Termodinamika

Stanja

Ekstenzivne spremenljivke X: $X_3 = X_1 + X_2$.
Intenzivne spremenljivke Y: $Y_3 = Y_1 = Y_2$.

Nabori TDS: $(p, V, T), (F, x, T), (\mathbf{p}_m, \mathbf{B}, T), (\mathbf{H}, \mathbf{M}, T)$, $(U, e, T), (\mathbf{E}, \mathbf{p}_e, T), (\mathbf{E}, \mathbf{P}, T)$.

$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p = V(\beta\,\mathrm{d}T - \chi_T\,\mathrm{d}p)$
$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$
$V_M = \frac{MV}{m}$

Idealni plin: $pV = \frac{m}{M}RT$
Realni plin: $\left(p + \frac{a}{V_M^2}\right)(V_m - b) = RT$ (van der Waals)
Brezdimenzijska oblika: $\left(\mathcal{P} + \frac{3}{\mathcal{V}^2}\right)(3\mathcal{V} - 1) = 8\mathcal{T}$
$\mathcal{P} = \frac{p}{p_c} = \frac{27b^2p}{a}, \quad \mathcal{V} = \frac{V_m}{V_m^c} = \frac{V_m}{3b}, \quad \mathcal{T} = \frac{T}{T_c} = \frac{27RbT}{8a}$

Dielektrik: $D = \varepsilon\varepsilon_0 E = \varepsilon_0 E + P$
$P = \chi\varepsilon_0 E$
Paramagnet: $M = \frac{aH}{T}$ (Curiejev zakon)
$B = \mu\mu_0 H = \mu_0(H + M)$
$M = \chi H$
Superprevodnik:
$\chi = -1$ v superprevodni fazi
$\chi = 0$ v normalni fazi

Energijski zakon

$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$

$H = U + pV$
$\mathrm{d}H = V\,\mathrm{d}p + \mathrm{d}Q$

$\mathrm{d}W = -p\,\mathrm{d}V = \mu_0 H\,\mathrm{d}(MV) = E\,\mathrm{d}(PV)$

$C_V = \left(\frac{\partial U}{\partial T}\right)_V$
$C_p = \left(\frac{\partial H}{\partial T}\right)_p$

Ideali plin:
$U = mc_V T$
$H = mc_p T$

Entropijski zakon

$\Delta S \geq \int \frac{\mathrm{d}Q}{T}$ (enakost pri reverzibilnih)

$\eta_c = 1 - \frac{T_2}{T_1}$ (Carnotov toplotni stroj)

Idealni plin:
$\Delta S = mc_v \ln\frac{T}{T_0} + \frac{mR}{M}\ln\frac{V}{V_0} = mc_p \ln\frac{T}{T_0} - \frac{mR}{M}\ln\frac{p}{p_0}$

Termodinamični potenciali

$F = U - TS$ (prosta energija)
$\mathrm{d}F \leq -p\,\mathrm{d}V - S\,\mathrm{d}T$

$G = H - TS$ (prosta entalpija)
$\mathrm{d}G \leq V\,\mathrm{d}p - S\,\mathrm{d}T$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\chi_T}$ (I. Maxwellova relacija)
$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -\beta V$ (II. Maxwellova relacija)

$\chi_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \frac{\chi_T}{\kappa}$
$c_p - c_V = \frac{T\beta^2}{\rho\chi_T}$
$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\beta T - 1}{\rho c_p}$ (Joule - Kelvinov koeficient)

Fazne spremembe

$\mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,p}$ (kemijski potencial)
Pri enofaznem sistemu $\mu = \frac{G}{m}$
Pri faznem ravnovesju $\mu_p = \mu_k$

$q_i = -\frac{T}{m}\left[\left(\frac{\partial g}{\partial T}\right)_{p,plin} - \left(\frac{\partial g}{\partial T}\right)_{p,kaplj}\right]$

Clausius - Clapeyronova enačba
$\frac{\mathrm{d}p_s}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{q_i}{T(\rho_p^{-1} - \rho_k^{-1})}$
$p_s(T) = p_s(T')\exp\left(-\frac{Mq_i}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right)$

