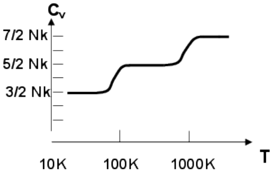
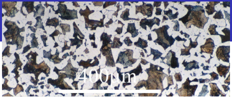
PREVIOUSLY ON ...Thermodynamics

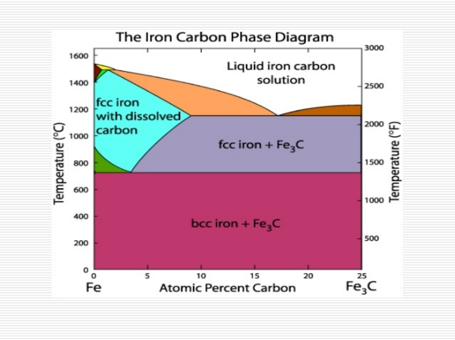
- Third Law of Thermodynamics
- Entropy, and its derivatives, go to zero as $T \to 0$.
- Zero heat capacity, thermal expansion.
- Entropy as counting states.
- "$T \to 0$" means thermal energy is close to quantum energy.
- diatomic ideal gas:



- Entropy as information

Gibbs phase rule





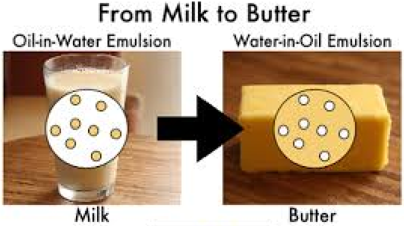
How much information is needed to specify system?

...equivalently...

How many independent variables (F) does a system have?

$$\boxed{F - 2 = C - N_P}$$

- C: Chemical species - reactions
- N_P: Number of phases present

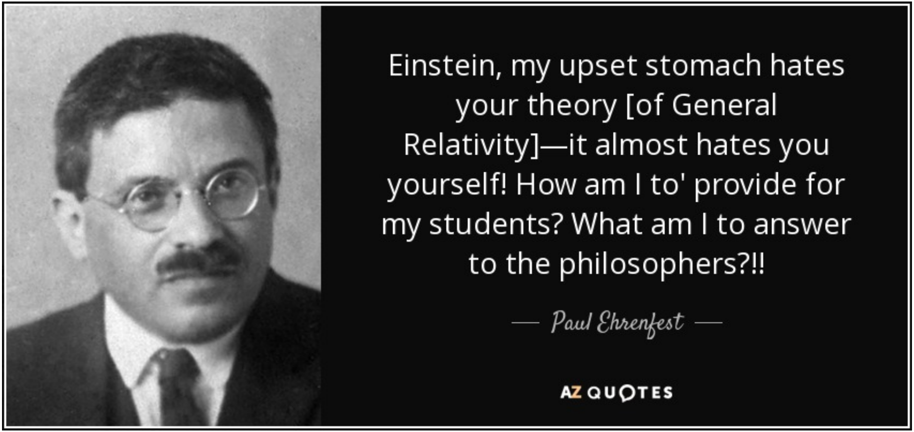


What must be given to define the state: Gibbs phase rule

$$\boxed{\text{F=C+2-}N_P}$$

- **Single phase water:** F = 1+2-1 =2. P and T must be specified.
- **Ice/water mix** F = 1+2-2 =1. Specifying P defines T.
- **Triple point** F = 1+2-3. no freedom, unique P,T.
- **Critical point** No freedom, unique P,T $\implies$ P=3. (!)
- **Gaseous O_2, H_2 and H_2O**: F = 3+2-1.
  Leaves four d.o.f, e.g. T, P, N_{O_2} N_{H_2}
- **...+reaction** $\frac{1}{2}O_2 + H_2 \Leftrightarrow H_2O$ F = 2+2-1,
  Leaves three d.o.f.
  (Assuming known reaction constant K, *q.v.*).

