

example: The ideal monatomic gas

$$\text{From expt: } PV = Nk_B T \Rightarrow \frac{P}{T} = \frac{N}{V} k_B = \frac{k_B}{v}$$

$$E = \frac{3}{2} Nk_B T \Rightarrow \frac{1}{T} = \frac{3}{2} k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{u}$$

if we can find  $\mu$ , then we have entropy  $S$  via

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N$$

From Gibbs-Duhem relation in entropy representation

$$d\left(\frac{\mu}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right)$$

$$= u \frac{3}{2} k_B d\left(\frac{1}{u}\right) + v k_B d\left(\frac{1}{v}\right)$$

$$d\left(\frac{\mu}{T}\right) = -\frac{3}{2} \frac{k_B}{u} du - \frac{k_B}{v} dv$$

integrate to get

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2} k_B \ln\left(\frac{u}{u_0}\right) - k_B \ln\left(\frac{v}{v_0}\right)$$

where  $u_0$  at  $v_0$  are some reference state, and  $(\mu/T)_0$  is an unknown constant of integration. Then one gets

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N = \frac{3}{2} \frac{k_B E}{(E/N)} + \frac{k_B V}{(V/N)}$$

$$+ \frac{3}{2} N k_B \ln\left(\frac{u}{u_0}\right) + k_B N \ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N$$

$$S = \frac{3}{2} k_B N + k_B N - \left(\frac{\mu}{T}\right)_0 N + N k_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right)\right]$$

$$E = uN, E_0 = u_0 N_0, V = vN, V_0 = v_0 N_0$$

$$S = \frac{N}{N_0} S_0 + N k_B \ln \left[ \left( \frac{E}{E_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-5/2} \right]$$

where  $S_0 = \frac{5}{2} k_B N_0 + \left( \frac{\mu}{T_0} \right) N_0$  a constant  
fundamental equation, expresses  $S$  in terms of  $E, V, N$

alternatively

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\Rightarrow d\alpha = \frac{1}{T} du + \frac{P}{T} dv$$

$$= \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv$$

$$\alpha - \alpha_0 = \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

$$\alpha = \alpha_0 + \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

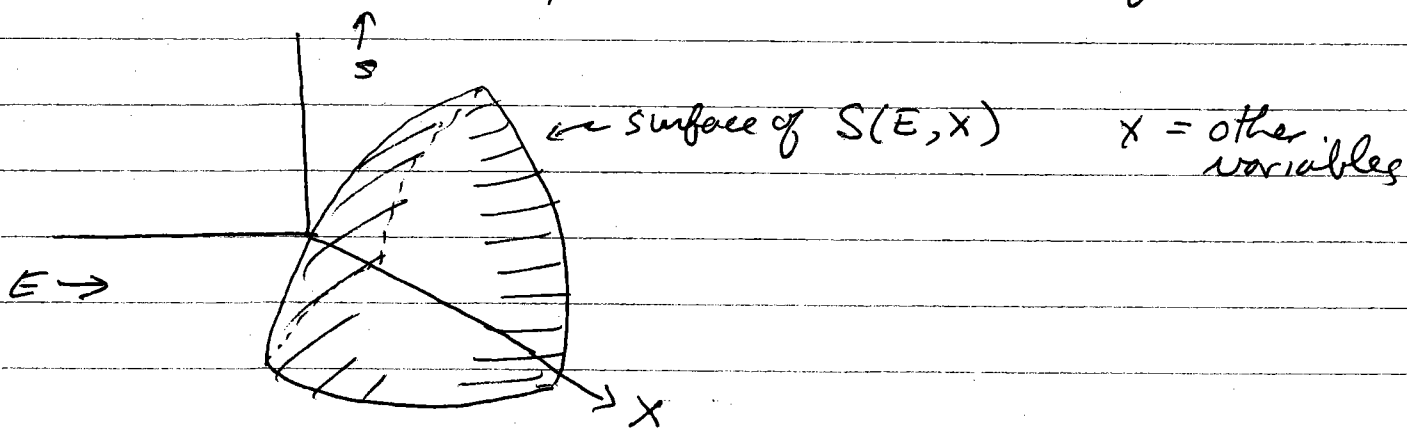
$$\alpha = \alpha_0 + k_B \ln \left[ \left( \frac{u}{u_0} \right)^{3/2} \left( \frac{v}{v_0} \right) \right] \text{ same as above}$$

