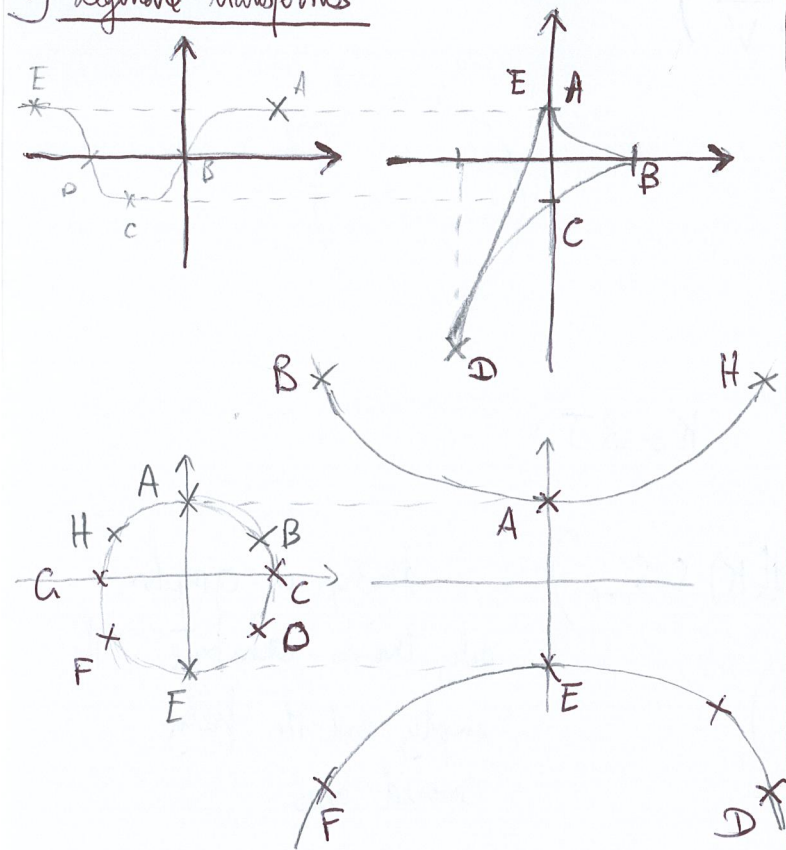


1) Legendre transforms



2) Phase transitions in hard sphere systems

1) The transition is entropy driven, and does not result from energy-entropy competition.

2) Let  $n = \frac{N}{V}$  :  $\mu = f'(n)$

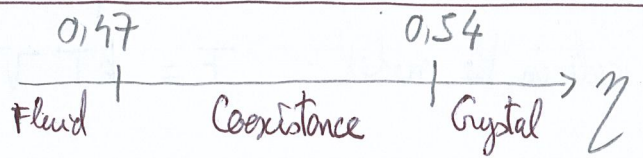
3)  $-P = f - n f'(n)$

$\Rightarrow \mu = \frac{4}{3} \pi \sigma^3 \frac{df}{dn}$

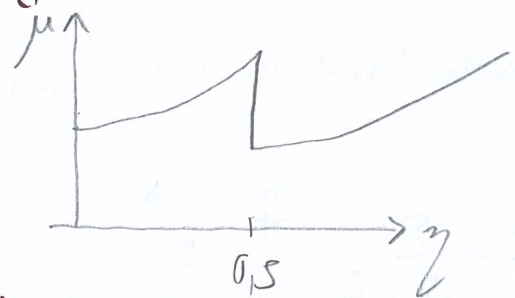
$-P = f(n) - n \frac{df}{dn}$

4) The one with triangles is stable at low  $\eta$ , and is for the fluid branch. The other is for the crystal branch (stable at large  $\eta$ )

