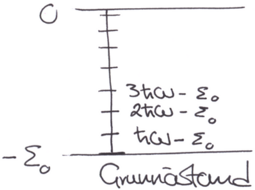
Dæmi líkan af uppgufun

fastefni með N-atóm
Hvert bundið með $\hbar\omega$
(Hreintóna sveifill) og
bindiorku ε_0



Kórsumman fyrir einn sveifil
í fastaefninu er

$$Z_s = \sum_n \exp\left\{-\frac{(n\hbar\omega - \varepsilon_0)}{\tau}\right\}$$

$$= e^{\frac{\varepsilon_0}{\tau}} \sum_n e^{-\frac{n\hbar\omega}{\tau}}$$

$$= \frac{e^{\frac{\varepsilon_0}{\tau}}}{1 - e^{-\frac{\hbar\omega}{\tau}}}$$

og

$$F_s = U_s - \tau\sigma_s = -\tau \ln Z_s$$

Frjáls orka Gibbs í fastaefninu
á atómer

$$G_s = U_s - \tau\sigma_s + pv_s = F_s + pv_s$$
$$= \mu_s$$

(2)

Þrýstingurinn er jafn í báðum fösum, en

$$v_s << v_g$$

sleppum pv_s-lið og fáum

$$\mu_s \simeq F_s$$

$$\rightarrow \lambda_s \equiv e^{\frac{\mu_s}{\tau}} \simeq e^{\frac{F_s}{\tau}}$$

$$= e^{-\ln Z_s} = \frac{1}{Z_s}$$

$$= e^{-\frac{\varepsilon_0}{\tau}} \left[1 - e^{-\frac{\hbar\omega}{\tau}}\right]$$

Gerum ráð fyrir kjörgasi og sleppum spuna

$$\lambda_g = \frac{n}{n_Q} = \frac{p}{\tau n_Q} = \frac{p}{\tau}\left(\frac{2\pi\hbar^2}{M\tau}\right)^{3/2}$$

því $pV = N\tau \rightarrow \frac{N}{V} = n = \frac{p}{\tau}$

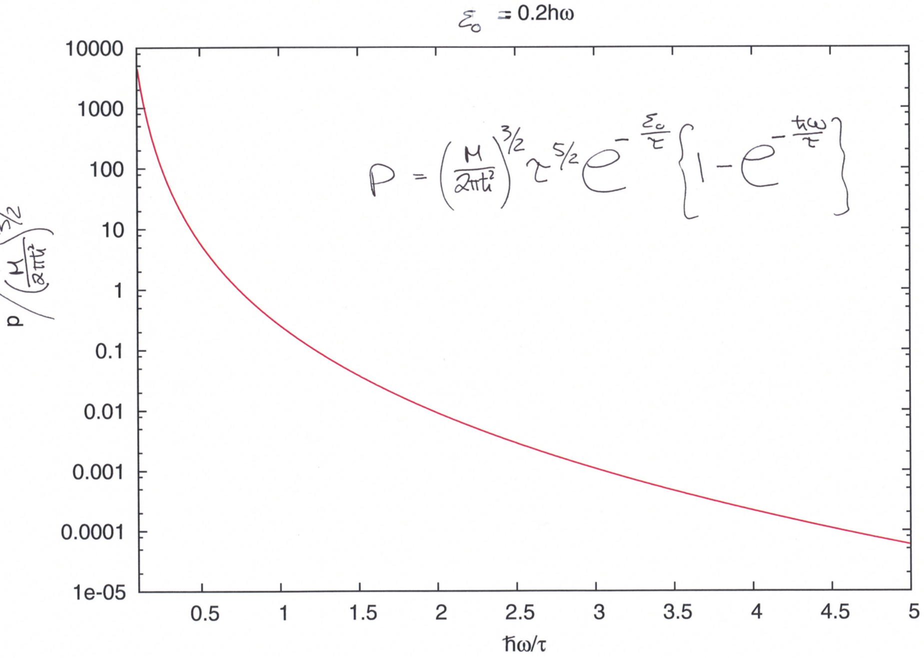
Fasarnir eru í jafnvægi

$$\rightarrow \lambda_g = \lambda_s$$

$$\rightarrow p = \tau n_Q e^{-\frac{\varepsilon_0}{\tau}} \left[1 - e^{-\frac{\hbar\omega}{\tau}}\right]$$

