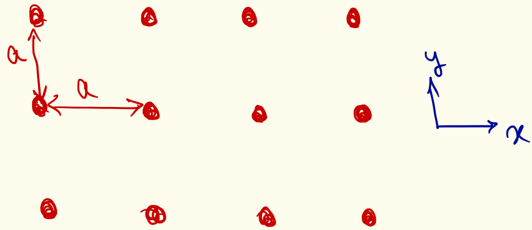
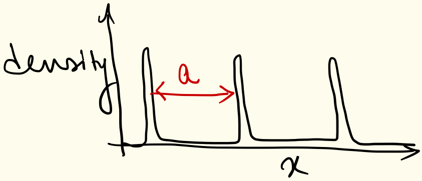
Phases of Matter

Naive notion of phases of matter:

Solid

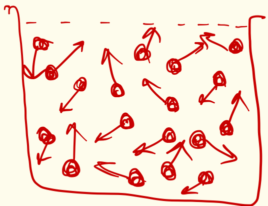


1. Periodic arrangement of atoms $\Rightarrow$ density <u>not</u> homogeneous.

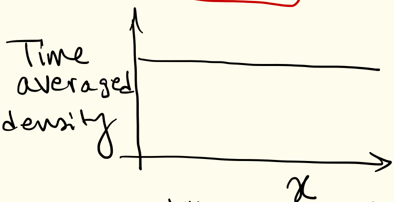


2. Non-zero shear modulus ('rigidity').
3. Presence of <u>Phonons</u>.

Liquid



1. Snapshot <u>not</u> periodic
   <u>Time-averged density homogeneous</u>.

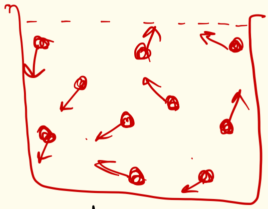


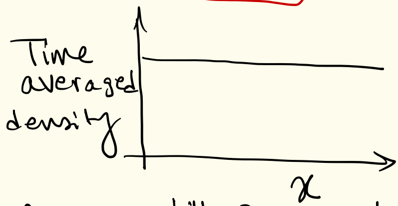
2. zero shear modulus.
3. No phonons but longitudinal sound waves can still propagate.

Gas

(1) Snapshot not periodic

Time-averaged density homogeneous.





(2) zero shear modulus.

(3) No phonons but longitudinal sound waves can still propagate.

(4) Less dense than liquid!

- Liquid and gas seem quite similar. Are they really distinct phases of matter?

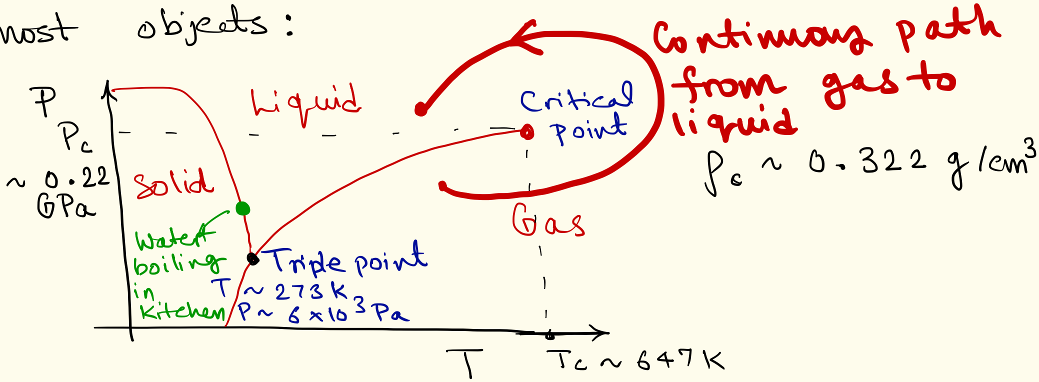
- If the answer to the above question is No, then are solid and liquid the only phases of matter?

- What is the precise definition of phase of matter anyway?

Let's discuss these questions one at a time.

- Liquid and gas seem quite similar. Are they really distinct phases of matter?

Phase diagram of water, or, for that matter, most objects:



The most striking thing in the above phase diagram is that one can convert water to gas without 'boiling'!

Therefore, it is very suggestive that liquid water and water vapor (gas) are the same phase of matter.

This is a consequence of the fact that the symmetries of the liquid water are exactly same as that of the water vapor.

