

PREVIOUSLY ON

...*Thermodynamics*

- Equation of state
- Phase Diagrams: stable phase by 2nd Law.
- System minimises (U,H,F or G) depending on boundary conditions
- Coexisting phases have same g
- Second Law prohibits negative Compressibility in equilibrium
- Second Law prohibits negative Heat Capacity in equilibrium

More permutations of Forbidden

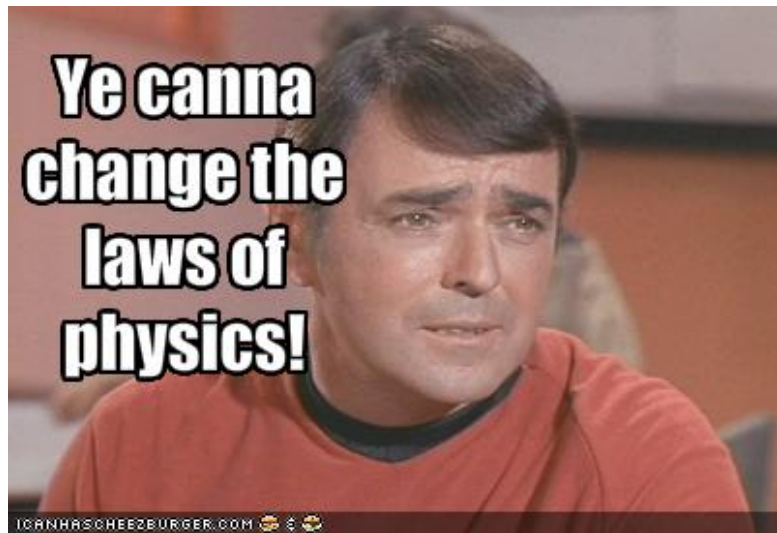
- Considering H in place of U gives $c_p > 0$.
- Using F gives positive isothermal bulk modulus. $K_T > 0$.
- Note this works for conjugate variables: PV, TS
- There is no similar argument for $\frac{dV}{dT}$ (thermal expansion).¹

All these derivations that quantities must be positive trace back to violations of the Second Law.

Negative modulus would allow heat to become work.

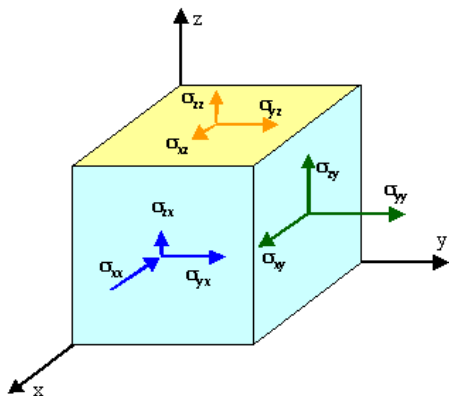
Negative heat capacity would allow heat to flow from hot to cold.

¹There is an assumption about homogeneous samples: for phase coexistence the bulk modulus is zero. Curious behaviour can be obtained for inhomogeneous metamaterials and self-gravitating clusters



Stress-strain relations: Negative elastic moduli

“What change of shape do you get for given stress?”



P and V are scalars,
 \implies K is scalar

Stress σ_{ij} and strain e_{kl} are

3x3 second rank tensors

Elasticity tensor C_{ijkl} (or 6×6 matrix)

C_{ij} is a material property.

σ_{ij} and e_{ij} depend on process.

Elastic Energy = $\sum_{ijkl} \frac{1}{2} C_{ijkl} e_{ij} e_{kl}$

σ_{ij} and e_{ij} are conjugate variables,
BUT energy is a *sum*.

Second Law means that
eigenvalues must be +ve

C_{ijkl} may have negative elements.

Calculating Entropy in Molecular Dynamics

P, V, T, U and H depend on atomic positions and velocities.

