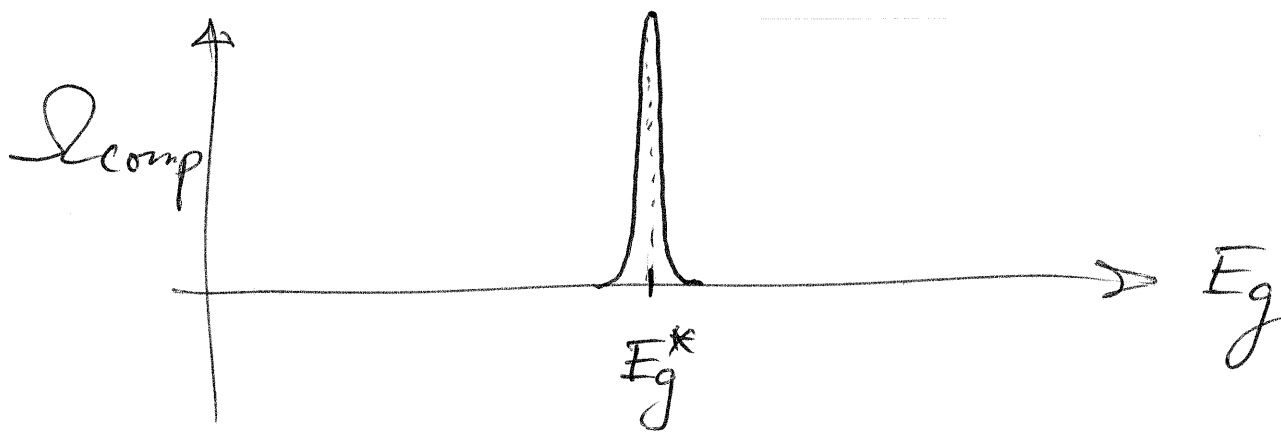


Lecture 37

(37.1)

The number of microstates of gas-solid compound system is the product of a very rapidly increasing function and a very rapidly decreasing function:

$$\Omega_{\text{comp}}(E_g) \propto (E_g)^{\frac{3}{2}N_g} (E - E_g)^{3N_s}$$



There are very many more microstates of the combined system when $E_g = E_g^*$ and so, according to

our central hypothesis, it (37.2) is much, much more likely to see the gas with energy E_g^* than any other energy.

We can efficiently locate the maximum of Ω_{comp} using logarithms.

$$\log \Omega_{\text{comp}} = \log \Omega_g(E_g) + \log \Omega_s(E - E_g)$$

$$0 = \frac{d}{dE_g} (\log \Omega_{\text{comp}}) =$$

$$\frac{d}{dE_g} (\log \Omega_g(E_g)) + \frac{d}{dE_g} \log \Omega_s(E - E_g)$$

$$- \frac{d}{dE_s} \log \Omega_s(E_s)$$

(Recall: $E_s = E - E_g$)

(87.3)

$$\Rightarrow \frac{d}{dE_g} \log \Omega_g(E_g) = \frac{d}{dE_s} \log \Omega_s(E_s)$$

In words: at the most probable partitioning of the energy, the energy-derivatives of the systems' $\log(\text{num. microstates})$ are equal.

The ~~the~~ reciprocal of this derivative defines the temperature of the system:

$$\text{temperature} = \left[\frac{d}{dE} \log \Omega(E) \right]^{-1}$$

$$= \frac{\Delta E}{\Delta(\log \Omega)}$$

We will use the "Kelvin" (37.4)
as our unit of temperature:

$$1\text{K} \approx \frac{1.38 \times 10^{-23} \text{ Joules}}{1 \text{ nat}}$$

(1 nat = change in natural logarithm
by 1)

So adding $1.38 \times 10^{-23} \text{ J}$ (a very small energy!) to a system at temperature 1K will increase the number of microstates it can access by a factor of $e = 2.718...$
If the system has temperature 1000K, then we would have to add $1.38 \times 10^{-20} \text{ J}$ of heat to increase

Q by the same factor.

(37.5)

Boltzmann's constant is a factor that converts between energy and temperature units :

$$k_B \approx \frac{1.38 \times 10^{-23} \text{ J}}{1 \text{ K}}$$

For example, if the temperature is $T = 1000 \text{ K}$, then $k_B T = 1.38 \times 10^{-20} \text{ J}$ of heat must be added to increase the number of microstates by a factor e .

The entropy in thermodynamics is usually defined in

terms of Boltzmann's
constant :

(37.6)

$$S = k_B \log \Omega .$$

Now, if $\Delta E = k_B T$ is the heat
needed for Ω to increase by a
factor e , then $\log \Omega$ increases
by 1 and

$$\frac{\Delta E}{\Delta S} = \frac{k_B T}{k_B} = T$$

gives the temperature in our
chosen system of units. Recall
that the "maximum Ω_{comp} " or
"most likely E_q " condition was
defined for arbitrarily small

energy changes (zero (37.7)
derivative). We should therefore
write the last equation as

$$\cancel{dS} \frac{dS}{dE} = \frac{1}{T} .$$

When a process also involves
volume changes, as in a gas,
we should include that part of
the microstate-count in the
definition of the entropy:

$$\text{gas: } \Omega(V, E) = C V^N E^{\frac{3}{2}N}$$

C = constant associated with
position and momentum grid,
energy resolution δE , etc.

$$S_{\text{gas}}(V, E) = k_B \log \Omega$$

(37.8)

$$= k_B N \log V + \frac{3}{2} k_B N \log E + S_0$$

$$S_0 = k_B \log C$$

The absolute entropy depends on the additive constant S_0 , but that is usually irrelevant since we are interested in entropy changes due to changes in V and E . For example, doubling the volume with E held fixed,

$$\Delta S = k_B N \log 2.$$