Tds Relations and Entropy Changes in Liquids and Solids

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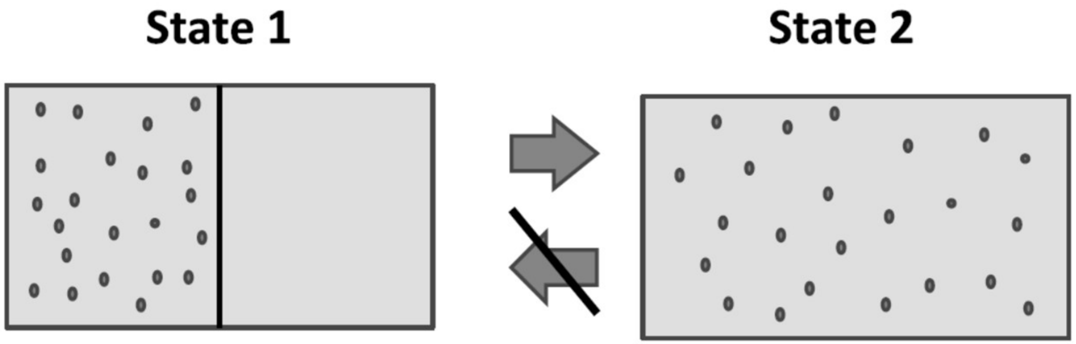
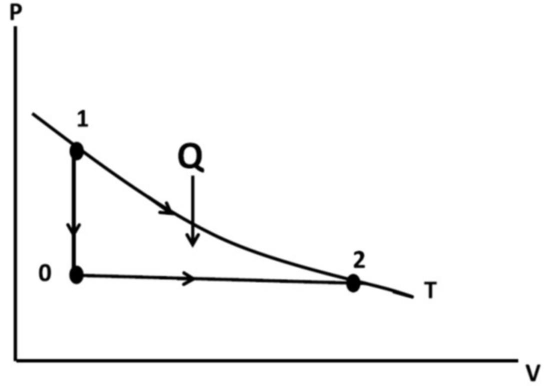
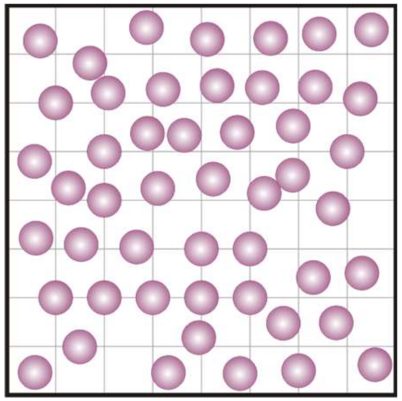
Previously: Microscopic Interpretation of Entropy





- Equivalent reversible path connects the 2 relevant states
- $\Delta S = NK^*\ln 2$; Result of macroscopic TD
- Each lattice has volume ~ r^3; (r ~ atomic radius)
- # of lattice points: $L_1 = (V_1/r^3)$; $L_1 >>> N$; $L_2 = 2L_1$
- $\Omega_1 = (L_1)^N$; $\Omega_2 = (2L_1)^N = 2^N * (L_1)^N$
- $\Delta S = S_2 - S_1 = K\ln\Omega_2(U,V,N) - K\ln\Omega_1(U,V,N) = K^*\ln 2^N$



- $(\Delta S)_{isolated} \geq 0$

$S(U,V,N) = K^*\ln\Omega(U,V,N)$

$F(T, V, N) = -KT^*\ln Z(T,V,N)$

Figs: Fundamentals of Physics-1, R. Shankar

Challenge with $\Delta s = \left(\frac{Q}{T}\right)_{rev}$

- Appropriate reversible path
- Implementation easy for isothermal reversible path
- Not straight forward when T is varying
- Can we a computational procedure that is not process dependent?

Not so tedious relationships!

$$\delta Q_{\text{int rev}} - \delta W_{\text{int rev,out}} = dU$$

$$\delta Q_{\text{int rev}} = T\,dS$$

$$\delta W_{\text{int rev,out}} = P\,dV$$

$$T\,dS = dU + P\,dV \qquad \text{(kJ)}$$

$$T\,ds = du + P\,dv \qquad \text{(kJ/kg)}$$

the first *T ds*, or *Gibbs equation*

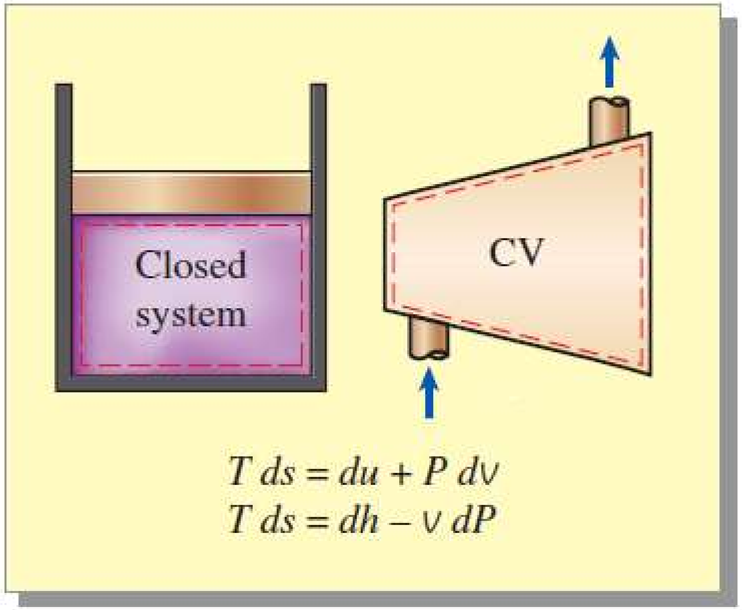
$$h = u + Pv$$

$$\left.\begin{aligned} dh &= du + P\,dv + v\,dP \\ T\,ds &= du + P\,dv \end{aligned}\right\} T\,ds = dh - v\,dP$$

the second *T ds equation*

$$ds = \frac{du}{T} + \frac{P\,dv}{T}$$

$$ds = \frac{dh}{T} - \frac{v\,dP}{T}$$



- Computational procedure dependent on the changes in state properties

Fig-TD: Cengel & Boles

Entropy changes in Solids & Liquids

$$ds = \frac{du}{T} + \frac{P\,d\text{v}}{T} \qquad d\text{v} \cong 0 \qquad ds = \frac{du}{T} = \frac{c\,dT}{T}$$

Liquids, solids: $$s_2 - s_1 = \int_1^2 c(T)\,\frac{dT}{T} \cong c_{\text{avg}} \ln\frac{T_2}{T_1} \qquad (\text{kJ/kg}\cdot\text{K})$$

For and isentropic process of an incompressible substance

Isentropic: $$s_2 - s_1 = c_{\text{avg}} \ln\frac{T_2}{T_1} = 0 \quad \rightarrow \quad T_2 = T_1$$

TD: Cengel & Boles

What's next?

- Entropy change of ideal gases