This leads us to ask,

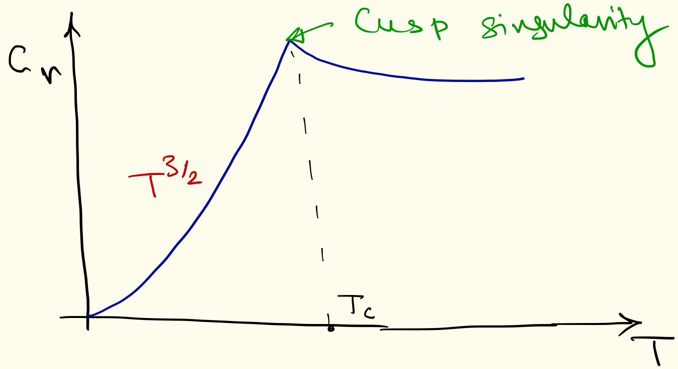
Are solid and liquid (= gas) the only two phases of matter for a given material?

The answer is an emphatic NO. In principle, there can exist an infinite number of phases of matter for a given system depending on how the symmetries are broken. For example, there are 230 kinds of solids in three dimensions which are all distinct from each other in the sense that one can't go from one to another without encountering a phase transition (to be made precise below).

Even more, there can exist other phases of matter which do not fall into the label solid / liquid at all.

We already encountered one such phase — Bose-Einstein Condensate for bosonic systems. The BEC is a distinct phase of matter from a high-temperature bose gas as signalled by the presence of

singularity in its free energy at T_c.
We won't derive this (see Dan Arovas lecture notes in Additional Resources), but the specific heat looks like:



Thus $\frac{dC_v}{dT}$ is discontinuous at $T = T_c$.

$\Rightarrow$ $\frac{d^3 F}{dT^3}$ is discontinuous at $T = T_c$.

Thus, free energy is not an analytic function of temperature.

This example leads us to a sharper definition of a phase:

Defining a phase of matter

Consider a system whose free energy is a function of several variables : $K_1, K_2, \cdots K_D$. Some of the K_i's could be thermodynamic variables e.g. T, P etc. and they can also be parameters in the underlying Hamiltonian. Let's define free energy density in the thermodynamic limit:

$$f\,[\{K\}] = \lim_{V\to\infty} \frac{F\,[\{K\}]}{V}.$$

Two points $K\ (= K_1, K_2, \cdots K_D)$ and $K'\ (= K'_1, K'_2, \cdots K'_D)$ are in the same phase if there exists a path from K to K' along which free energy is analytic i.e. does not develop any singularity in itself or its derivatives.

This definition also leads to a sharp definition of phase boundaries between potentially different phases.

Phase boundaries:

Consider the regions in this D-dimensional space $(K_1, K_2, \ldots K_D)$ where the free energy is singular. If such a given region has dimensionality D_s $(\leq D)$, then the co-dimension of singular region is:

$$C = D - D_s.$$

C denotes number of directions which are not singular.

The regions with $C = 1$ are called phase boundaries.

Why $C = 1$ required? $\Rightarrow$ Need to separate two regions (e.g. need a two-dimensional plane ($D_s = 2$) to separate a three-dimensional room into two regions).

How are more than one phase even possible?

As discussed above, existence of more than one phase requires that the free energy be singular as a f^n of parameters $\{K\}$.

The expression for free energy is:

$$e^{-\beta F} = \sum_{\{\vec{v}\}} e^{-\beta H\{\vec{v}\}} \quad \text{(Classical)}$$

or

$$\mathrm{Tr}\, e^{-\beta \hat{H}(\{v\})} \quad \text{(Quantum)}$$

In either case if $\beta \neq \infty$, and the number of particles / Hilbert space dimension is finite then, F cannot be singular.

Therefore there are only two ways that F can be singular:

① Thermodynamic limit :

As the number of particles go to infinity, the number of terms in the sum corresponding to the partition fn Z diverge $\rightarrow$ This allows F to be singular (but doesn't enforce singularity of course).

② $\beta \rightarrow \infty$ (Zero temperature) :

If the number of particles are finite, then F can 'still be singular if $\beta \rightarrow \infty$ since the function $e^{-\beta E[\{V\}]}$ is potentially singular at $\beta = \infty$.

e.g consider the $f^n(x) = e^{-\beta(x-v)}$

when $x > V$ as $\beta \to \infty$ $f^n(x) = 0$

$x < V$ as $\beta \to \infty$ $f^n(x) = \infty$

Clearly this is singular behavior.