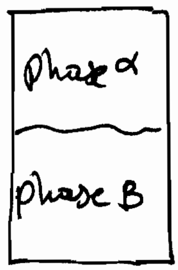
Tracing Coexistence Curves §9.2 F+S



1-component system: α-β coexistence

$$d\mu^\alpha = -S^\alpha dT + V^\alpha dP$$

$$d\mu^\beta = -S^\beta dT + V^\beta dP$$

$$d(\mu^\alpha - \mu^\beta) = -(S^\alpha - S^\beta)dT + (V^\alpha - V^\beta)dP = 0$$

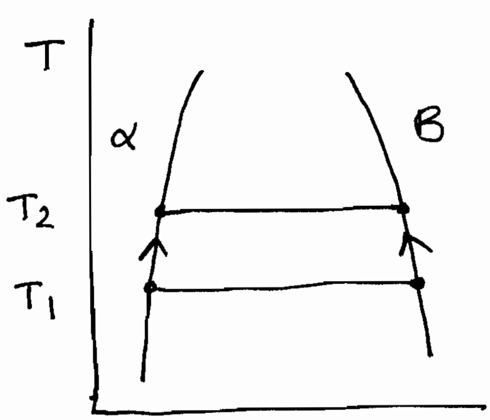
at coex.; $\mu^\alpha = \mu^\beta$

$$\Rightarrow \left.\frac{dP}{dT}\right)_{\substack{\alpha\text{-}\beta \\ \text{Coex}}} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta S}{\Delta V}$$

since $G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S = 0$ at coexistence $\Rightarrow$

$$\Rightarrow \boxed{\left.\frac{dP}{dT}\right)_{\substack{\alpha\text{-}\beta \\ \text{Coex}}} = \frac{\Delta H}{T\Delta V}}$$ (1) Clapeyron equation; exact

$\left.\begin{matrix}\Delta H \\ \Delta V\end{matrix}\right\}$ "mechanical" quantities can be obtained simply in NVT/NPT simulations ($H = U + PV$)



Kofke, Mol. Phys. 68:931 (1989)

Gibbs-Duhem integration:
Numerically integrate (1), starting from point on coexistence envelope;

For VLE, better accuracy using a modified version of (1):

$$\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta H}{P\Delta V/T} \quad ②$$

[If we assume $V_G \gg V_L$, $V_G = RT/P$, ② is the approx. Clausius-Clapeyron equation]

The R.H.S. of ② varies a lot slower w/ T for VLE. (But no need to use Gibbs-Duhem for VLE!)

Method is <u>much</u> more useful for equilibria involving solids, <u>provided that</u> a single coexistence point has been calculated using the methods described in the next chapter.

<u>Example:</u> Freezing of soft spheres

$$u(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n$$

$n \to \infty$: hard spheres

$n = 1$: one-component plasma

Parameter $s = 1/n$

$$dG = -SdT + VdP + \lambda ds$$

λ: thermodynamic conjugate to s

$$d(\mu^\alpha - \mu^\beta) = (V^\alpha - V^\beta)dP + (\lambda^\alpha - \lambda^\beta)ds \quad \text{Const. } T$$

$$\left.\frac{dP}{ds}\right|_{coex} = -\frac{\Delta\lambda}{\Delta V}$$

: Generalized Clapeyron

How is λ determined? Connection to thermodynamics

$$\lambda = \left.\frac{\partial A}{\partial s}\right)_{T,P} = \frac{1}{Q(N,V,T)} \frac{\partial Q(N,V,T)}{\partial s}$$

$$Q = \sum_{\text{all states}} \exp(-\beta U)$$

$$\left.\begin{aligned} Q &= \sum_{\text{all states}} \exp(-\beta U) \\ \frac{\partial Q}{\partial s} &= \sum_{\text{all states}} -\beta \frac{\partial U}{\partial s} \exp(-\beta U) \end{aligned}\right\} \Rightarrow \lambda = -\beta \left\langle \frac{\partial}{\partial s} \left(\varepsilon \left(\frac{\sigma}{r} \right)^{1/s} \right) \right\rangle$$

$$= \frac{\varepsilon \beta}{s^2} \left\langle \left(\frac{\sigma}{r} \right)^{1/s} \ln \left(\frac{\sigma}{r} \right) \right\rangle = \frac{\beta}{s^2} \left\langle u(r) \ln\left(\frac{\sigma}{r} \right) \right\rangle$$

Agrawal + Kofke

PRL 74:122 (1995)

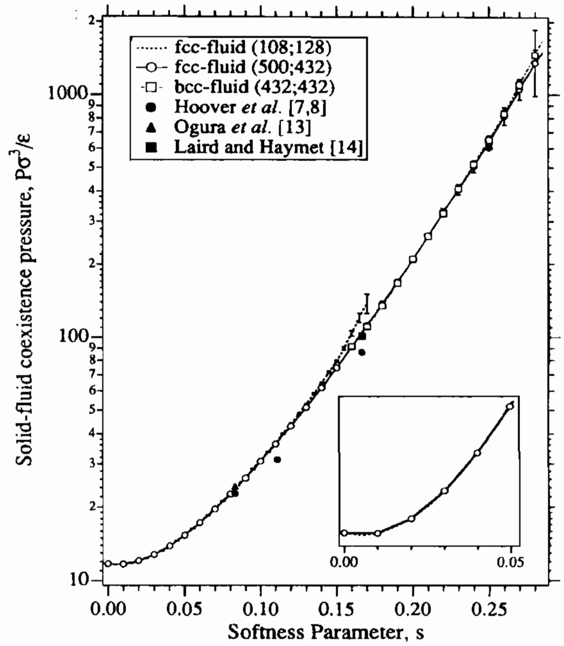


FIG. 1. Coexistence lines determined in this study. Confidence limits (67%) are indicated where they are larger than the plotting symbol. Numbers in the legend refer to the number of spheres used to simulate each phase (solid, fluid). The inset is an expansion of the region near $s = 0$.