Toplotne osobina čvrstih tela i adsorpcija

Debajev model kristala

$N \longrightarrow 3N-6 \approx 3N$

$T \to \infty \qquad C_v \sim 3Nk$

$T \to 0 \qquad C_v \sim T^3$

$\vec{k} = \frac{\pi}{L}\left(n_x\vec{e}_x + n_y\vec{e}_y + n_z\vec{e}_z\right) \qquad n_x, n_y, n_z = 1,2,3,\dots$

$\vec{k}\cdot\vec{k} = k^2 = \frac{\pi^2}{L^2}\left(n_x^2+n_y^2+n_z^2\right) \Rightarrow n_x^2+n_y^2+n_z^2 = \left(\frac{kL}{\pi}\right)^2$

ν_D

$C_v = ?$

$\Phi(k) = \frac{1}{8}\,\frac{4}{3}\pi\left(\frac{kL}{\pi}\right)^3 = \frac{k^3 V}{6\pi^2} \quad ; \ V = L^3 \qquad \lambda\cdot\nu = \vartheta \Rightarrow \nu = \frac{\vartheta}{\lambda}\cdot\frac{2\pi}{2\pi} = \frac{\vartheta k}{2\pi}$

$Q = \prod_{i=1}^{3N} \frac{e^{-\frac{1}{2}\beta h\nu_i}}{1-e^{-\beta h\nu_i}}$

$g(k) = \frac{d\Phi(k)}{dk} = \frac{k^2 V}{2\pi^2} \qquad g(\nu)\,d\nu = g(k)\,dk$

$g(\nu) = g(k)\frac{dk}{d\nu}$

$\ln Q = \sum_{i=1}^{3N}\left[-\frac{1}{2}\beta h\nu_i - \ln\left(1-e^{-\beta h\nu_i}\right)\right] \longrightarrow \int_0^{\nu_D} g(\nu)\left(-\frac{1}{2}\beta h\nu - \ln\left(1-e^{-\beta h\nu}\right)\right)d\nu$

$g(\nu) = \frac{4\pi V}{\vartheta^3}\nu^2 \sim \nu^2$

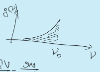
$g(\nu) = 2\cdot\underbrace{\frac{4\pi V}{\vartheta_T^3}\nu^2}_{} + \underbrace{\frac{4\pi V}{\vartheta_L^3}\nu^2}_{}$

$+ \quad -$

$\vartheta_T = \vartheta_L = \vartheta_0$

$\int_0^{\nu=\nu_D} g(\nu)\,d\nu = 3N$

$g(\nu) = \frac{12\pi V}{\vartheta_0^3}\nu^2$



$\boxed{g(\nu) = 9N\frac{\nu^2}{\nu_D^3}}$

$\frac{12\pi V}{\vartheta_0^3} = \frac{9N}{\nu_D^3}$

$\ln Q = \int_0^{\nu_D} \frac{9N}{\nu_D^3}\nu^2\left(-\frac{1}{2}\beta h\nu - \ln\left(1-e^{-\beta h\nu}\right)\right)d\nu =$

$= \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[-\frac{1}{2}\beta h\nu^3 - \nu^2\ln\left(1-e^{-\beta h\nu}\right)\right]d\nu$

$\langle E\rangle = -\left(\frac{\delta \ln Q}{\delta\beta}\right) = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[\frac{1}{2}h\nu^3 + \nu^2\,\frac{-e^{-\beta h\nu}(-h\nu)}{1-e^{-\beta h\nu}}\right]d\nu$

$\langle E\rangle = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[\frac{1}{2}h\nu^3 + \frac{h\nu^3}{e^{\beta h\nu}-1}\right]d\nu$

$C_v = \left(\frac{\delta\langle E\rangle}{\delta T}\right)_{V,N} = \frac{9Nk}{\nu_D^3}(h\beta)^2\int_0^{\nu_D}\frac{\nu^4 e^{\beta h\nu}}{\left(e^{\beta h\nu}-1\right)^2}d\nu$