S, F and G depend on states never seen: can't be calculated

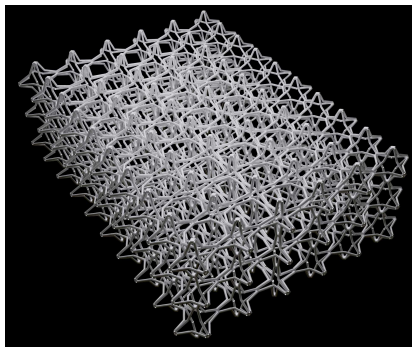
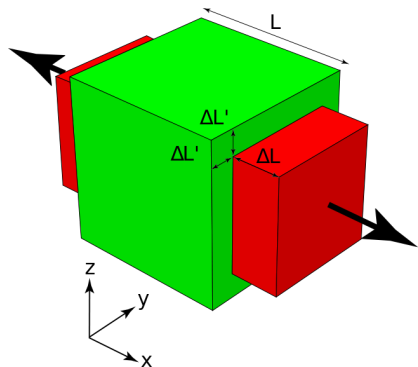
Consider

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{(G + TS)}{T^2} = -\frac{H}{T^2}$$

$$\int_1^2 d\left(\frac{G}{T}\right) = \frac{G_2}{T_2} - \frac{G_1}{T_1} = -\int_{T_1}^{T_2} \frac{\langle H \rangle}{T^2} dT$$



Negative Poisson Ratio $\nu = -de_y/de_x$



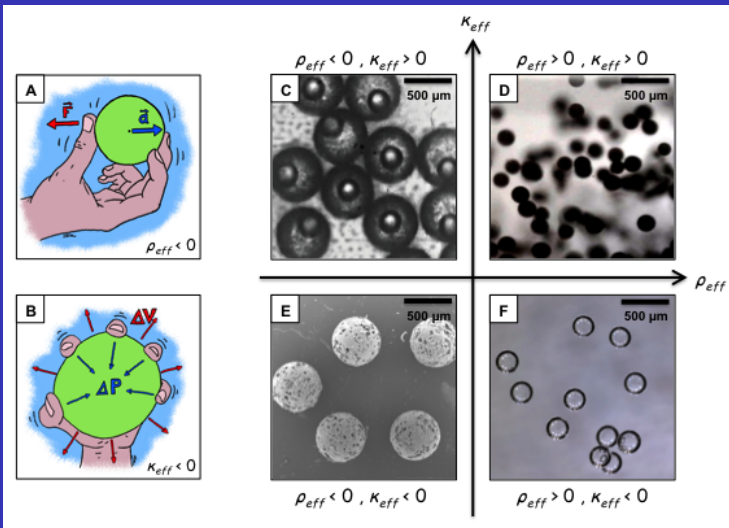
No theoretical limits

e.g. porous polytetrafluoroethylene reported $\nu = -12$ (Nature 2003).

e.g. O^{2-} ion retains sp^3 spherical symmetry.

<http://www.bbc.co.uk/news/science-environment-35818924> [Link](#)

Acoustic Metamaterials



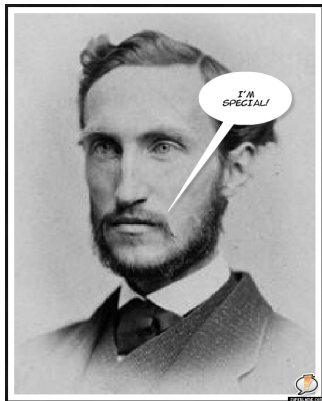
core-shell particles, “slow-oil droplets, polymer porous beads, air bubbles
Science 342 6156 323

“first-order” phase changes

Gibbs is special.

$$g_1 = g_2$$

Mechanical (P) and Thermal (T) equilibrium



Clausius-Clapeyron equation: “first-order” phase changes

Phase Boundary Slope?

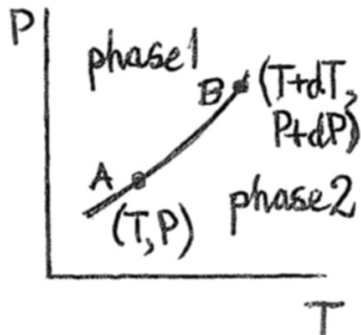
Consider points A and B on phase boundary,

$$\text{at A } g_1(T, P) = g_2(T, P)$$

$$\text{at B } g_1(T+dT, P+dP) = g_2(T+dT, P+dP)$$

$$dg = vdP - sdT$$

$$g_1 = g_2 \text{ on phase boundary}$$



Taylor expand g to get $g(P + dP, T + dT)$

$$\begin{aligned} & g_1(T, P) + \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP + \text{higher order terms} \\ &= g_2(T, P) + \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP + \text{higher order terms} \end{aligned}$$

from which,

$$\left[\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P \right] dT = \left[\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T \right] dP$$

Using $dg = -sdT + vdP$

$$\left(\frac{dP}{dT}\right)_{\text{pb}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{S_2 - S_1}{V_2 - V_1}$$

Where the suffix pb means we are at the phase boundary.

