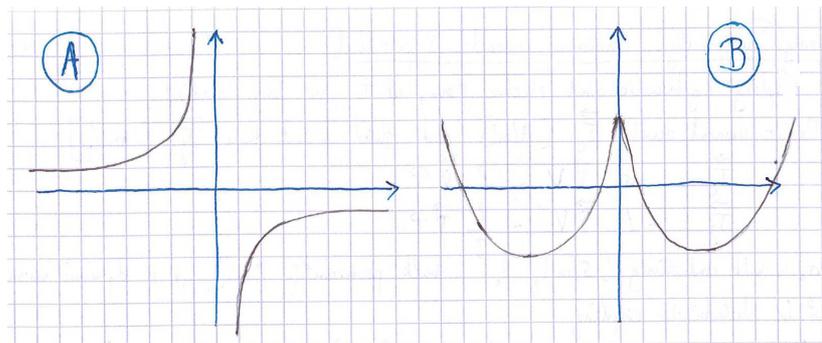


Should be written on a separate paper.
Concise but explicative answers expected throughout. No bonus for verbosity

1 Basic questions

- 1) What does *universality* mean in the statistical physics treatment of phase transitions?
- 2) Discuss competing effects that may be at work in phase transitions. Propose two different scenarios where in each case, the mechanisms would differ (different competing effects in the two situations).
- 3) Are there phase transitions for which temperature plays no role and if so, which ones?
- 4) Sketch graphically the Legendre transform of function A in the graph below. Comments?
- 5) Take $f(x) = -1/x$ for $x > 0$. Compute analytically the corresponding Legendre transform $\hat{f}(p)$. Is this compatible with the answer to the previous question?
- 6) Sketch graphically the Legendre transform of function B in the graph below



2 Partially miscible liquids - take 1

A two component mixture of species A and B may exist either in a fully mixed, or in a partially demixed state. Figure 1 displays how the thermodynamic potential \mathcal{R} describing the experimental situation under study depends on the molar fraction of species B (varying between 0 and 1). Delineate the region of AB miscibility in a schematic temperature versus molar fraction diagram. Explain.

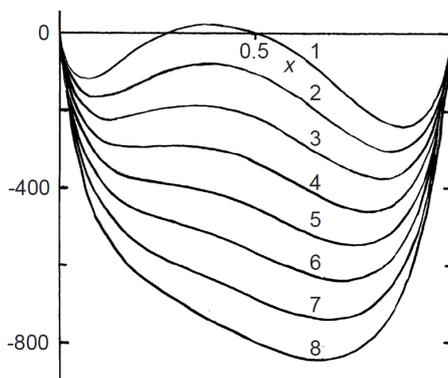


Figure 1: Plot of \mathcal{R} as a function of x , the molar fraction of species B, for different temperatures: (1) 270 K; (2) 275 K; (3) 280 K; (4) 285 K; (5) 290 K; (6) 295 K; (7) 300 K; (8) 305 K. From S.R. Logan, *J. Chem. Educ.* **75**, 339 (1998).

3 Partially miscible liquids - take 2

We are interested in mixing water and phenol (or methanol/decane etc.) at a given pressure. Quite a number of pairs of partially miscible liquids do lead to the same behaviour, shown in Fig. 2, in a temperature-concentration diagram (note that here, the concentration is dimensionless).

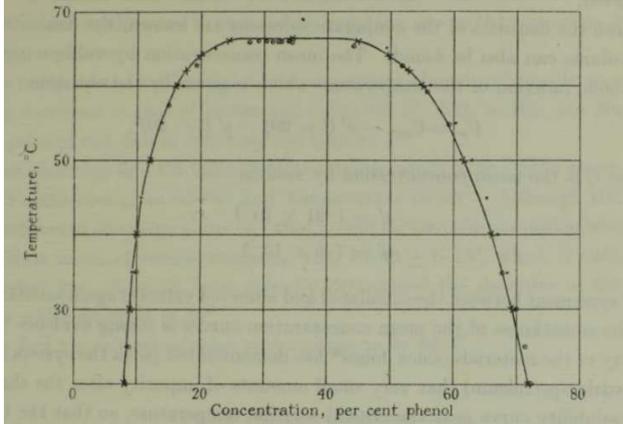


Figure 2: Water-phenol solubility curve at room pressure, from O.R. Howell, *Proc. R. Soc. Lond. A* **137**, 418 (1932). The x -axis is for the phenol concentration c , that ranges from 0 to 100%.

- 1) The curve in Fig. 2 defines two regions: inside the “bell”, and outside. One is for complete miscibility, the other for partial miscibility. On physical grounds, which is which ?
- 2) What is the thermodynamic potential suited to describe such a situation? Specify the variables.
- 3) Apply the Gibbs phase rule in each region. What do you conclude?

4 Partially miscible liquids - take 3

We seek for a simple framework that would rationalize the water/phenol miscibility measures. We write the thermodynamic potential as

$$\beta\mathcal{R} = \chi c(1 - c) + c \log c + (1 - c) \log(1 - c). \quad (1)$$

where $1/\beta$ is the thermal energy kT .

- 1) What do the last two terms on the right hand side remind you of? What can we then surmise concerning the origin of the other contribution in $\chi c(1 - c)$?
- 2) For which χ value χ^* is \mathcal{R} a convex-up function for all $0 < c < 1$?
- 3) Plot the typical \mathcal{R} -profiles for $\chi < \chi^*$ and $\chi > \chi^*$.
- 4) How does this relate to the measures reported in Fig. 2?

◇

5 Correlation function in an Ising chain

Take an open Ising one-dimensional chain (free boundary conditions), without a magnetic field, such that the couplings between nearest neighbors are all different. Starting from the direct calculation of the partition function, propose a method to compute the correlation function $\langle S_i S_j \rangle$. What is the correlation length here? Does this quantity signal a phase transition?