Paul Ehrenfest (1880-1933)



Ehrenfest's order of phase transitions

$$g_1 = g_2$$

- First order: discontinuous change of state variables (e.g. s or v)

$$\frac{\partial g_1}{\partial T} \neq \frac{\partial g_2}{\partial T}$$

- Second order: continuous change of state variables, but discontinuous derivatives (e.g. c_v, K, β)

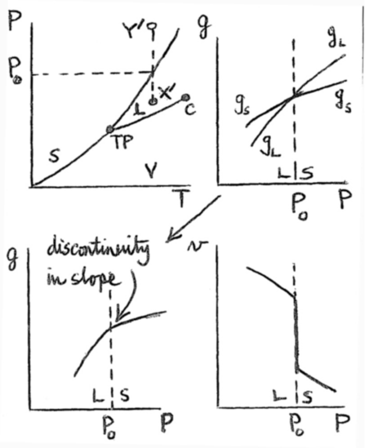
$$\frac{\partial g_1}{\partial T} = \frac{\partial g_2}{\partial T}$$

$$\frac{\partial^2 g_1}{\partial T^2} \neq \frac{\partial^2 g_2}{\partial T^2}$$

- Third order: continuous change of state variables and derivatives.

Discontinuous $\equiv 1^{st}$ order transitions

Isothermal process traverse X'Y'



At the phase boundary.

$$g_1 = g_2 \text{ always } \ldots$$

For first order, derivatives change...

$$-\left(\frac{\partial g_1}{\partial T}\right)_P \neq -\left(\frac{\partial g_2}{\partial T}\right)_P$$

$$\left(\frac{\partial g_1}{\partial P}\right)_T \neq \left(\frac{\partial g_2}{\partial P}\right)_T$$

$$s_1 \neq s_2 \text{ and } \quad v_1 \neq v_2$$

Discontinuous transition $\equiv 1^{st}$ order

Second derivatives?

Isobaric Heat Capacity $T\left(\frac{\partial s}{\partial T}\right)_P = T\left(\frac{\partial^2 g}{\partial T^2}\right)_P$

Thermal Expansivity $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial^2 g}{\partial T_P \partial P_T}\right)$

Isothermal Compressibility $\frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{-1}{V}\left(\frac{\partial^2 g}{\partial P^2}\right)_T$

The ‘discontinuities’ at continuous phase changes

In a second order transition

$$-\left(\frac{\partial g_1}{\partial T}\right)_P = -\left(\frac{\partial g_2}{\partial T}\right)_P \text{ and } \left(\frac{\partial g_1}{\partial P}\right)_T = \left(\frac{\partial g_2}{\partial P}\right)_T$$

$\Delta S = 0$ means no latent heat. $\Delta V = 0$ means no volume change.

S and V are anyway related by $\left(\frac{\partial s}{\partial P}\right)_T \overset{Maxwell}{=} -\left(\frac{\partial v}{\partial T}\right)_P$

No latent heat or volume change: same internal energy $dU = TdS - PdV$

Clausius Clapeyron $= 0/0$.

What sort of thing?

Two types of transition look like "second order"

"Critical fluctuation" is where regions of the system fluctuate into the other phase in an uncorrelated way.
e.g. ferromagnet.

"Coexistence" is where one phase the system is effectively two-component.
e.g. Bose condensate.

The Ehrenfest equations

Equivalent of Clausius-Clapeyron for second order boundary.
Consider entropy at points (T, P) and $(T + dT, P + dP)$ on phase boundary.
No change in s or v.

$$\text{at A} \quad s_1(T, P) = s_2(T, P)$$

$$\text{at B} \quad s_1(T + dT, P + dP) = s_2(T + dT, P + dP)$$

use a Taylor expansion on B

$$\left(\frac{\partial s_1}{\partial T}\right)_P dT + \left(\frac{\partial s_1}{\partial P}\right)_T dP = \left(\frac{\partial s_2}{\partial T}\right)_P dT + \left(\frac{\partial s_2}{\partial P}\right)_T dP$$

Identify heat capacity c_P, thermal expansion β: "first Ehrenfest equation":

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{c_{P,1} - c_{P,2}}{Tv(\beta_1 - \beta_2)} = \frac{C_{P,1} - C_{P,2}}{TV(\beta_1 - \beta_2)}$$

Second Ehrenfest equation

"Second Ehrenfest equation"

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

Similar derivation starting from $v_1 = v_2$
Slope of transition line relates to $\Delta\beta$, $\Delta\kappa$, ΔC_P.

