Lanford on StatMech, Jan 15 2010

January-15-10
10:06 AM

Stance: A "manifold" of equilibrium states with "state functions: p, V, E, T, S

In the 2D case, can choose two of these to identify with (a piece of) $\mathbb{R}^2$.

Notation $E^{(V,T)}: \mathbb{R}^2 \to \mathbb{R}$ is E, written as a function of V &, .

So $E^{(V,T)}(V(A), T(A)) = E(A$ for any state A.

Another piece of notation:

$\left(\frac{\partial E}{\partial V}\right)_T$ means "partial rel V, holding T fixed

i.e., $= \frac{\partial E^{(V,T)}}{\partial V}$

$dE = \delta Q - \delta W = T\,dS - p\,dV \Rightarrow$

$$dS = \frac{1}{T}\left(\left(\frac{\partial E}{\partial V}\right)_T + p\right)dV + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT \quad \text{or}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\left(\frac{\partial E}{\partial V}\right)_T + p\right) \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V$$

Now use $\partial_V \partial_T = \partial_T \partial_V$ to get

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Application In an ideal gas $(pV = nRT)$,

$$T\left(\frac{\partial p}{\partial T}\right)_V = p \quad \text{so} \quad \left(\frac{\partial E}{\partial V}\right)_T = 0.$$

"Energy of an ideal gas depends only on temp.".

$$dS = \frac{1}{T} dE + \frac{p}{T} dV \quad \text{so} \quad \left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \quad \left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}$$

So if we know $S(V,E)$, we can derive T & p.
So "everything's encoded in $S(V,E)$".

The "Helmholtz Free Energy": $F := E - TS$

$$dF = dE - TdS - SdT = -pdV - SdT$$

So $\left(\frac{\partial F}{\partial V}\right)_T = -p \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$

$$\Rightarrow \frac{\partial p}{\partial T} = \frac{\partial S}{\partial V} \quad \text{"Maxwell's relation"}$$

Also, "Everything's encoded in $F(V,T)$".

The Gibbs potential $G := E - TS + pV$
$\Rightarrow$ "Everything's encoded in $G(p,T)$".

(V,T,p) <u>does</u> <u>not</u> "specify everything"
$(V,T) \longrightarrow p$ is "the eq'n of state".

<u>Magnetism</u>: Magnetically susceptible matter: If you apply a magnetic field $\vec{H}$ it acquires a magnetic moment $\vec{M}$ "dipoles get lined up".
Assume $\vec{M}$ & $\vec{H}$ are co-linear so drop the vector notation. The space of equilibrium states is 2D w/ state functions H, M, E, T, S [or 3D if p, V are included]

From magnetostatics,

$$\delta W = -\vec{H} \cdot d\vec{M} = -H dM$$

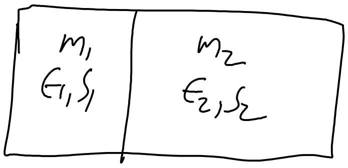
So $dE = T\,dS + H\,dM \quad (\text{c.w. } dE = T\,dS - p\,dV)$

$$\ldots \quad \left(\frac{\partial S}{\partial E}\right)_M = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial M}\right)_E = -\frac{H}{T} \quad \ldots$$

Concavity: $V \to v := V/M = 1/\rho$

$E \to \epsilon$

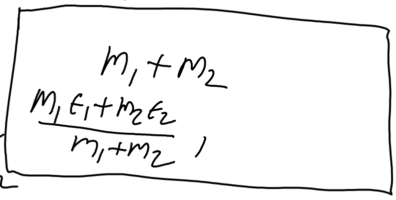
$S \to s$



Consider two samples, m_1 grams at (ϵ_1, s_1)

m_2 —"— (ϵ_2, s_2)

Remove the wall:



$V_{final} = V_1 + V_2$

$E_{final} = E_1 + E_2$ $\Rightarrow$ $v_f = \alpha v_1 + (1-\alpha) v_2$ w/ $\alpha = m_1/m_1+m_2$, likewise for ϵ, l.w. ineq. for s.

$S_{final} \geq S_1 + S_2$

So
$$s\left(\alpha\begin{pmatrix}\epsilon_1\\ v_1\end{pmatrix} + (1-\alpha)\begin{pmatrix}\epsilon_2\\ v_2\end{pmatrix}\right) \geq \alpha\, s\begin{pmatrix}\epsilon_1\\ v_1\end{pmatrix} + (1-\alpha)\, s\begin{pmatrix}\epsilon_2\\ v_2\end{pmatrix}$$

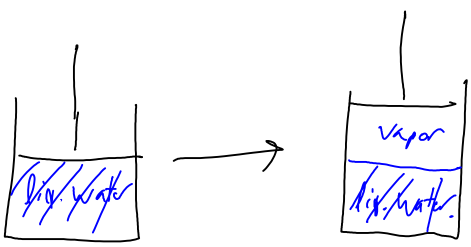
So s is concave.

So $\left(\frac{\partial s}{\partial \epsilon}\right)_v$ is decreasing; yet $\frac{\partial s}{\partial \epsilon} = \frac{1}{T}$

So T is an increasing function of ϵ at fixed density

Phase Transitions: Discontinuities in state functions.

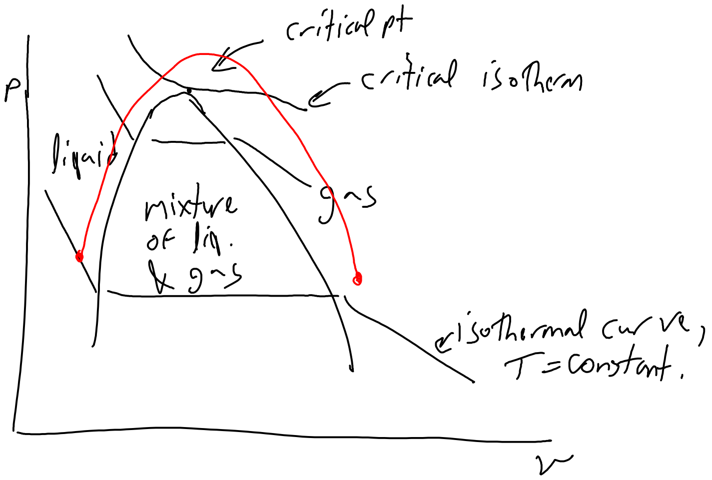
Water.



Fact: if piston is pushed back down, part of the vapor recondenses & pressure remains constant.

$\Rightarrow$ water at a given T has a definite vapor pressure.

So



moving along red we see that there is no qualitative difference between liquid and gas.