$\beta h\nu = x$

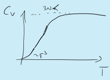
$\nu = \frac{x}{\beta h} \qquad d\nu = \frac{dx}{\beta h}$

$C_v = \frac{9Nk}{\nu_D^3}(h\beta)^2\int_0^{\beta h\nu_D}\frac{x^4}{(\beta h)^4}\,\frac{e^x}{\left(e^x-1\right)^2}\,\frac{dx}{\beta h} \qquad \underbrace{\frac{h\nu_D}{k} = \Theta_D}_{}$

$\boxed{C_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4 e^x}{\left(e^x-1\right)^2}dx}$

1) $T \to 0$, $\frac{\Theta_D}{T} \to \infty$, $x \to \infty$

$C_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3\underbrace{\int_0^{\frac{\Theta_D}{T}}\frac{x^4 e^x}{\left(e^x-1\right)^2}dx}_{\neq f(T)} \sim T^3$



2) $T \to \infty$, $x \to 0$, $\frac{\Theta_D}{T} \to 0$

$C_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4\left(1+x+\dots\right)dx}{\left(1+x+\dots-1\right)^2} \approx$

$\approx 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4}{x^2}dx = \overset{3}{\cancel{9}}Nk\cancel{\left(\frac{T}{\Theta_D}\right)^3}\,\frac{1}{\cancel{3}}\cancel{\left(\frac{\Theta_D}{T}\right)^3}$

$C_v \approx 3Nk$

Mi-Griajyerova jednacina

$P = -\frac{d\Phi}{dV} + \gamma\frac{U}{V} \qquad \frac{d\ln\nu_j}{d\ln V} = -\gamma$

$E(V) = \Phi(V) + \sum_{j=1}^{3N}\left(n_j+\frac{1}{2}\right)h\nu_j(V) \qquad g_i = 1$

$Q = \sum_i g_i e^{-\beta E_i} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\dots\sum_{n_j=0}^{\infty} e^{-\frac{E_i}{kT}} = e^{-\frac{\Phi(V)}{kT}}\underbrace{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\dots\sum_{n_j=0}^{\infty} e^{-\frac{\left(n_j+\frac{1}{2}\right)h\nu_j(V)}{kT}}}_{}$

$Q = e^{-\frac{\Phi(V)}{kT}}\cdot g_{vib} = \underbrace{e^{-\frac{\Phi(V)}{kT}}\prod_{j=1}^{3N}\frac{e^{-\frac{1}{2}\beta h\nu_j}}{1-e^{-\beta h\nu_j}}}_{} \qquad \prod_{j=1}^{3N}\frac{e^{-\frac{1}{2}\beta h\nu_j}}{1-e^{-\beta h\nu_j}}$

$F = -kT\ln Q$

$P = -\left(\frac{\delta F}{\delta V}\right)_{T,N} = +kT\left(\frac{\delta \ln Q}{\delta V}\right)_{T,N} = kT\frac{\delta}{\delta V}\left[-\frac{\Phi(V)}{kT} + \sum_{j=1}^{3N}\left[-\frac{1}{2}\frac{h\nu_j}{kT} - \ln\left(1-e^{-\beta h\nu_j}\right)\right]\right] =$

$= -\frac{d\Phi(V)}{dV} + \cancel{kT}\sum_{j=1}^{3N}\left[-\frac{1}{2}\frac{h}{\cancel{kT}}\frac{d\nu_j}{dV} - \frac{-e^{-\beta h\nu_j}\left(-\frac{h}{\cancel{kT}}\right)\frac{d\nu_j}{dV}}{1-e^{-\beta h\nu_j}}\right] =$

$= -\frac{d\Phi(V)}{dV} - \underbrace{\sum_{j=1}^{3N}\left(\frac{1}{2}h\nu_j - \frac{h\nu_j}{e^{\beta h\nu_j}-1}\right)}_{}\frac{1}{\nu_j}\frac{d\nu_j}{dV} =$

$-\left(\frac{\delta \ln Q}{\delta\beta}\right) = \langle E\rangle = \sum_{j=1}^{3N}\langle E_j\rangle$

