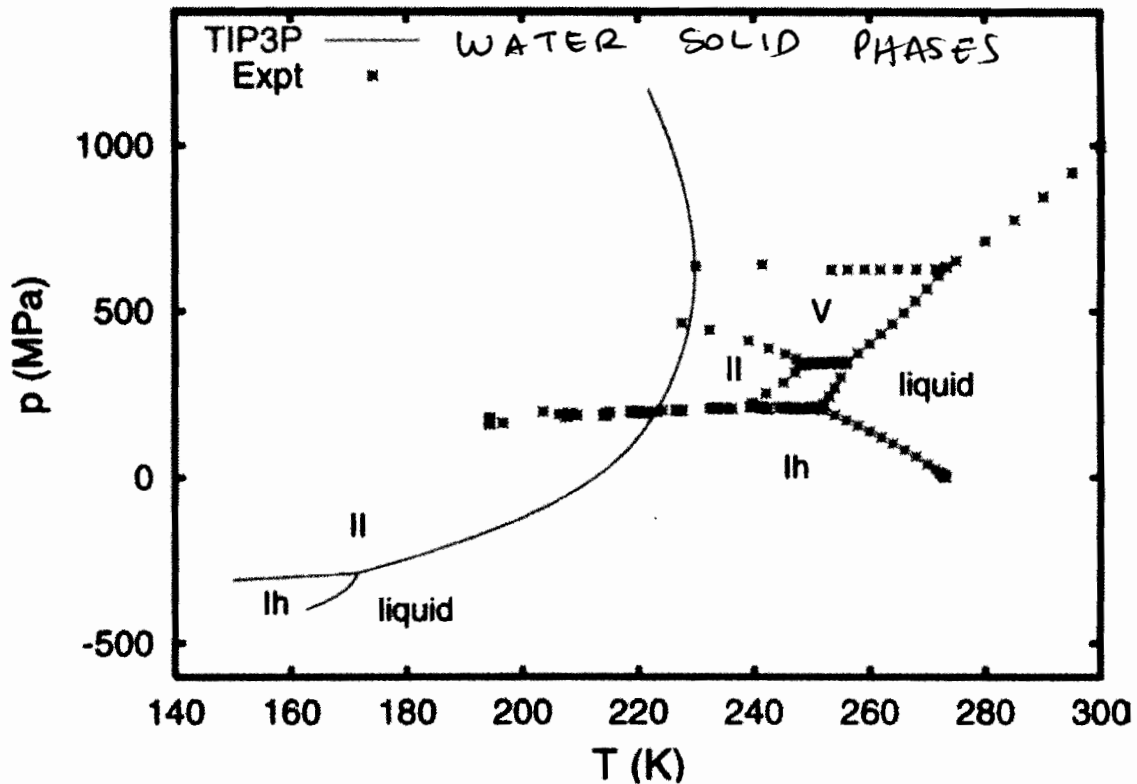


## Free Energies of Solids (Ch. 10 in f+s)

- \* Melting / freezing (fluid/solid)
  - \* Solid / Solid transitions
- } no critical point  
} rare exceptions  
} for solid-solid between  
} same crystal class



C. Vega et al. J. Chem. Soc. Faraday Disc. 141:251 (2009)

Methods discussed up to this point (e.g. GCMC, Gibbs ensemble) do not work for solids because they require particle transfers.

### Thermodynamic Integration

As already suggested, one can obtain the Helmholtz free energy  $A$

$$dA = -SdT - PdV$$

$$\left. \frac{\partial A}{\partial V} \right|_T = -P \Rightarrow A(V_2) - A(V_1) = \int_{V_1}^{V_2} -P dV \quad (1)$$

Need to link unknown state to a state of known free energy. For fluids, natural choice is

$V_2 \rightarrow \infty$  for which the fluid is an ideal gas,

$$A(V \rightarrow \infty) = A^{id}(T, V) = kT \ln \rho + \text{const}(T) \quad \rho = \frac{N}{V}$$

Direct integration of (1) is inconvenient because

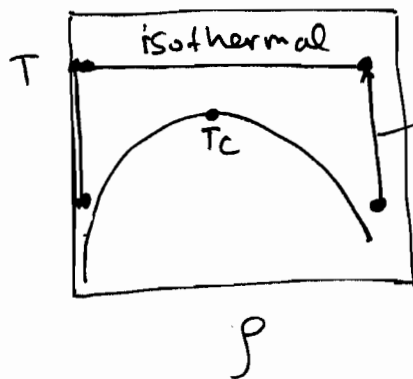
$$A(V \rightarrow \infty) \rightarrow -\infty \text{ as } \rho \rightarrow \phi$$

$$\text{Instead, one computes } A(V) - A^{id}(V) = - \int_V^\infty P dV + \int_\infty^V P^{id} dV \\ = \int_0^\infty (P^{id} - P) dV$$

$$\text{Transform } \rho = 1/V \quad d\rho = -\frac{1}{V^2} dV = -\rho^2 dV$$

$$\Rightarrow A(\rho) - A^{id}(\rho) = \int_0^\rho \frac{P - P^{id} kT}{\rho'^2} d\rho' \quad (2)$$