$$= \left(\frac{M}{2\pi\hbar^2}\right)^{3/2} \tau^{5/2} e^{-\frac{\varepsilon_0}{\tau}} \left[1 - e^{-\frac{\hbar\omega}{\tau}}\right]$$

gufuþrýstingur kerfisins



$\varepsilon_0 = 0.2h\omega$
$p \Big/ \left(\frac{M}{2\pi\hbar^2}\right)^{3/2}$
$p = \left(\frac{M}{2\pi\hbar^2}\right)^{3/2} \tau^{5/2} e^{-\frac{\varepsilon_0}{\tau}} \left\{1 - e^{-\frac{\hbar\omega}{\tau}}\right\}$
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
1e-05
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
$\hbar\omega/\tau$

Ástandsjafna van der Waals

Fyrir kjörgas höfðum við

$$pV = N\tau$$

Engar fasabreytingar verða án víxlverkunar eindanna

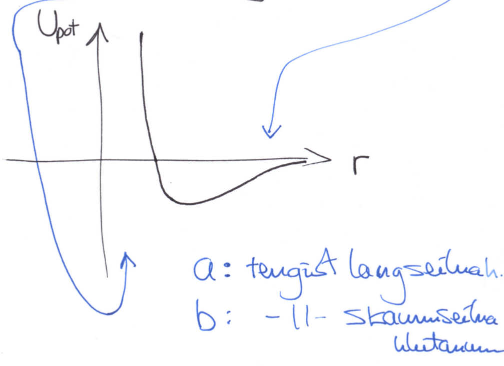
Við munum nú athuga hvernig ástandsjafna van der Waals

$$\left(p - \frac{N^2 a}{V^2}\right)(V - Nb) = N\tau$$

er mótuð af víxlverkunum og hvaða eiginleika hún hefur

a og b eru fastar sem tengjast víxlverkun

Almennt búumst við við að víxlverkun atóma (ekki jóna) hafi veikan aðdráttarhluta og sterka fráhrindingu fyrir skemmri fjarlægðir



Fyrir kjörgas var

$$F = -N\tau\left\{\ln\left(\frac{n_Q}{n}\right) + 1\right\}$$

Nálgum skammseilna hluta víxlverkunarinnar sem harðan vegg þannig að heildarrúmmál kerfisins skerðist um Nb þ.s.

b er rúmmálið sem harði „kjarni" hverrar eindar útilokar

$$V \to V - Nb$$

og $n = \frac{N}{V} \to \frac{N}{V-Nb}$

$$\to F = -N\tau\left\{\ln\left[\frac{n_Q(V-Nb)}{N}\right] + 1\right\}$$

Notum meðalsviðsnálgun t.þ.a. meta a

$\phi(r)$ er mættisorka tveggja atóma í fjarlægð r

Meðal mættisorka atómanna í gasinu með þéttleika n er

$$\int_b^\infty dV\, \phi(\bar{r})\, n(\bar{r}) \simeq n\int_b^\infty dV\, \phi(\bar{r}) = -2na$$

þ.s. við höfum sett

$$a = -\frac{1}{2}\int_b^\infty dv\, \phi(r)$$

nálgunin $n(r) \sim n$ er fyrstastigs nálgun hér sem má endurbæta (með al sviðs fræði)

Hún veldur því að við sleppum ýmsum fylgnihrifum

Orka sameindanna er breytt

$$\rightarrow \Delta F \simeq \Delta U = -\frac{1}{2}(2Nan)$$
$$= -\frac{N^2 a}{V}$$

$$\rightarrow F^{vdW} = -N\tau\left\{\ln\left[\frac{n_Q(V-Nb)}{N}\right]+1\right\} - \frac{N^2 a}{V}$$

og því

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau N} = \frac{N\tau}{V-Nb} - \frac{N^2 a}{V^2}$$

$$\downarrow$$

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = N\tau$$

Ástandsjafna van der Waals

Markpunktar fyrir van der Waals gas

skilgreinum

$$p_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad \tau_c = \frac{8a}{27b}$$

þá verður ástandsjafna vdW

$$\left(\frac{p}{p_c} + \frac{3}{\left(\frac{V}{V_c}\right)^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8\tau}{3\tau_c}$$