Introduce Latent Heat

From previous slide....

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{S_2 - S_1}{V_2 - V_1}$$

Consider the phase change at temperature T from phase 1 to 2,

$$\text{latent heat} = l = T(s_2 - s_1)$$

If $s_2 > s_1$, l is positive and heat must be put INTO the system.

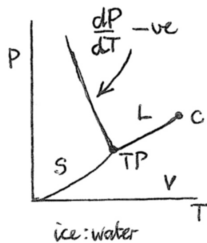
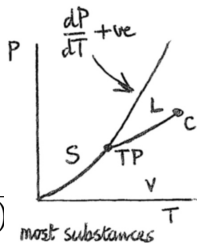
Clausius-Clapeyron equation for slope of a phase boundary line.

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{l}{T(v_2 - v_1)} = \frac{L}{T(V_2 - V_1)}$$

Clausius-Clapeyron equation

Clausius-Clapeyron equation, from combination of latent heat and relation for $(dP/dT)_{pt}$

$$\left(\frac{dP}{dT}\right)_{pt} = \frac{l}{T(v_2 - v_1)} = \frac{L}{T(V_2 - V_1)}$$



- l is always positive going from low T (solid) to high T phase (liquid).
- For $v_L > v_S$ (solid expands on melting), dP/dT is positive.
- For $v_L < v_S$ (solid – like ice – contracts on melting) dP/dT is negative.
- REMEMBER THE SMALL PRINT:
It's $\frac{dP}{dT}$ along the phase boundary line. "Isophaseboundaryic"

Horrible tea



I am sorry to report that occasionally in a tearoom I have been brought a pot of hot water with a cup and teabag on the side. This has been both painful and distressing, very much like standing on an upturned plug

<http://lornastearoomdelights.com>



Following their successful ascent of Mount Everest in 1953, Tenzing Norgay and Edmund Hillary take tea out of tin mugs.

How does the boiling point vary with pressure

Tin itself is subject to a solid-solid phase transition from ductile metal to brittle insulator on cooling.

<https://www.youtube.com/watch?v=FUoVEmHuykM>

Speeded up video for 20 hours at -40degC

How does the boiling point vary with pressure

Specific volumes v_s and v_L , for vapour and liquid.

Assume $v_v \gg v_L$: $v_v - v_L = v_v = RT/P$, giving

$$\frac{dP}{dT} \approx \left(\frac{l}{T} \right) \left(\frac{P}{RT} \right)$$

Integrate, assuming that the specific latent heat l is constant to get the equation for the vapourization line on a PT diagram.

$$\ln P = -\frac{l}{RT} + \text{constant}$$

Boiling point changes logarithmically with pressure.

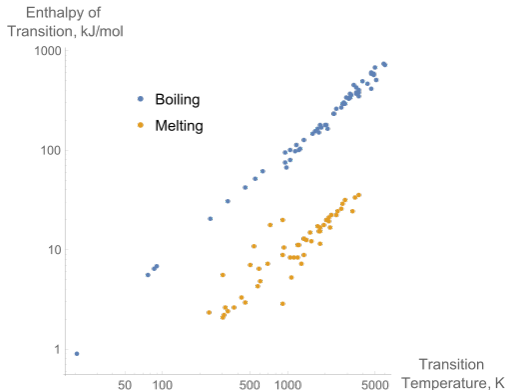
Logs and fires



“Quit whinging Ed, it’d be a lot worse without the logarithm”

Trouton's Rule (1884)

If the structure of all liquids were the same, the entropy would be similar.
Entropy of vaporization = $10.5R$. Latent heat = $10.5RT_{vap}$ (not constant!)