To integrate (2), we need the equation-of-state  $P(T, \rho)$  for the fluid between the state of interest and the ideal-gas state. This can be done by simulation provided that there are no phase transitions along the path. If there are such transitions, need to "go around" them by integrating over the critical point:



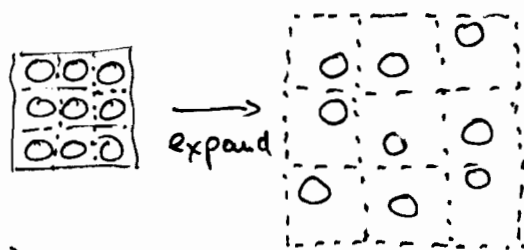
Constant-volume step

$$\left. \frac{\partial(A/T)}{\partial(1/T)} \right|_V = U \Rightarrow$$

$$\frac{A(T_2)}{T_2} - \frac{A(T_1)}{T_1} = \int_{T_1}^{T_2} U(T, V, N) d\left(\frac{1}{T}\right)$$

For solids, one does not have a "natural" reversible path. Instead, various Hamiltonian-scaling approaches can be used - e.g.

Single-occupancy cell  
Hoover + Ree JCP 49:3609 (1968)



Cool to  $T \rightarrow 0$ ,  
Harmonic solid

Hoover et al.

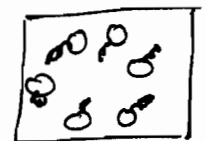
JCP 55:1228 (1971)

Issues arise because of transitions long paths

Best current approach: Frenkel + Ladd, JCP 81:3188 (1984)

→ Reversibly transform into Einstein (harmonic) crystal

Atomic solids, Continuous potentials



$$\tilde{U}(\vec{r}^N) = U(\vec{r}^N) + (1-\lambda) [U(\vec{r}^N) - U(\vec{r}_0^N)] + \lambda \sum_{i=1}^N \alpha_i (\vec{r}_i - \vec{r}_{0,i})^2$$

→  $\vec{r}_0$ : equilibrium lattice positions

$U(\vec{r}_0^N)$ : static contributions to energy when particles are at equil. position

$$\text{For } \lambda=0 \quad \tilde{u} = u(\vec{r}^N)$$

$$\lambda=1 \quad \tilde{u} = u(\vec{r}_0^N) + \sum \alpha_i (\vec{r}_i - \vec{r}_{0,i})^2 \quad (\text{harmonic})$$

$$A = A_{\text{Einstein Crystal}} + \int_0^1 d\lambda \left\langle \frac{\partial u(\alpha)}{\partial \lambda} \right\rangle_{\lambda} =$$

$$= A_{\text{Einstein Crystal}} + \int_0^1 d\lambda \left\langle \sum_{i=1}^N \alpha_i (\vec{r}_i - \vec{r}_{0,i})^2 - [u(\vec{r}^N) - u(\vec{r}_0^N)] \right\rangle_{\lambda} \quad (1)$$

The configurational free energy of the Einstein crystal is

$$A_{\text{Einstein Crystal}} = u(\vec{r}_0^N) - \frac{d}{2B} \sum_{i=1}^N \ln \frac{\pi K T}{\alpha_i}$$

d : dimensionality of space  
B = 1/kT

The spring constants  $\alpha_i$  are chosen to minimize differences between Einstein and real crystal in positions at  $\lambda=0$  and  $\lambda=1$ :

$$\left\langle \sum_{i=1}^N (\vec{r}_i - \vec{r}_{0,i})^2 \right\rangle_{\lambda=0} = \left\langle \sum_{i=1}^N (\vec{r}_i - \vec{r}_{0,i})^2 \right\rangle_{\lambda=1}$$

$$\Rightarrow \left\langle (\vec{r}_i - \vec{r}_{0,i})^2 \right\rangle_{\lambda=0} = \frac{3}{2B\alpha_i}$$

mean-square displ. of atom  $i$  in real crystal

mean-square displ. in Einst. crystal

Implementation issue: for  $\lambda=0$  there is no penalty for moving crystal as a whole  $\rightarrow$  drift!  
(com)  
 $\rightarrow$  solution: constrain center-of-mass or compute actual position of COM + calculate harmonic terms from

shifted position.

