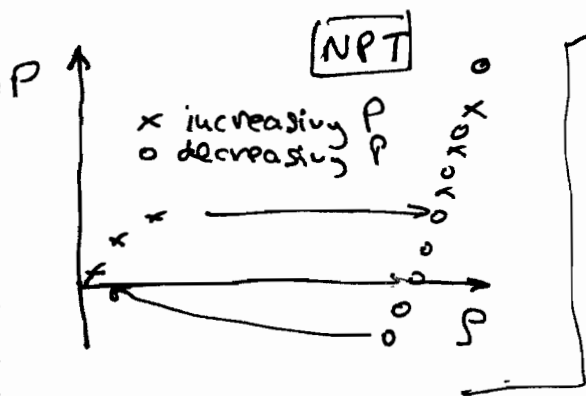
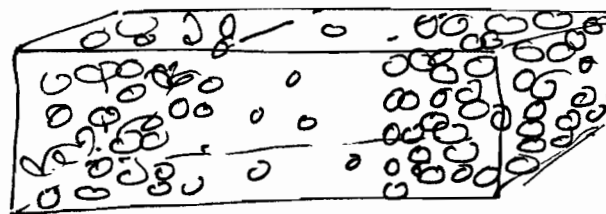


# Interfacial Simulations

We have seen previously that phase transitions are associated with hysteresis - e.g.



Possible solution: explicit 2-phase simulations



## Issues involved:

- \* large systems required
- \* long-range corrections in inhomogeneous systems
- \* slow equilibration via diffusion (for  $\mu$ )
- \* inhomogeneous pressure (tensorial)

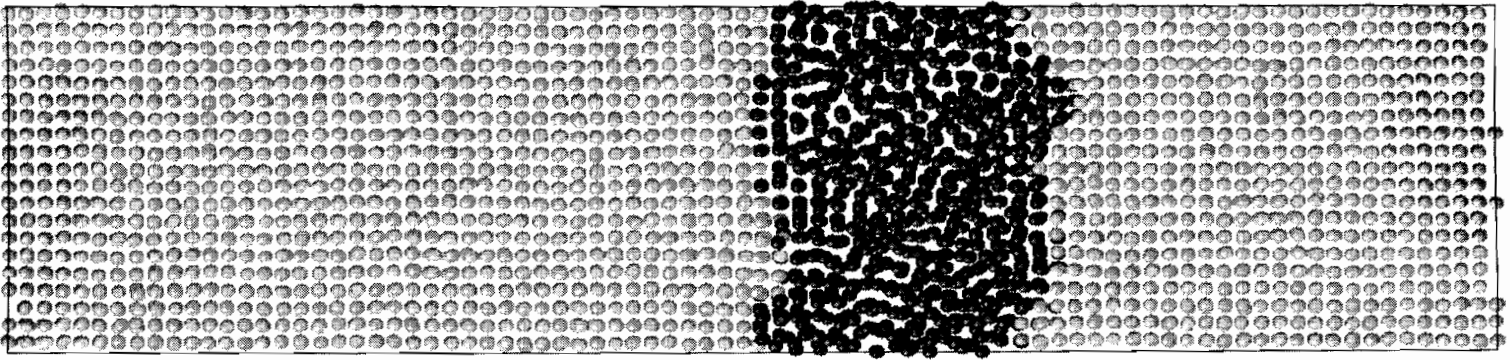
$$P_{\perp} = P_{\parallel} - \frac{2\gamma}{L_{\parallel}} \leftarrow \text{surface tension}$$

$\uparrow$                        $\uparrow$   
 perpendicular to interface      pressure on plane  $\parallel$  to interface  $\rightarrow$  coexistence  $P$

$\rightarrow$  need to vary  $L_{\perp}$  to set pressure

Pressure inhomogeneity / equilibration issues are particularly pronounced for solid-fluid equilibria. Solid-Solid impossible to do.

Advantages: easy to set up, if near melting temperature system "self-adjusts"



- Prepare solid, liquid regions separately at NPT conditions
- Connect together, switch to NVE
- If energy too high, solid melts, if too low liquid solidifies
- "read off" equilibrium  $T, P$

J. Chem. Phys. J. R. Morris and X. Song  
116: 9352-8 (2002)

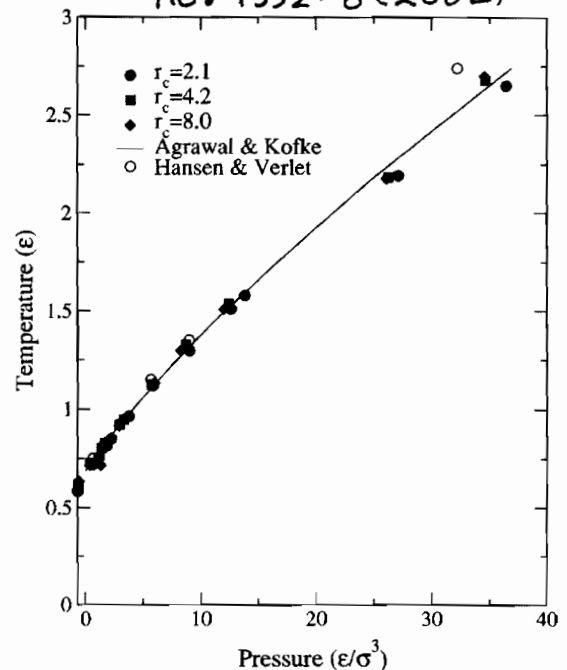
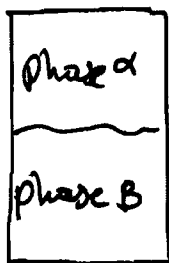


FIG. 5. The pressure-temperature diagram for the LJ system. We have included results for all cutoffs of the LJ potential. The solid line is the fit from the results of Ref. 12, while the large open squares indicate the results of Ref. 9. Error bars for the calculations are approximately equal to the symbol size.