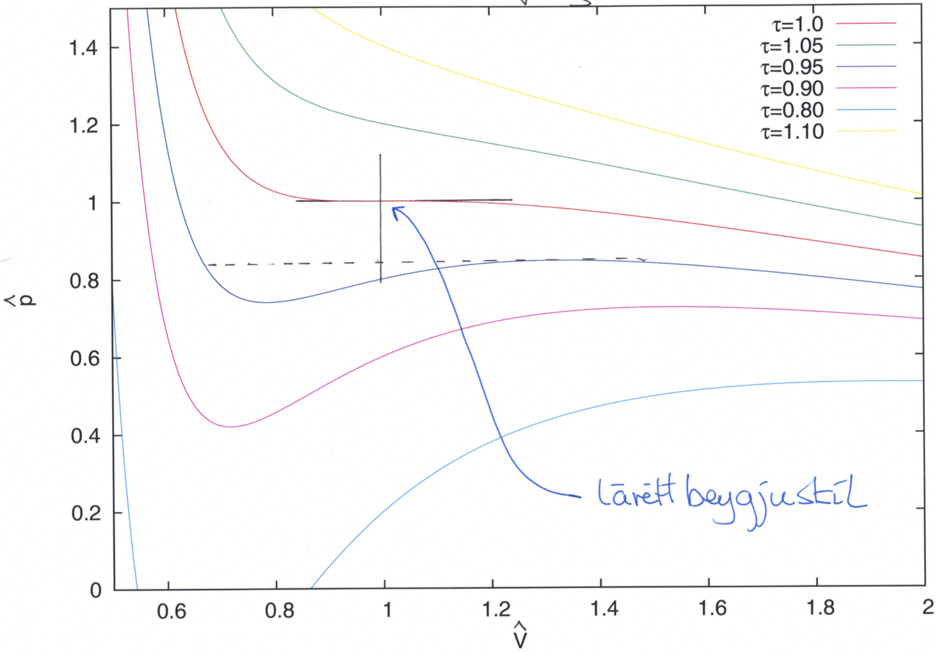
skilgreinum síðan

$$\hat{p} \equiv \frac{p}{p_c}, \quad \hat{V} \equiv \frac{V}{V_c}, \quad \hat{\tau} \equiv \frac{\tau}{\tau_c}$$

$$\rightarrow \left(\hat{p} + \frac{3}{\hat{V}^2}\right)\left(\hat{V} - \frac{1}{3}\right) = \frac{8}{3}\hat{\tau} \quad \text{eða}$$

$$\boxed{\hat{p} = \frac{\frac{8}{3}\hat{\tau}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}}$$

van der Waals $\hat{p} = \frac{\frac{8}{3}\hat{\tau}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}$



Í markpunktinum $(\hat{p}, \hat{V}, \hat{\tau})$ eru beygjuskilin lárétt

$$\left(\frac{\partial \hat{p}}{\partial \hat{V}}\right)_{\hat{\tau}} = 0, \quad \left(\frac{\partial^2 \hat{p}}{\partial \hat{V}^2}\right)_{\hat{\tau}} = 0 \qquad \text{ef } \hat{p} = 1,\ \hat{V} = 1,\ \hat{\tau} = 1$$

Skalaða vdW-jafnan er lýsir lögmáli samsvarandi ástanda

↳ með skölunninni virðast öll gös haga sér eins

fyrir neðan τ_c er til bil í $\hat{V}$ þannig að $\hat{p}$ sé ekki einhlítt ákvarðað, tveir fasar í kerfinu. Fyrir ofan τ_c er aðeins einn fasi

(könnum betur)

Skoðum G hér

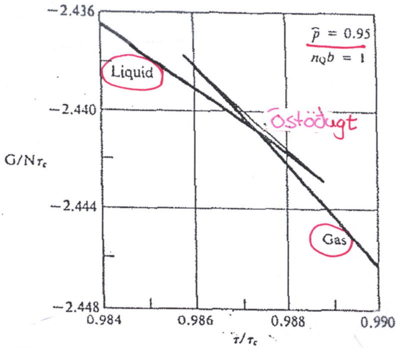
$$G = F + pV$$

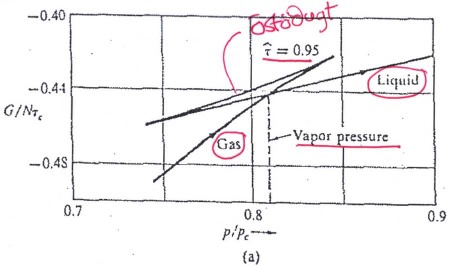
$$G(\tau,V,N) = \frac{N\tau V}{V-Nb} - \frac{2N^2 a}{V} - N\tau\left\{\ln\left[\frac{n_Q(V-Nb)}{N}\right]+1\right\}$$