fundamental equation, expresses  $\alpha$  in terms of  $u$  and  $v$

## Energy Minimum Principle

Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy  $S(E, V, N, \dots)$

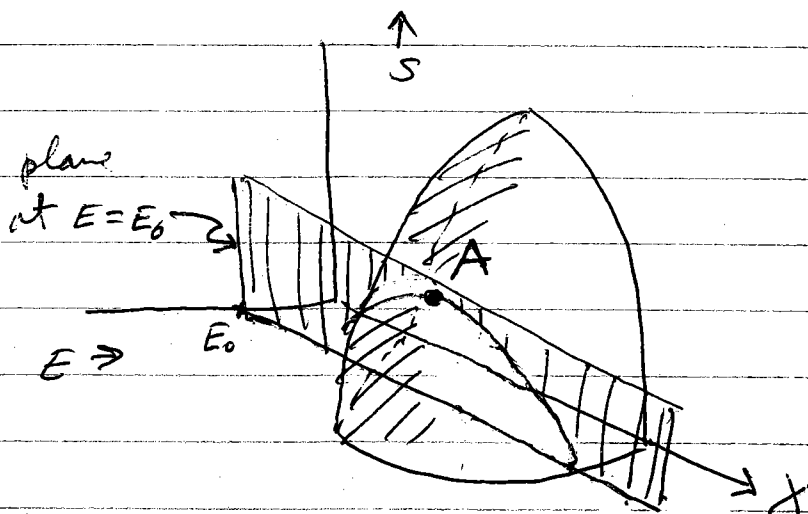
We saw that entropy is a <sup>concave</sup> convex function of its variables



For a situation where the total  $E$  is held fixed, at value  $E_0$ , then if  $X$  is an unconstrained degree of freedom, it will take in equilibrium that value  $X_0$  that maximizes  $S$  for the given fixed  $E_0$ . This is determined by the intersection of the surface  $S(E, X)$  with the plane at fixed  $E = E_0$ .

$X_0$  is given by the point  $A$  that maximizes  $S$  along this curve of intersection

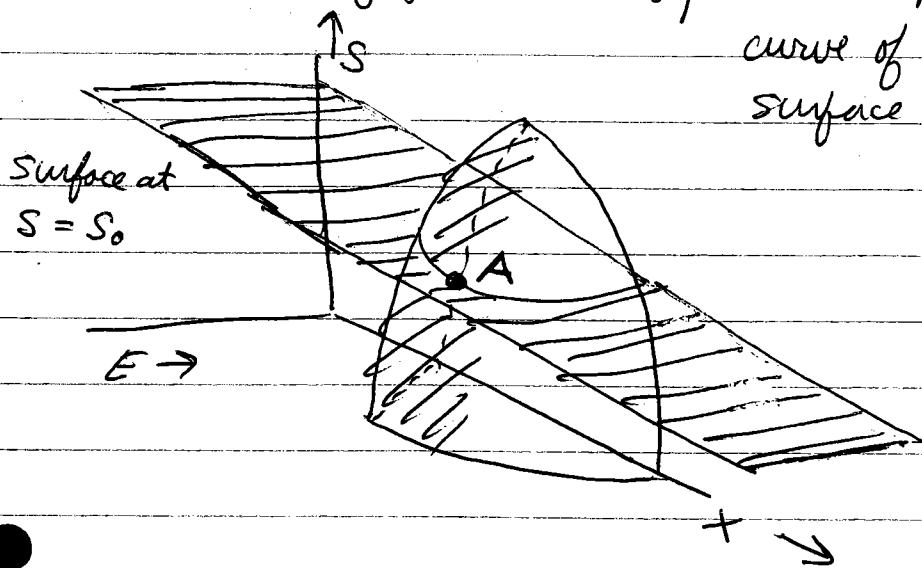
$$S_0 = \max_X [S(E_0, X)]$$



Callen Fig 5.1

Suppose now an alternative situation in which the total entropy  $S$  is held fixed at value  $S_0$ .

Then if  $X$  is an unconstrained degree of freedom we see that the equilibrium state at  $S_0, E_0$  corresponds to minimizing the energy with respect to  $X$ , along the curve of intersection between  $S(E, X)$  surface and plane of const  $S = S_0$ .



Callen Fig 5.2

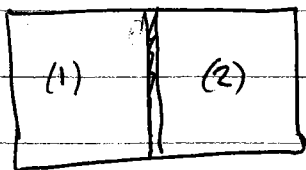
$$E_0 = \min_X [E(S_0, X)]$$

We thus have two contrasting formulations:

Entropy formulation: fundamental function is  $S(E, X_1, X_2, \dots)$   
 if constraint on some  $X_i$  is removed,  $X_i$  will take the value that maximizes  $S$  for the fixed total energy  $E$ . In equilib,  $d^2S < 0$ .  $S$  ~~convex~~ <sup>concave</sup>

Energy formulation: fundamental function is  $E(S, X_1, X_2, \dots)$   
 if constraint on some  $X_i$  is removed,  $X_i$  will take the value that minimizes  $E$  for the fixed total entropy  $S$ . In equilib  $d^2E > 0$   
 $E$  ~~concave~~ <sup>convex</sup>

Example



$$\underline{dQ = T_1 ds_1 = T_2 ds_2 = 0}$$

thermally insulating wall  
allowed to slide

Since wall is thermally insulating, no heat flows across it.  $\Rightarrow dQ = T ds = 0$  So entropy on each side remains constant.  $S_1, S_2$  fixed... or  $ds_1 = ds_2 = 0$ . What condition determines equilib?