Fluctuations, Instability and Scaling Laws

In critical region close to the transition, $\pm\Delta T_{crit}$ around T_c
e.g. Heat Capacity

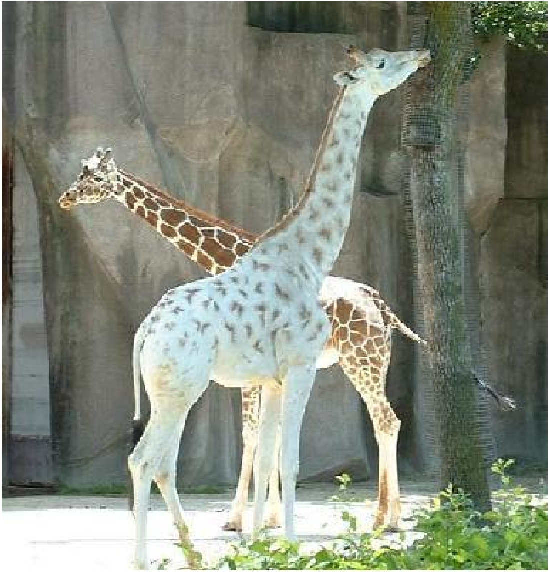
$$C_V \propto (T - T_C)^{-\alpha}$$

e.g. correlations between magnetic spins

$$< S_i.S_j > \propto r^{-\nu}$$

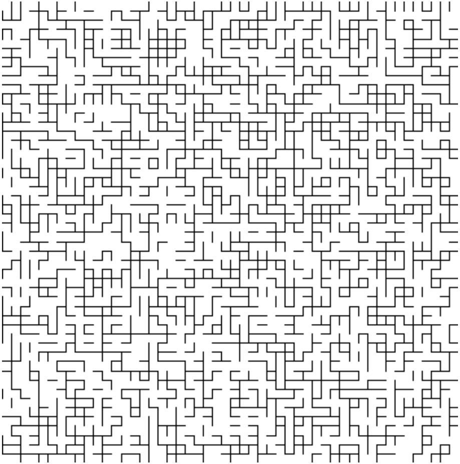
Power Law dependence implies there is no characteristic scale.
Universality: conjecture that α, ν are independent of material.
In Economics and Ecology, as in Physics, forthcoming transitions often characterized by big fluctuations.

Giraffe (Phase coexistence)



Animal skin patterns come from phase separation between pigmented and non-pigmented cells.

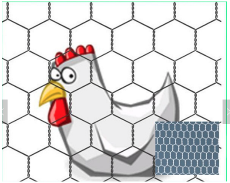
Percolation: cutting a chicken wire



How many random bonds give a connection?

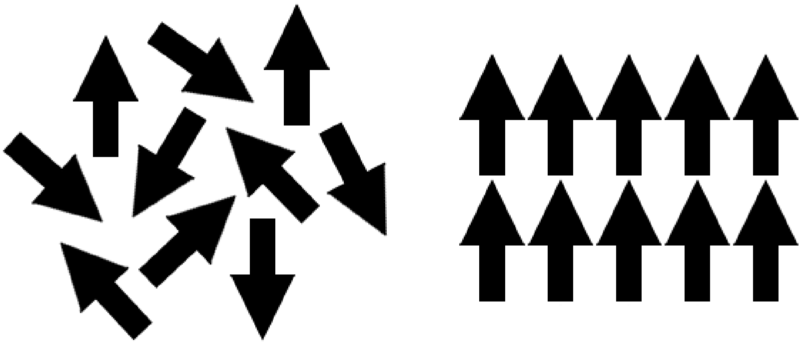
Imagine links are wires

- discontunity in conductivity..

