}$: $d\Gamma_{mód} = 2\frac{V\,d\mathcal{V}_p}{(2\pi\hbar)^3} = d\Gamma_1$ & $d\Gamma_{mód} \propto \varepsilon^2 d\varepsilon \Rightarrow \omega_1 \propto \varepsilon^2$, NIE $\varepsilon^{1/2}$); UV katastrofa (Rayleigh-Jeans 1900): ∀ mód ↔ $\bar\varepsilon = k_B T$ (ekvipartičná teoréma) ⇒ $u = \frac{1}{V}\int \bar\varepsilon\, d\Gamma_{mód} = \frac{k_B T}{\pi^2 c^3}\int_0^\infty \omega^2 d\omega = \infty$ ZLE;

Planckov zákon (P. 1900): módy = 1-časticové stavy s en. $\varepsilon = \hbar\omega$ a stredným počtom častíc $\nu = \nu_{BE} = 1/[e^{\beta(\varepsilon-\mu)} - 1]$ ⇒ $u = \frac{1}{V}\int \nu\varepsilon\, d\Gamma_{mód} = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \nu\,\omega^3 d\omega$ / μ?: fotóny sa vyžarujú a pohlcujú ⇒ N nie je fixované, $N = N(V,T)$ ⇒ $\boxed{\mu = 0}$ (zostrojenie ν: ∀ člen ∝ N v $\mathcal{S}$ / určenie μ: ∀ podm. $\sum \nu_i = N$),



$\boxed{u_\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/(k_B T)} - 1}}$ (1) $\Omega = \frac{1}{\hbar}k_B T$: $u_\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\times\begin{cases}\Omega/\omega, & \text{ak } \omega \ll \Omega \text{ (R.-J.)}\\ e^{-\omega/\Omega}, & \text{ak } \omega \gg \Omega \text{ (Wien)}\end{cases}$ & u_ω má max. pri $\boxed{\omega_m = 2.82\,\Omega}$ (I_λ má max. pri $\lambda_m = 0.20\,\Lambda$, $\Lambda = 2\pi c/\Omega \propto T^{-1}$ O.K.), (2) $\boxed{u = a T^4}$, $\boxed{a = \frac{\hbar}{\pi^2 c^3}\cdot\frac{k_B^4}{\hbar^4}\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2}{15}\frac{k_B^4}{\hbar^3 c^3}}$ ($I = \sigma T^4$, $\sigma = \frac{1}{4}ca$ O.K.),

(3) $n = \frac{1}{\pi^2 c^3}\int_0^\infty \nu\,\omega^2 d\omega$ → na 1 fotón pripadá kocka s hranou $\sim\lambda$, viď $n = \int \underbrace{\nu}_{\sim 1}\cdot 2\frac{d^3k}{(2\pi)^3} \sim \frac{k^3}{(2\pi)^3} = \lambda^{-3}$

Debyeova teória merných tepiel

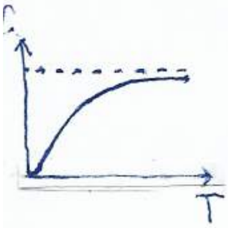
mriežka: $3N$ normálnych módov: ∀ mód ↔ $\bar\varepsilon = k_B T$ ⇒ $E = 3N k_B T$, $\boxed{C = 3N k_B}$ (Dulong-Petit 1819); QM: módy = stavy fonónov s $\varepsilon = \hbar\omega$, $\nu = 1/(e^{\beta\varepsilon} - 1)$ ($\mu = 0$ ako pri fotónoch!) / $k \ll a^{-1}$: módy = zvukové vlny s $\omega = v_{zv} k$, $v_{zv} = \begin{cases} v_L \text{ pre pozdĺžne vlny } (\lambda = 1)\\ v_T \text{ pre priečne vlny } (\lambda = 2,3)\end{cases}$ ⇒ $d\Gamma_{mód} = 3\frac{V\,d\mathcal{V}_k}{(2\pi)^3} = \frac{3}{2\pi^2 \overline{v_{zv}^{2}}} V\omega^2 d\omega$ & $k_B T \ll \varepsilon_{max}$: v $\int$ cez

$d\Gamma_{mód}$ stačí uvažovať módy s $\omega \ll \omega_{max}$, v kt. $\omega = \overline{v}_{zv} k$ + $\int$ sa dá rozšíriť do ∞-na $\rightarrow E \doteq \frac{3}{2} E_{EM}(c \rightarrow \overline{v}_{zv}) = AVT^4$,

$A = \frac{\pi^2}{10} \frac{k_B^4}{\hbar^3 \overline{v}_{zv}^3} \Rightarrow \boxed{C = 3AVT^3}$; Debyeova teória (D.1912):

módy vĺn sa nachádzajú vnútri k_D (Debyeoro vlnove číslo)

+ majú $\omega = \overline{v}_{zv} k \Rightarrow E$ = predchádzajúci $\int$ obrezaný pri $\omega_D = \overline{v}_{zv} k$



$$\rightarrow C \doteq \begin{cases} 3Nk_B, & \text{ak } T \gg T_D = \hbar\omega_D / k_B \\ 3AVT^3, & \text{ak } T \ll T_D \end{cases}$$