Total  $S = S_1 + S_2$  is const. Use energy for minimization

$$E = E_1(S_1, V_1, N_1) + E_2(S_2, V_2, N_2) \quad \left. \begin{array}{l} N_1, N_2 \\ S_1, S_2 \end{array} \right\} \text{fixed}$$

$$V_1 + V_2 = V \text{ fixed} \Rightarrow dV_1 = -dV_2$$

$$dE = \left( \frac{\partial E_1}{\partial S_1} \right)_{VN} ds_1 + \left( \frac{\partial E_1}{\partial V_1} \right)_{SN} dV_1 + \left( \frac{\partial E_1}{\partial N_1} \right)_{SV} dN_1 \\ + \left( \frac{\partial E_2}{\partial S_2} \right)_{VN} ds_2 + \left( \frac{\partial E_2}{\partial V_2} \right)_{SN} dV_2 + \left( \frac{\partial E_2}{\partial N_2} \right)_{SV} dN_2$$

$$= T_1 ds_1 - p_1 dV_1 + \mu_1 dN_1 + T_2 ds_2 - p_2 dV_2 + \mu_2 dN_2$$

$$= -p_1 dV_1 - p_2 dV_2 \quad \text{as } ds_1 = ds_2 = dN_1 = dN_2 = 0$$

$$= (-p_1 + p_2) dV_1$$

as expected

at equilib,  $E$  is minimum,  $dE = 0 \Rightarrow \boxed{p_1 = p_2}$   
energy is lowered as system does work by moving wall

We could also do this in the entropy formulation

$$\begin{aligned} ds_1 &= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 = 0 \\ ds_2 &= \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 = 0 \end{aligned} \quad \left. \begin{array}{l} \text{since wall is} \\ \text{thermally insulating} \end{array} \right\}$$

$$\text{wall impermeable} \Rightarrow dN_1 = dN_2 = 0$$

$$ds_1 = 0 \Rightarrow dE_1 + P_1 dV_1 = 0$$

$$ds_2 = 0 \Rightarrow dE_2 + P_2 dV_2 = 0$$

$$P_1 = - \frac{dE_1}{dV_1} \quad P_2 = - \frac{dE_2}{dV_2}$$

$$V_1 + V_2 = V \text{ fixed} \Rightarrow dV_1 = -dV_2$$

$$\text{at equilibrium, } E \text{ is a minimum} \Rightarrow dE = dE_1 + dE_2 = 0$$

$$\Rightarrow dE_1 = -dE_2$$

$$\Rightarrow P_1 = P_2 \quad \text{same as by energy method.}$$

Suppose we had some equilib state for which  $E$  was not the minimum possible value for the given  $S$ .

Then can withdraw energy from the system by doing mechanical work (for example drive a piston) while keeping  $S$  constant.

$$\begin{array}{ccccc} \text{start} & \text{do mechanical} & & \text{add heat} & \\ & \text{work} & & & \\ E_0, S_0 & \xrightarrow{\quad} & E_1, S_0 & \xrightarrow{\quad} & E_0, S_1 \\ & & \text{where } E_1 < E_0 & & \text{where } S_1 > S_0 \end{array}$$

now return this energy to the system in the form of heat  $E_0 - E_1 = dQ = T dS$ . The energy is now back to  $E_0$ , but the entropy has increased by  $dS = (E_0 - E_1)/T$ .

The system is restored to its original energy but with a higher value of entropy. But this contradicts the requirement that the original equilib state was a maximum of entropy.  $\Rightarrow$  original  $E$  had to have been the minimum.

We have now two equivalent representations

- 1) entropy  $S(E, V, N)$  energy  $E$ , volume  $V$ , number  $N$  held fixed
- 2) energy  $E(S, V, N)$  entropy  $S$ , volume  $V$ , number  $N$  held fixed

In certain cases it is more natural to regard temperature  $T$  as held constant, rather than  $S$ ; or to regard pressure  $p$  as held constant, rather than  $V$ ; or to regard chemical potential  $\mu$  as held constant, rather than  $N$ .

We therefore wish to develop new formulations of thermodynamics that will allow us to regard  $T$ ,  $p$ , or  $\mu$  as a fundamental variable rather than  $S$ ,  $V$ , or  $N$ . These new formulations will lead to the Helmholtz and Gibbs free energies that play the role of ~~entropy~~ <sup>energy</sup> analogous to ~~entropy~~ as the fundamental thermodynamic function of these new formulations.

For example, we have  $E(S, V, N)$  with  $T = \left(\frac{\partial E}{\partial S}\right)_{V, N}$

How can we make a thermodynamic "potential" that contains all the information of  $E(S, V, N)$  but depends on  $T$  rather than  $S$ .