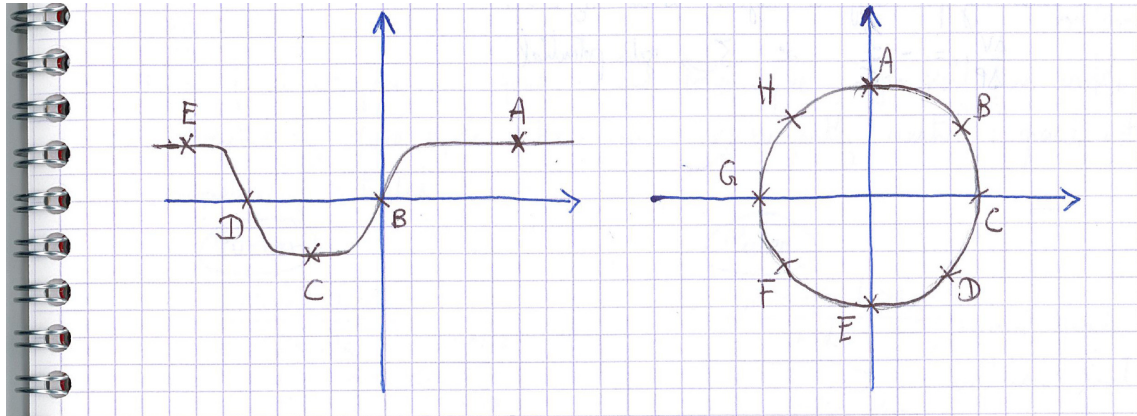


Should be written on a separate paper.
Concise but explicative answers expected throughout. No bonus for verbosity

1 Legendre again

Sketch graphically the Legendre transform of the two functions in the graph below. Locate the images of the points indicated (A,B,C...).



2 Phase transition in hard sphere systems

In a hard-sphere system, the pair potential for interaction between “molecules” is such that there is an infinite energy penalty whenever two spheres do overlap, and a vanishing energy otherwise. The notations are as follows: N hard spheres with radius σ are confined in a system of volume V . The volume fraction is defined as

$$\eta = \frac{4N}{3V} \pi \sigma^3$$

and f denotes the free energy density $f = F/V$ where F is the total free energy. Temperature is fixed throughout.

- 1) The hard-sphere system does exhibit a phase transition, between a fluid phase, and a crystal one. What does drive this phase transition? Does it result from an energy-entropy competition?
- 2) Express the chemical potential μ as some derivative of f with respect to η
- 3) Same question for the pressure P .
- 4) A recent study has computed the free energy of various phases, see the results in Fig. 1. Which branch is for the fluid and which one is for the crystal? Explain.
- 5) What is the meaning of the dashed red line in the upper graph of Fig 1? What consequences can be draw for the phase behaviour of the system? Give the η -range for which the fluid phase is stable, the range for which there is phase coexistence and the range for which the solid phase is stable.
- 6) What is the connection between the two grey regions in the chemical potential graph in Fig. 1? What is such a construction reminiscent of?