Tracing Coexistence Curves

§ 9.2 F+S

1-component system:  $\alpha$ - $\beta$  coexistence

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

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

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

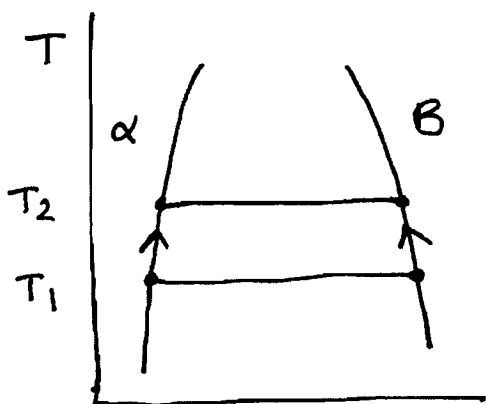
at coex.;  $\mu^\alpha = \mu^\beta$ 

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

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

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

$\Delta H$   
 $\Delta V$  } "mechanical" quantities can be obtained  
Simply in NVT/NPT simulations ( $H = U + PV$ )

Kofke, Mol. Phys. 78:1331 (1992)

Gibbs-Duhem integration:

Numerically integrate ①,  
Starting from point on  
coexistence envelope;

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

$$\frac{d(\ln P)}{d(1/T)} = - \frac{\Delta H}{P \Delta V / T} \quad (2) \quad \left[ \begin{array}{l} \text{If we assume } V_G \gg V_L, \\ V_G = RT/P, \text{ (2) is the approx.} \\ \text{Clausius-Clapeyron equation} \end{array} \right]$$

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

Example: Freezing of soft spheres

$$U(r) = \epsilon \left( \frac{\sigma}{r} \right)^n \quad \begin{array}{l} n \rightarrow \infty : \text{hard spheres} \\ n = 1 : \text{one-component plasma} \end{array}$$

Parameter  $s = 1/n$

$$dG = -SdT + v dP + \lambda ds \quad \begin{array}{l} \lambda : \text{thermodynamic} \\ \text{conjugate to } s \end{array}$$

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

$$\left. \frac{dP}{ds} \right|_{\text{coex}} = - \frac{\Delta \lambda}{\Delta V} \quad : \text{Generalized Clapeyron}$$

How is  $\lambda$  determined? Connection to thermodynamics

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

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

$$\frac{\partial Q}{\partial s} = \sum_{\text{all states}} -\beta \frac{\partial U}{\partial s} \exp(-\beta U) \Rightarrow \lambda = -\beta \left\langle \frac{\partial}{\partial s} \left( \epsilon \left( \frac{\sigma}{r} \right)^{12} \right) \right\rangle$$

$$= \frac{\epsilon \beta}{s^2} \left\langle \left( \frac{\sigma}{r} \right)^{12} \ln \left( \frac{\sigma}{r} \right) \right\rangle = \frac{\beta}{s^2} \langle u(r) \ln \left( \frac{\sigma}{r} \right) \rangle$$

Agrawal +  
Kofke

PRL 74:122 (1995)

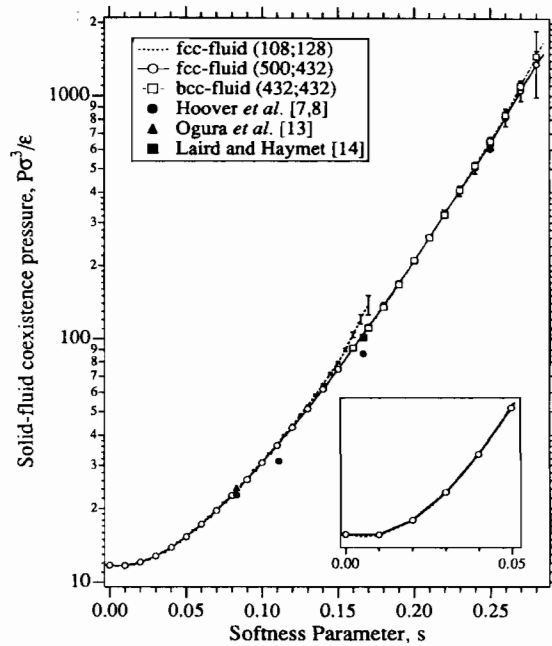


FIG. 1. Coexistence lines determined in this study. Confidence limits (67%) are indicated where they are larger than the plotting symbol. Numbers in the legend refer to the number of spheres used to simulate each phase (solid, fluid). The inset is an expansion of the region near  $s = 0$ .