$\frac{1}{V}\,\frac{\frac{d\nu_j}{\nu_j}}{\frac{dV}{V}} =$

$= -\frac{d\Phi(V)}{dV} - \sum_{j=1}^{3N}\langle E_j\rangle\cdot\frac{1}{V}(-\gamma) =$

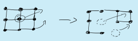
$= \frac{1}{V}\underbrace{\frac{d\ln\nu_j}{d\ln V}}_{} = -\gamma\cdot\frac{1}{V}$

$= -\frac{d\Phi(V)}{dV} + \gamma\frac{\langle E\rangle}{V} = P$

Defekti

ФРЕНКЕЛОВИ

ШОТКИЈЕВИ



АДСОРПЦИЈА

Langmirova adsorpciona izoterma

$\Theta = \frac{N}{M} = \frac{K(T)\cdot P}{1+K(T)\cdot P}$

1) $(N,V,T) \to (N,M,T)$

$Q = Q(M,N,T)$

$Q = \frac{M!}{N!(M-N)!}g_{ads}^N \qquad g_{ads}\ g_{vib}\ g_{el} = g_{vib}^0\, e^{\beta\varepsilon_0} \ \ \varepsilon_0 \approx 1eV$

$Q = \underbrace{\frac{M!}{N!(M-N)!}}_{\text{ЕНТРОПИЈСКИ ЧЛАН}}\left(g_{vib}^0\right)^N\underbrace{\left(e^{\beta\varepsilon_0}\right)^N}_{\text{ЕНЕРГИЈСКИ ЧЛАН}} \rightarrow F \rightarrow \mu \rightarrow N = f(\mu)$

$F = -kT\ln Q = \dots$

$\mu = \left(\frac{\delta F}{\delta N}\right)_{M,T} = kT\ln\left(\frac{N}{M-N}\right) - kT\ln g_{ads}$

$e^{\frac{\mu}{kT}+\ln g_{ads}} = \frac{N}{M-N} = \frac{1}{\frac{1}{\Theta}-1} \qquad \frac{N}{M} = \Theta$

$g_{ads}\,e^{\frac{\mu}{kT}} = \frac{1}{\frac{1}{\Theta}-1} \Rightarrow \boxed{\Theta = \frac{N}{M} = \frac{g_{ads}e^{\frac{\mu_{ads}}{kT}}}{1+g_{ads}e^{\frac{\mu_{ads}}{kT}}}}$

$A_{(g)} \rightleftarrows A_{(ads)}$

$\mu_{gas} = \mu_{ads} = -kT\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right) = \qquad \frac{V}{N} = \frac{kT}{P}$

$= -kT\ln\left[\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] = \qquad \lambda_T = \frac{h}{\sqrt{2\pi mkT}}$

$= -kT\ln\left[\frac{kT}{P}\,\frac{1}{\lambda_T^3}\right]$

$\boxed{\mu_{ads} = kT\ln\left[\frac{\lambda_T^3}{kT}\cdot P\right]}$

$\Theta = \frac{g_{vib}^0 e^{\beta\varepsilon_0}e^{+\ln\left(\frac{\lambda_T^3}{kT}\cdot P\right)}}{1+g_{vib}^0 e^{\beta\varepsilon_0}e^{+\ln\left(\frac{\lambda_T^3}{kT}\cdot P\right)}} = \frac{g_{vib}^0 e^{\beta\varepsilon_0}\frac{\lambda_T^3}{kT}\cdot P}{1+\underbrace{g_{vib}^0 e^{\beta\varepsilon_0}\frac{\lambda_T^3}{kT}}_{K(T)}\cdot P} = \frac{K(T)P}{1+K(T)P}$

$N_{2(g)} \rightleftarrows 2N_{(ads)} \qquad H_2 \rightleftarrows 2H$

$\mu_{ads} = \frac{1}{2}\mu_{gas} \qquad \boxed{g_{tr}\,g_{vib}\,g_{rot}\,g_{el}}$