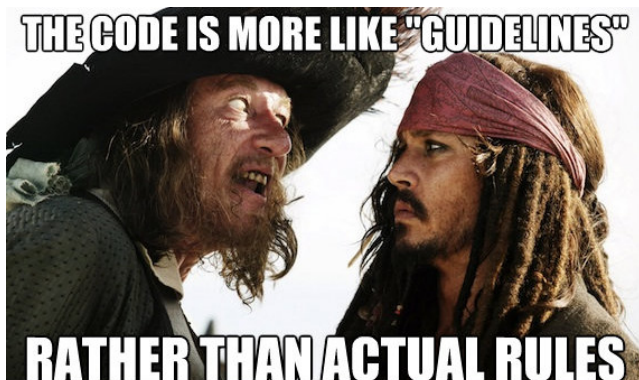
Measure enthalpy, because...
Gibbs: $g = h - Ts$
Phases have equal g , $\Delta g = 0$
 $\Delta h_{vap} = T_{vap}\Delta s_{vap}$

$$\frac{dP}{dT} \approx \left(\frac{I}{T}\right) \left(\frac{P}{RT}\right) \approx \left(\frac{10.5P}{T}\right) \implies P/P_0 \approx (T/T_0)^{10.5}$$

Trouton's Rule, with pirates

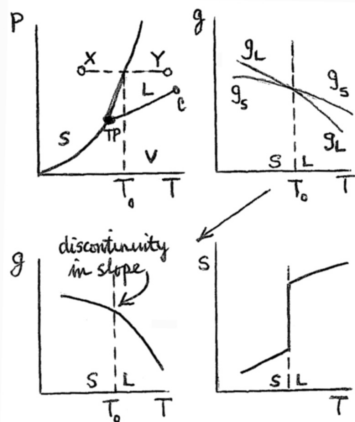
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Variation of state functions at first-order transitions

Consider isobaric process XY,



- g vs T curve always has negative slope,

$$\left(\frac{\partial g}{\partial T}\right)_P = -s < 0$$

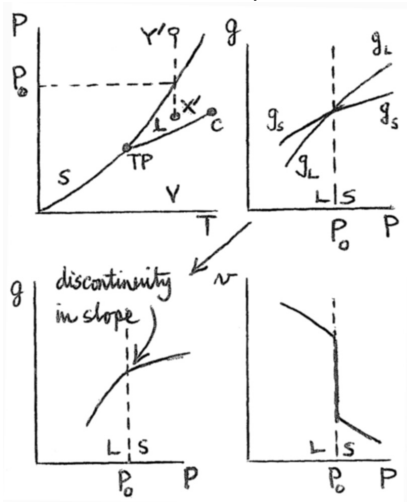
- slope becomes steeper as T increases

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T} < 0$$

- $g_L(T_0) = g_S(T_0)$, so for $T < T_0$ $g_S(T) < g_L(T)$ and vice versa.
- Discontinuity at T_0
 $\Delta s = -\Delta(\partial g/\partial T)_P$.
- $S_{Liquid} > S_{Solid}$
... larger entropy means less "order".

Isothermal freezing

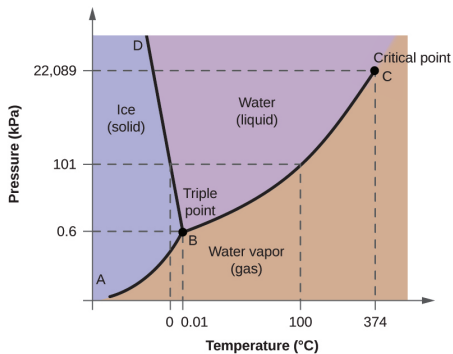
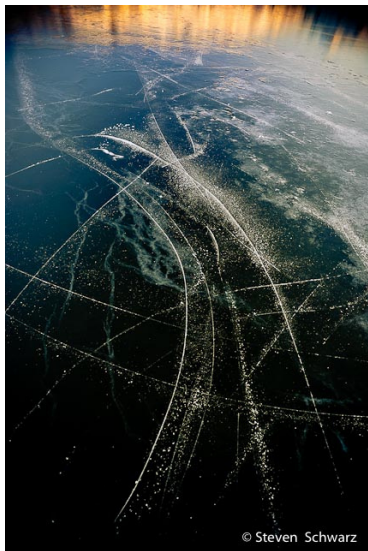
Consider isothermal process X'Y'



$g(P)$ is

- continuous across transition
- discontinuous in slope at P_0
 $\Delta v = -\Delta(\partial g / \partial P)_T$.
- $v_{Liquid} > v_{Solid}$
 ...not always true - slope may be negative.

Isothermal melting of water



It is widely known that the pressure of ice skates melts water.
Simple thermodynamics shows it is possible: water is denser than ice.
Putting in actual numbers shows it is impossible