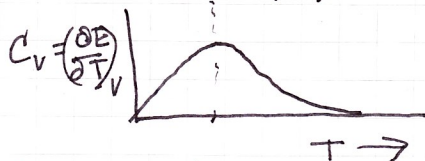
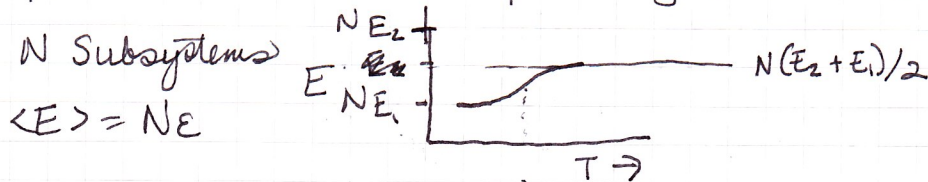


Lecture 6 Fundamental Thermodynamic Identity 25 Sept. 2008

Going over Mandl 2.2 N interacting systems, temperature dependence of \bar{E} , C_V
 Take one system as the subsystem and one as the heat bath

$$P_r = \frac{1}{Z} e^{-\beta E_r} \quad P \downarrow \text{ exponentially as } E_r \uparrow \quad \begin{array}{l} \text{--- } \bar{E}_2 \\ \text{--- } E_1 \end{array}$$



Can get an exact expression

$$\bar{E} = \sum_r E_r P_r = \frac{E_1 e^{-E_1/kT}}{Z} = \frac{E_1 e^{-E_1/kT} + E_2 e^{-E_2/kT}}{e^{-E_1/kT} + e^{-E_2/kT}}$$

$$\bar{E} = N\bar{E} \quad C_V = \frac{\partial \bar{E}}{\partial T} \quad \text{in terms of atoms all the } \bar{E}'\text{s are at the lowest state}$$

Electronic states are not normally excited at room temperature. It is completely unintelligible in classical physics. Statistical mechanics is the motivation for discovery. Boltzmann's tombstone $\sigma = k \log \Omega$

Last time, we showed that the magnetic moment of a paramagnetic solid as a function of T is inversely proportional to T for most temperature ranges. We can use this result to measure low T . by measuring the magnetic moment. Each atom has

$$L_{TOT} = \hbar/2$$

Slightly more complex for higher spins

Starting Mandl Chapter 4

The Fundamental Thermodynamic Identity ways to derive the result. Look at the entropy of an isolated system:

$$S \equiv S(E, V, N)$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V, N} dE + \left(\frac{\partial S}{\partial V} \right)_{E, N} dV \quad \text{assume } N = \text{constant}$$

$$dS = \left(\frac{1}{T} \right) dE + \left(\frac{P}{T} \right) dV$$

$$T dS = E + P dV \rightarrow$$

Fundamental Thermodynamic Identity

$$dE = T dS - P dV$$

Constant Entropy

back to
$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV$$

in general E, S vary together

Constant Entropy

If $dS=0$

$$dS=0 = \left(\frac{\partial S}{\partial E}\right)_{V,N} \delta E + \left(\frac{\partial S}{\partial V}\right)_{E,N} \delta V$$

$$0 = \left(\frac{\partial S}{\partial E}\right)_{V,N} \left(\frac{\partial E}{\partial V}\right)_S^{-1} + \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

Consider a large number of particles in a box n_x, n_y, n_z are positive integers

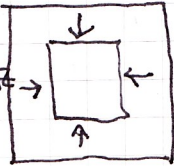
$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2 \pi^2}{2mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

Every particle will be in a different quantum state n_x, n_y, n_z

$$\langle E \rangle = \frac{1}{V^{2/3}}$$

as you increase the volume E decreases

Change $\langle E \rangle$ at a constant entropy, decrease V by a small amount
Compress slowly so no transition in quantum states
 \therefore number of microstates doesn't change

The force is balanced by the pressure: $PA \Delta x$ $PA \Delta y$ $PA \Delta z$ \rightarrow  Δx

The total work done: $\Delta W = PA(\Delta x + \Delta y + \Delta z)$

When $\Delta x < 0$ then $\Delta W > 0 \therefore \Delta W = -PA \Delta V$ appears as increase in energy

$$P = -\left(\frac{\Delta E}{\Delta V}\right)_S \text{ in the limit } \Delta V \rightarrow 0 = -\left(\frac{\partial E}{\partial V}\right)_S$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV \Rightarrow \boxed{-\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}}$$

Lecture 6 continued...