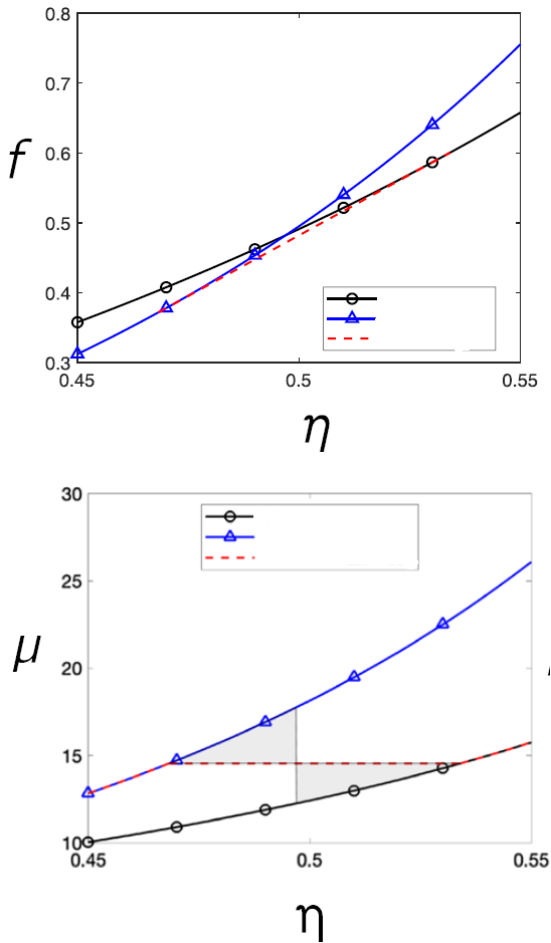


Figure 1: In each of these two plots, one branch is for the fluid phase, another one is for the crystal phase. The upper graph shows the free energy density $f(\eta)$; the bottom graph shows the chemical potential. You have to match triangles/circles to either fluid/crystal, then make sense of the red dashed line in the upper graph and finally establish the correspondence between the upper and bottom graphs. This provides a geometric construction to discuss the phase transition scenario in terms of the information embedded in the $\mu(\eta)$ relation. From T.G. Fai, J.M. Taylor, E.G. Virga, X. Zheng and P. Palffy-Muhoray *J. Chem. Phys.* **154**, 104505 (2021).

- 7) Some real-world colloidal systems feature interactions that are very close to those of hard spheres, see Fig. 2. In this figure, a complication arises though: at the highest densities displayed, the system forms a glass, which destroys the regular ordering of the crystal phase. Describe the experimental results, pure phases versus phase coexistence, discussing the time scales, and what the intrusion of the glass into the game does change compared to the scenario with a mere fluid/crystal competition.
- 8) In which sense does the phase behaviour depend on temperature?

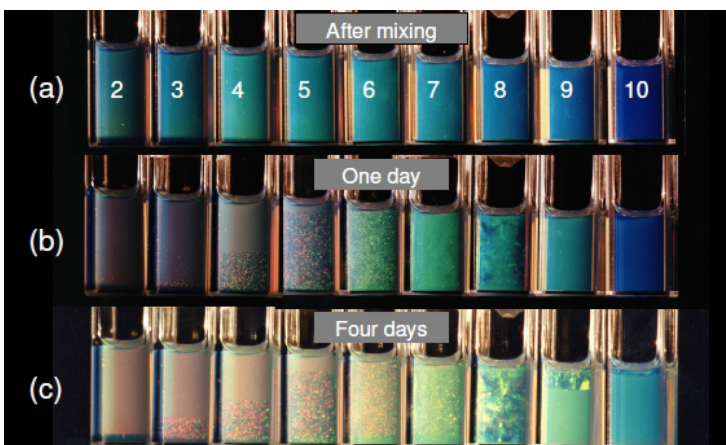


Figure 2: Phase behaviour of hard sphere colloids, as obtained in experiments. The samples, numbered from 2 to 10, are displayed in order of increasing η , from left to right a) Immediately after preparation, b) after one day and c) after 4 days. The colloids used have a radius $\sigma \simeq 300$ nm. From Pusey and van Megen (1986, 1987).

◇

3 Ising 1D: correlation function

We aim at computing the correlation function $\langle S_i S_j \rangle$ for the one-dimensional ferromagnetic Ising model with coupling constant ($J > 0$), without a magnetic field. The hamiltonian reads

$$H = -J \sum_{i=1}^N S_i S_{i+1}, \quad (1)$$

and we shall assume periodic boundary conditions. We will make use of the relation

$$e^{K S_i S_{i+1}} = \cosh(K) + S_i S_{i+1} \sinh(K), \quad (2)$$

to proceed, as in the tutorials, with a graphical method for computing the partition and correlation functions.

- 1) We have a system of $N + 1$ spins. What does “periodic boundary conditions” mean here?
- 2) Write and then compute the partition function. How does it compare to its free boundary counterpart?
- 3) What is the free energy per spin in the thermodynamic limit? How does it compare to its free boundary counterpart?
- 4) Compute the correlation function.
- 5) What is it in the thermodynamic limit?
- 6) (bonus) Propose a transfer matrix approach to compute the same quantities for free boundary conditions.