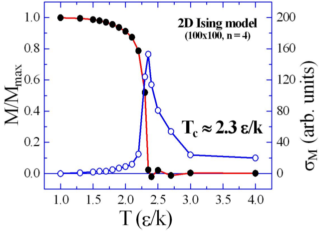


EM Quiz: infinite square/cubic lattice of resistors, what is the resistance between opposite corners?

Ferromagnet



Ising Ferromagnet

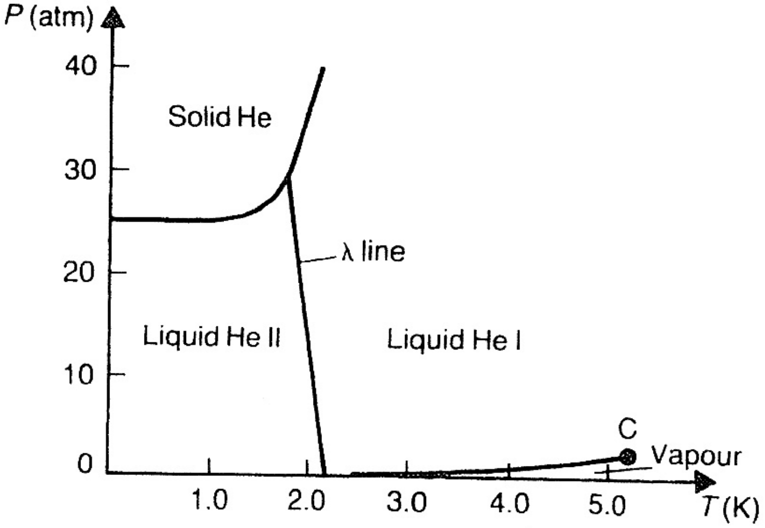


$$U = \epsilon \sum_{i,j} \sigma_i \sigma_j$$

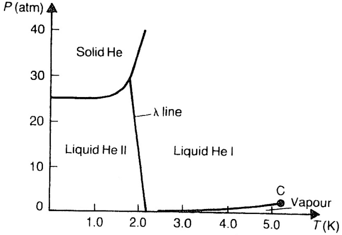
- Equation of state: $M = (T - T_c)^\beta$ and $\chi = \frac{dM}{dB} = \left(\frac{C}{T - T_c}\right)^\gamma$
- MACRO: zero magnetisation to finite magnetisation
- MICRO: transition from aligned spins to randomly oriented spins.
- $\left(\frac{\partial M}{\partial T}\right)_{B,P}$ massive near transition.

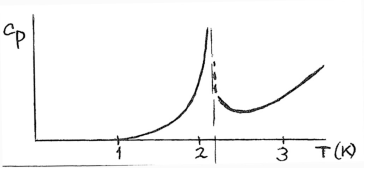
Liquid Helium

https://www.youtube.com/watch?v=2Z6UJbwxBZI

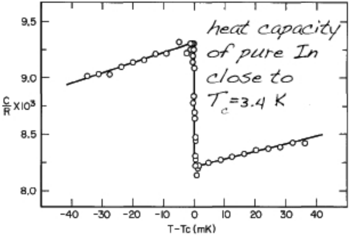


Liquid Helium





- At $T_\lambda = 2.2$ K, on cooling (He I) to "superfluid" (He II)
- Only for ^{4}He (Bosons)
- Finite fraction of atoms in same (ground) quantum state (S=0).
- He II phase: no viscosity.
- Peak in C_P at transition.
- Looks like a λ, hence T_λ.
- Heat capacity continuous: third order