### Atomic Solids, Discontinuous potentials

E.g., Hard Spheres  $u_0(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$

Cannot use linear coupling as before; instead,

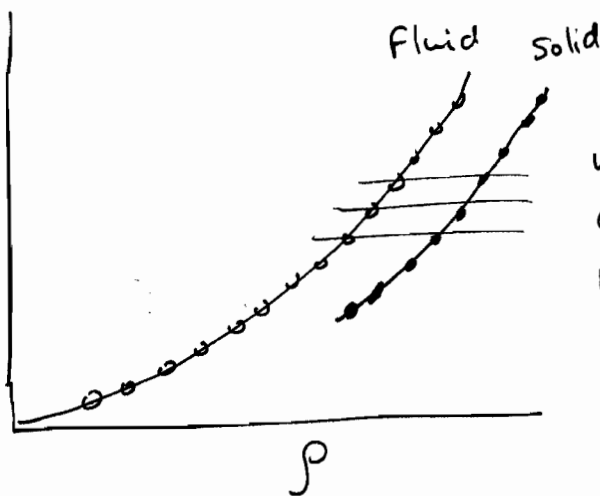
could use:  $u(r) = u_0 + \lambda u_{\#} = u_0 + \lambda \sum_{i=1}^N \alpha_i (r_i - r_{0,i})^2$

$$\lambda = 0 \quad u = u_0 \quad \lambda = 1 \quad u = u_{\#} + u_0$$

If  $\alpha_i$  large enough, particles are always close to their equilibrium positions and "never" feel hard-core repulsions  $\rightarrow$  error prop. to  $\alpha(1/\lambda)$  in  $A(\lambda)$

Application

BP



where is  
coexistence?  
need  $A$  for  
solid

Fluid E.O.S. (Speedy, 1997)  
[or Carnahan-Starling, 1969]  $\rightarrow \frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}$

$\eta = \frac{\pi \rho}{6}$ , "packing fraction" less accurate, more elegant

Solid E.O.S. (Speedy, 1998)  $\frac{\beta P}{\rho} = \frac{3}{1 - \rho} - 0.5921 \frac{\rho - 0.7072}{\rho - 0.601}$

$\Delta A(\text{solid})$  from E.O.S., but need absolute  $A$  for some  $\rho$ .

Careful integrations using high values of  $\beta$  & the coupling constant  $a$  + analytical corrections + finite-size corrections (Polson et al., JCP 112: 5339 (2000))

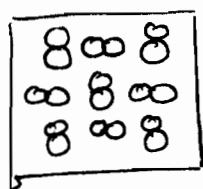
$$\text{give } \left\{ \begin{array}{l} P_L = 0.9391 \quad P_S = 1.0376 \\ BP = 11.567 \end{array} \right\} \text{ for H.S.}$$

## Molecular Solids

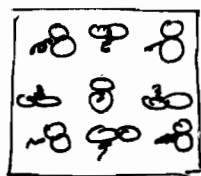
e.g. 7 crystal phases for  $N_2$ , many for  $H_2O$

Two-step process to avoid phase transitions:

Lattice-coupling expansion method [Meijer et al., JCP 92 (1990)]



→

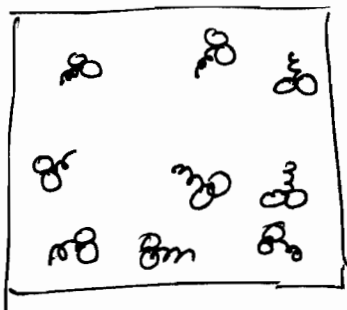


①

$$U_I(\vec{r}^N, \underline{0}^N, \lambda) = U(\vec{r}^N, \underline{0}^N) + \lambda \sum_{i=1}^N \alpha_i (\vec{r}_i - \vec{r}_{i,0})^2$$

Coupling to positions on lattice w/ harmonic springs (but keeping original potential to maintain orientations)  $\Delta A_I = \int_0^1 d\lambda \left\langle \sum_{i=1}^N \alpha_i (\vec{r}_i - \vec{r}_{i,0})^2 \right\rangle_\lambda$

② Expand to large  $V \rightarrow \infty$



Expansion factor  $\gamma = (V/V_0)^{1/3}$

$$\Delta A_{II} = \int_1^\infty d\gamma \left\langle \sum_{i < j}^N \frac{\partial u(r_{ij}, \underline{0}_{ij})}{\partial r_{ij}} \frac{\vec{r}_{ij} \vec{r}_{ij}}{r_{ij}} \right\rangle$$

for pair-wise potentials

## Integration Method

Typically, Gauss-Legendre quadrature with  $n=10$  points is adequate for the integrations

$$\int_{-1}^1 f(x) dx \approx \sum_{i=1}^n w_i f(x_i) \quad w_i: \text{weights}$$

exact for polynomial functions of degree  $\leq n$

e.g.  $n=3$  points  $\{x_i\} = \left\{ -\frac{\sqrt{3}}{3}, 0, \frac{\sqrt{3}}{3} \right\}$   $\{w_i\} = \left\{ \frac{5}{9}, \frac{8}{9}, \frac{5}{9} \right\}$