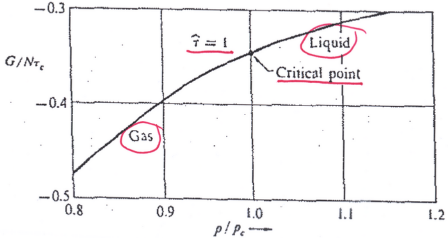
en eðlilegar breytur eru p, τ og N, breytuskiptin leiða til óbeinnar jöfnu, notum tölulegar niðurstöður

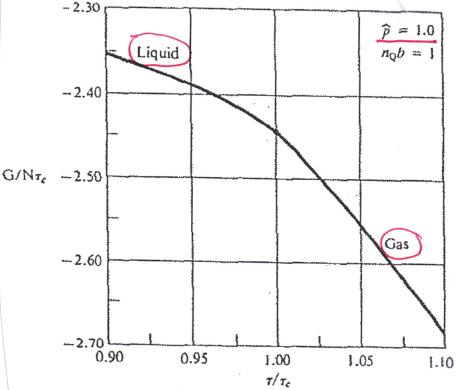
þurfum $\mu(\tau,p) = \dfrac{G(\tau,p,N)}{N}$

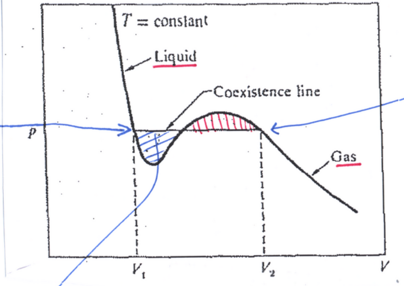
því þá fást upplýsingar um $\mu_l = \mu_g$


−2.436
−2.440
−2.444
−2.448
G/Nτ_c
0.984
0.986
0.988
0.990
τ/τ_c
p̂ = 0.95
n_Q b = 1
Liquid
Gas
ostödugt


−0.40
−0.44
−0.45
G/Nτ_c
0.7
0.8
0.9
p/p_c
τ̂ = 0.95
Liquid
Gas
Vapor pressure
ostödugt
(a)


−0.3
−0.4
−0.5
G/Nτ_c
0.8
0.9
1.0
1.1
1.2
p/p_c
τ̂ = 1
Liquid
Gas
Critical point


−2.30
−2.40
−2.50
−2.60
−2.70
G/Nτ_c
0.90
0.95
1.00
1.05
1.10
τ/τ_c
p̂ = 1.0
n_Q b = 1
Liquid
Gas



$\mu_\ell(\tau, p) = \mu_g(\tau, p)$

$dG = -\sigma d\tau + Vdp + \mu dN$

$= Vdp$ því N, τ eru ~~fastar~~

$G_g - G_\ell = \int dp \cdot V = 0$

á línunni

$\rightarrow G_g(\tau, p) = G_\ell(\tau, p)$

$\mu_g(\tau, p) = \mu_\ell(\tau, p)$

Jafnvægi

Kjörnun

gas

dropi

$\Delta\mu = \mu_g - \mu_\ell$

$\Delta G = G_\ell - G_g = -\left(\frac{4\pi}{3}\right)R^3 n_\ell \Delta\mu + 4\pi R^2 \gamma$

dropinn

yfirborðsliður vegna yfirborðsspennu

dropinn vex ef

$$G_l < G_g$$

(G tekur lággildi í jafnvægi)

$$\frac{d\Delta G}{dR} = -4\pi R^2 n_l \Delta\mu + 8\pi R \gamma$$

$$\rightarrow R_c = \frac{2\gamma}{n_l \Delta\mu}$$

er markgeisli dropans

$R < R_c$

Dropinn gufar upp

$R > R_c$

Dropinn vex

Orku þröskuldurinn

$$(\Delta G)_c = \left(\frac{16\pi}{3}\right)\frac{\gamma^3}{n_l^2(\Delta\mu)^2}$$