Transportni pojavi

$\frac{\partial \rho_i}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{j}_i$
$\mathbf{j}_i = -D\,\boldsymbol{\nabla}\rho_i$
$\frac{\partial \rho_i}{\partial t} = D\,\nabla^2\rho_i$
Rešitev za $\rho_1(z, t = 0) = c\delta(z)$:
$\rho_1(z, t) = \frac{m_1}{A\sqrt{4\pi Dt}}\exp\left(-\frac{z^2}{4Dt}\right)$

$\frac{\partial T}{\partial t} = -\frac{1}{\rho c_p}\boldsymbol{\nabla}\cdot\mathbf{j}_Q$
$\mathbf{j}_Q = -\lambda\,\boldsymbol{\nabla}T$
$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_p}\nabla^2 T$
S toplotnimi izvori/ponori: $q = \frac{\partial P}{\partial V}$
$\frac{\partial j}{\partial z} = q - \rho c_p\frac{\partial T}{\partial t}$

Termočlen: $U = a\Delta T$
Peltierjev pojav: $P = \pi I$
$\frac{\mathrm{d}\pi}{\mathrm{d}T} = a - (\sigma_A - \sigma_B) \implies \pi \approx aT$

Klasična statistična fizika

V ravnovesnem stanju $\rho = \rho(E(\mathbf{r}, \mathbf{p}))$

Mikrokanonična porazdelitev:
$\sum E_i =$ konst.
$\int \rho(E)\,\mathrm{d}\Gamma = \int \rho(E)g(E)\,\mathrm{d}E = 1$
$\rho = \begin{cases}(g(E)\Delta E)^{-1} & E_0 - \Delta E < E < E_0 + \Delta E\\ 0 & \text{sicer}\end{cases}$

Klasična kanonična porazdelitev:
$T =$ konst.
$\rho(E) \propto \exp[-\beta(E - F)]$
$\beta = \frac{1}{k_B T}$

Fazni integral/vsota:
$Z = \exp(-\beta F) = C\int\exp(-\beta E)\,\mathrm{d}\Gamma$
$\langle Y\rangle = C\int Y(\mathbf{r}, \mathbf{p}, \dots)\exp[-\beta(E - F)]\,\mathrm{d}\Gamma$
$\langle E\rangle = \frac{\mathrm{d}(\beta F)}{\mathrm{d}\beta}$

Ekviparticijski izrek:
Povprečna energija vsake kvadratične, neomejene in neodvisne prostorske stopnje je enaka $\frac{1}{2}k_B T$.

Fluktuacije energije:
$\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = -\frac{\mathrm{d}^2(\beta F)}{\mathrm{d}\beta^2} = k_B T^2 C_V \propto N$

Enačba stanja

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

Virialni razvoj:
$\frac{\beta pV}{N} = 1 + \sum_{i=2}^{\infty} B_i\left(\frac{N}{V}\right)^{i-1}$
Če vzamemo samo $i = 2$:
$e^{-\beta F} = C\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} I$
$I = V^N(1 - \frac{N^2 B_2}{V})$
$\frac{N^2 B_2}{V} \ll 1 \implies \ln I \approx N\ln V - B_2\frac{N^2}{V}$
$B_2 = \frac{1}{2}\int\left[1 - e^{-\beta\phi(\mathbf{r}_{i,j})}\right]\mathrm{d}\mathbf{r}_{i,j}$
V sferičnih koordinatah: $B_2 = \frac{1}{2}\int_0^\infty\left[1 - e^{-\beta\phi(r)}\right]4\pi r^2\,\mathrm{d}r$
$p = \frac{N}{V\beta} + \frac{N^2 B_2}{V^2\beta}$

Entropija

$S = \frac{\langle E\rangle - F}{T}$
$S = k_B\langle\beta(E - F)\rangle$
Kanonična porazdelitev (Gibbs):
$S = -k_B\langle\ln\frac{\rho}{C}\rangle = -k_B\int\rho\ln\frac{\rho}{C}\,\mathrm{d}\Gamma$
Mikrokanonična porazdelitev (Boltzmann):
$S = k_b\ln(\Delta\Gamma C)$