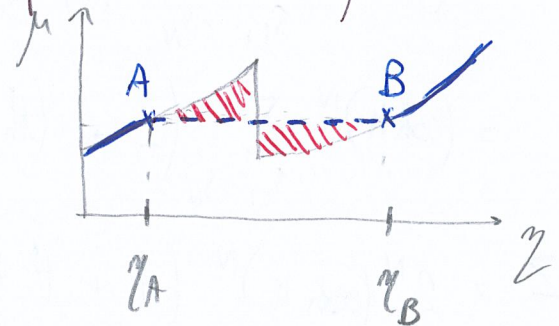
5) Double-tangent. Hence the phase diagram



6) If we restrict to stable branches:

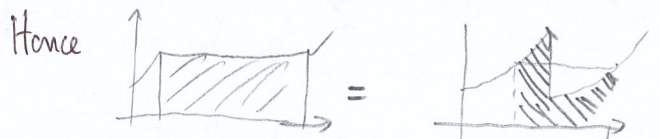


This does not account for demixtion  $\rightarrow$  a plateau at constant  $\mu$ .



We can go from A to B in 2 ways, either taking the plateau, or taking the  $f$

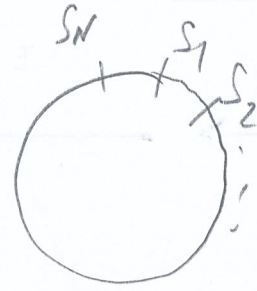
$\int_A^B \mu d\eta = \int_A^B \left. \frac{df}{dn} \right|_T d\eta = \frac{4}{3} \pi \sigma^3 (f(B) - f(A))$



Thus like areas above and  $\rightarrow$  reminiscent of Maxwell construction

7) Samples 2 and 3 are fluid after 1 day. 4 shows phase coexistence, 5 also. 6 " crystallites. After 4 days: 2 remains fluid, 3, 4 and 5 show fluid-crystal coexistence; 6, 7 and 8  $\rightarrow$  crystals; 9 and 10: core glass + crystal

8°) the phase behavior does not depend on temperature, because there is no energy scale in the model.  $F = kT \ln \left( \frac{Z}{V} \right)$



### 3- Ising 1D - correlation functions

1°) Periodic boundaries mean  $S_{N+1} = S_1$

$$2°) Z = \sum_{S_1, \dots, S_N} \prod_{i=1}^N e^{K S_i S_{i+1}} \quad K = \beta J$$

$$= (\cosh K)^N \sum_{S_1, \dots, S_N} \prod_{i=1}^N (1 + (\tanh K) S_i S_{i+1})$$

$$= (\cosh K)^N \sum_{S_1, \dots, S_N} (1 + (\tanh K)^N)$$

develop in graphs only two do contribute, the empty and the fully covered ones

$$Z = 2^N (\cosh K)^N (1 + (\tanh K)^N)$$

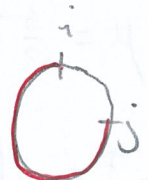
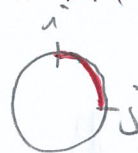
$$3°) \frac{F}{N} \xrightarrow{N \rightarrow \infty} -kT \ln 2 \cosh K$$

same result as with free b.c.

$$4°) \langle S_i S_j \rangle = \frac{1}{Z} \sum_{S_1, \dots, S_N} S_i S_j \prod_{k=1}^N e^{K S_k S_{k+1}}$$

$$= \frac{1}{Z} (\cosh K)^N \sum_{S_1, \dots, S_N} S_i S_j \prod_{k=1}^N [1 + S_k S_{k+1} (\tanh K)]$$

only 2 graphs contribute



$$= \frac{1}{Z} (\cosh K)^N \left[ (\tanh K)^{|j-i|} + (\tanh K)^{N-|j-i|} \right] 2^N$$

$$5°) \langle S_i S_j \rangle \xrightarrow[N \rightarrow \infty]{i \text{ and } j \text{ fixed}} (\tanh K)^{|j-i|}$$

hence a correlation length

$$\xi = -\frac{1}{\ln(\tanh K)}$$

or result we already knew.