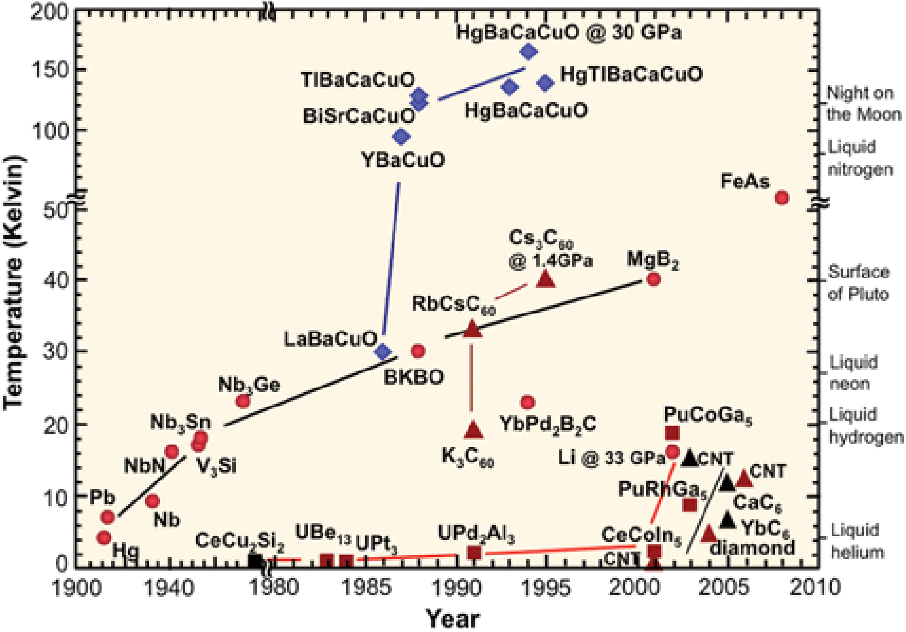
- Heat capacity of In: no singularity
- No latent heat
- 2nd order Transition,

- Below $T_c = 3.4$K electrical resistance is zero.
- "Two component model"
- Electrons couple to form "Cooper pairs" (bosons).
- Finite fraction of electrons (N_1) in ground state (S=0)

Why is the average R zero?
Consider resistors in parallel:

$$\frac{1}{R} = \frac{N_1}{R_1} + \frac{N_2}{R_2}$$

$$R_1 = 0 \implies R = 0$$


HgBaCaCuO @ 30 GPa
TlBaCaCuO
HgTlBaCaCuO
HgBaCaCuO
BiSrCaCuO
YBaCuO
FeAs
Cs_3C_{60} @ 1.4GPa
MgB_2
$RbCsC_{60}$
LaBaCuO
BKBO
Nb_3Ge
Nb_3Sn
NbN
V_3Si
K_3C_{60}
$YbPd_2B_2C$
$PuCoGa_5$
Li @ 33 GPa
CNT
CNT
$PuRhGa_5$
CaC_6
YbC_6
diamond
Pb
Nb
Hg
$CeCu_2Si_2$
UBe_{13}
UPt_3
UPd_2Al_3
$CeCoIn_5$
CNT
Night on the Moon
Liquid nitrogen
Surface of Pluto
Liquid neon
Liquid hydrogen
Liquid helium
Temperature (Kelvin)
Year
0
10
20
30
40
50
100
150
200
1900
1940
1980
1985
1990
1995
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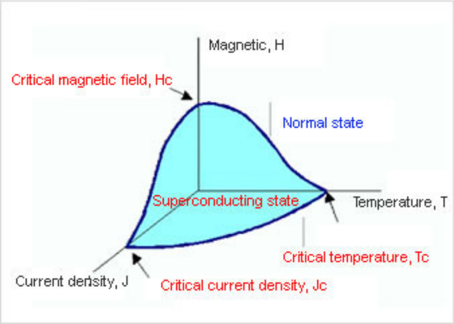
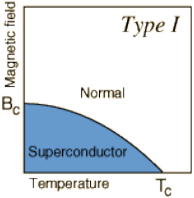
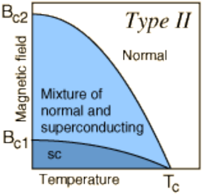
2005
2010







Superconductivity suppressed by

- High temperature
- High field
- High current
- Type I excludes all magnetic fields
- Type II allows some magnetic field