Kvantna statistična fizika

Bozoni imajo cel spin.
Fermioni imajo polovičen spin, za njih velja Paulijevo načelo.
$\Psi^F(\mathbf{r}_1\dots\mathbf{r}_n) \propto \sum_\sigma \mathrm{sgn}(\sigma)\varphi_\alpha(\mathbf{r}_\sigma(1))\varphi_\beta(\mathbf{r}_\sigma(2))\cdots$
$\Psi^B(\mathbf{r}_1\dots\mathbf{r}_n) \propto \sum_\sigma \varphi_\alpha(\mathbf{r}_\sigma(1))\varphi_\beta(\mathbf{r}_\sigma(2))\cdots$

$\oint p\,\mathrm{d}q = nh$ (Bohr - Sommerfeldovo kvantizacijsko pravilo)
$C = \frac{(2j+1)^N}{N!h^{3N}}$

Enačbe za fazno vsoto veljajo tudi tukaj, le da seštevamo po diskretnih stanjih.

Paramagnetizem

$p_{m_z} = \gamma\hbar j_z = g\mu_B j_z$
$j_z = -j, -j+1 \dots j-1, j \quad ((2j+1)$ kratna degeneracija$)$
$E = -\mathbf{p}_m \cdot \mathbf{B} = -p_{m_z} B$

Isingov model

$H = -J \sum_{i,j \text{ soseda}} s_{i_z} s_{j_z} = -\sum_i \gamma\hbar s_{i_z} \sum_{j \text{ sosed } i} \frac{J s_{j_z}}{\gamma\hbar} =$
$= -\sum_i \gamma\hbar s_{i_z} B_{\text{lok}_i}$
$\langle B_{\text{lok}} \rangle = z \frac{J\langle s_z \rangle}{\gamma\hbar} \quad$ (približek povprečnega polja)

Velekanonična porazdelitev

$\rho(E,N) \propto \exp\left[\beta\mu N - \beta E\right]$
$C_N = \frac{(2j+1)^N}{N! h^{3N}}$
$Z = \exp\left[-\beta q\right] = \sum_{N=0}^{\infty} C_N \int \exp\left[\beta(\mu N - E)\right] \mathrm{d}\Gamma_N$
$\langle Y \rangle = \sum_{N=0}^{\infty} C_N \int Y(\mathbf{r}, \mathbf{p}, \dots) \exp\left[\beta(\mu N - E + q)\right] \mathrm{d}\Gamma_N$
$\langle E \rangle = \frac{\mathrm{d}(\beta q)}{\mathrm{d}\beta}$
$\langle p \rangle = -\left(\frac{\partial q}{\partial V}\right)_{\beta,\mu} = -\left(\frac{\partial(\beta q)}{\partial(\beta V)}\right)_{\beta,\mu}$
$\langle N \rangle = -\left(\frac{\partial(\beta q)}{\partial(\beta\mu)}\right)_{\beta}$
$q = -pV$

Enoatomni idealni plin:
$e^{\beta\mu} = \frac{h^3}{(2j+1)(2\pi m)^{\frac{3}{2}} k_B^{\frac{5}{2}}} \frac{p}{T^{\frac{5}{2}}} = \frac{1}{J} \frac{p}{T^{\frac{5}{2}}}$

Fermi - Diracova porazdelitev

$e^{-\beta q} = \prod_j \left[1 + \exp\left(\beta\mu - \beta E_j\right)\right]$
$\langle N \rangle = \sum_j \frac{1}{\exp\left(\beta E_j - \beta\mu\right) + 1}$

Bose - Einsteinova porazdelitev

$e^{-\beta q} = \prod_j \frac{1}{1 - \exp\left(\beta\mu - \beta E_j\right)}$
$\langle N \rangle = \sum_j \frac{1}{\exp\left(\beta E_j - \beta\mu\right) - 1}$

Kinetična teorija plinov

$p = n k_B T$
$\rho(v) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left[-\frac{mv^2}{2k_B T}\right]$
$\langle v \rangle = \sqrt{\frac{8 k_B T}{\pi m}}$
$j = \frac{n\langle v \rangle}{4}$
$l_p = (\sqrt{2}\pi\sigma^2 n)^{-1}$
$D = \frac{6}{10} \langle v \rangle l_p$
$\eta = \frac{1}{2} \rho_m \langle v \rangle l_p$
$\lambda = \frac{3}{4} n \langle v \rangle l_p k_B$