Another derivation of the Fundamental Thermodynamic Identity

The fluctuation of E is so small that $d\bar{E} = dE$

$$d\bar{E} = dE = \sum_r E_r p_r + \sum_r p_r dE_r$$

System in equilibrium with heat bath: $p_r = \frac{1}{Z} e^{-\beta E_r}$

$$E_r = -\frac{1}{\beta} (\ln Z - \ln p_r) = -kT (\ln Z + \ln p_r) \quad \hookrightarrow E_r = -\frac{1}{\beta} \ln(Z p_r)$$

$$d\bar{E} = dE = \sum_r \left\{ -kT (\ln Z + \ln p_r) dp_r \right\} + \sum_r p_r \left(\frac{\partial E_r}{\partial V} \right) dV$$

$$= -kT \sum_r (\ln p_r) dp_r - \sum_r p_r P_r dV$$

pressure in that particular quantum state r

$$\bar{P} = \langle P \rangle = \sum_r p_r P_r$$

$$S = -k \sum_r p_r \ln p_r$$

$$dS = -k \sum_r p_r \frac{1}{p_r} dp_r - k \sum_r \ln(p_r) dp_r$$

$$\therefore dE = T dS - \sum_r p_r P_r dV = T dS - P dV \rightarrow \boxed{dE = T dS - P dV}$$

Mandel's derivation: Equate to pressure if you try to decrease volume too rapidly.

$$dW = -P dV \quad \text{for a quasistatic reversible process}$$

$$\text{but in general} \quad dW \geq -P dV$$

Fundamental Thermodynamic Identity: $dE = dQ + dW$

since $dW = -P dV$ for a reversible process $dQ = T dS$ for a reversible process, but S should remain constant for quasistatic processes

$$dS = \frac{dQ}{T} \quad \text{for a reversible infinitesimal process.}$$

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ}{T} = S_2 - S_1$$

Thus a change in entropy of a process doesn't depend on the process only on the initial and final state.

Clausius Inequality

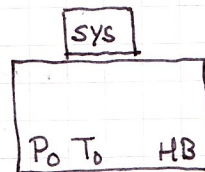
Constant Volume
Condition of equilibrium with Heat Bath

$\therefore F = E - TS$ is a minimum

$$S_{\text{TOTAL}} = S_{\text{SYS}} + S_{\text{HB}} = S_{\text{SYS}} + S_0$$

Quasistatic $\therefore \Delta S_{\text{TOTAL}} \geq 0$

$$\Delta S + \Delta S_0 \geq 0$$



diathermal
moveable
piston
glass of
very warm
water

The heat bath remains in the same state although it exchanges heat, $P, T,$ stay the same \therefore the system is reversible

$$\Delta S_0 = -\frac{Q}{T_0}$$

$$\Delta S - \frac{Q}{T_0} \geq 0 \quad \Delta W = -P_0 \Delta V \quad \Delta E = Q + \Delta W$$

$$Q = \Delta E - \Delta W = \Delta E + P_0 \Delta V$$

$$\boxed{\Delta S - \frac{(\Delta E + P_0 \Delta V)}{T_0} \geq 0} \quad \text{Clausius Inequality}$$

Some people write as

$$T_0 \Delta S - (\Delta E + P_0 \Delta V) \geq 0$$

$$\Delta E + P_0 \Delta V - T_0 \Delta S \leq 0$$

$$A \equiv E + P_0 V - T_0 S = \text{availability}$$

$$\Delta A \leq 0$$