Ch.3 Boltzmann Distribution and Helmholtz Free Energy.
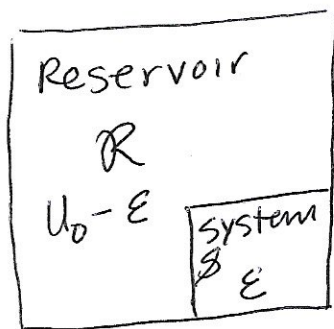
We have been looking at systems with subsystems of similar size, but it is offten more convenient to consider an __open__ system that can exchange energy and particles with the environment.

The environment is called the __reservoir__ and it is comparatively huge, could be the rest of the Universe. The system is comparatively tiny.

Consider a system with only 2 energy states, each with multiplicity 1, so there is only one configuration with that energy:

$$—\quad \varepsilon_2$$
$$—\quad \varepsilon_1 \quad \leftarrow \text{lower}$$

The system can get energy from the reservoir to move from ε_1 to ε_2, and this changes the multiplicity of the reservoir. The ratio of probabilities is

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{g_R(U_0 - \varepsilon_1)}{g_R(U_0 - \varepsilon_2)} \qquad \text{KK Eq. 3.2}$$

$$\exp\left\{\ln\left[\frac{g_R(U_0-\varepsilon_1)}{g_R(U_0-\varepsilon_2)}\right]\right\}$$

$\frac{P(\varepsilon_1)}{P(\varepsilon_2)}$ is the ratio of the probability of finding the system in quantum state 1 to prob. finding it in quantum state 2, as a function of τ !!

$$= \exp\left\{\ln g_R(U_0-\varepsilon_1) - \ln g_R(U_0-\varepsilon_2)\right\}$$

$$= \exp\left[\sigma_R(U_0-\varepsilon_1) - \sigma_R(U_0-\varepsilon_2)\right]$$

with $\Delta\sigma_R \equiv \sigma_R(U_0-\varepsilon_1) - \sigma_R(U_0-\varepsilon_2)$, **KK Eq. 3.4** $\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = e^{\Delta\sigma_R}$ **KK Eq. 3.5**

Let's now Taylor expand about $\sigma_R(U_0)$. Recall

KK Eq. 3.6

$$f(x_0+a) = f(x_0) + a\left(\frac{df}{dx}\right)_{x=x_0} + \frac{1}{2!}a^2\left(\frac{d^2f}{dx^2}\right)_{x=x_0} + \cdots$$

then

$$\sigma_R(U_0 - \varepsilon_1) = \sigma_R(U_0) - \varepsilon_1\left(\frac{d\sigma_R}{dU}\right)_{U=U_0} {}^{\swarrow 1/\tau} + \frac{1}{2}\varepsilon_1^2\left(\frac{d^2\sigma_R}{dU^2}\right)_{U=U_0} + \cdots$$

$$-\sigma_R(U_0 - \varepsilon_2) = -\sigma_R(U_0) + \varepsilon_2\left(\frac{d\sigma_R}{dU}\right)_{U=U_0} {}^{\nwarrow 1/\tau} - \frac{1}{2}\varepsilon_2^2\left(\frac{d^2\sigma_R}{dU^2}\right)_{U=U_0} - \cdots$$

$$\Delta\sigma_R = -\frac{\varepsilon_1}{\tau} + \frac{\varepsilon_2}{\tau} + \frac{1}{2}\varepsilon_1^2\frac{d}{dU}\left(1/\tau\right) - \frac{1}{2}\varepsilon_2^2\frac{d}{dU}\left(1/\tau\right)$$

$$\Delta\sigma_R = -(\varepsilon_1 - \varepsilon_2)/\tau \quad \text{KK Eq. 3.8}$$

↑ intensive   ↑ extensive

So they go to zero in the limit of an infinitely large reservoir.

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}}$$

$e^{-\varepsilon_1/\tau}$ is the Boltzmann factor

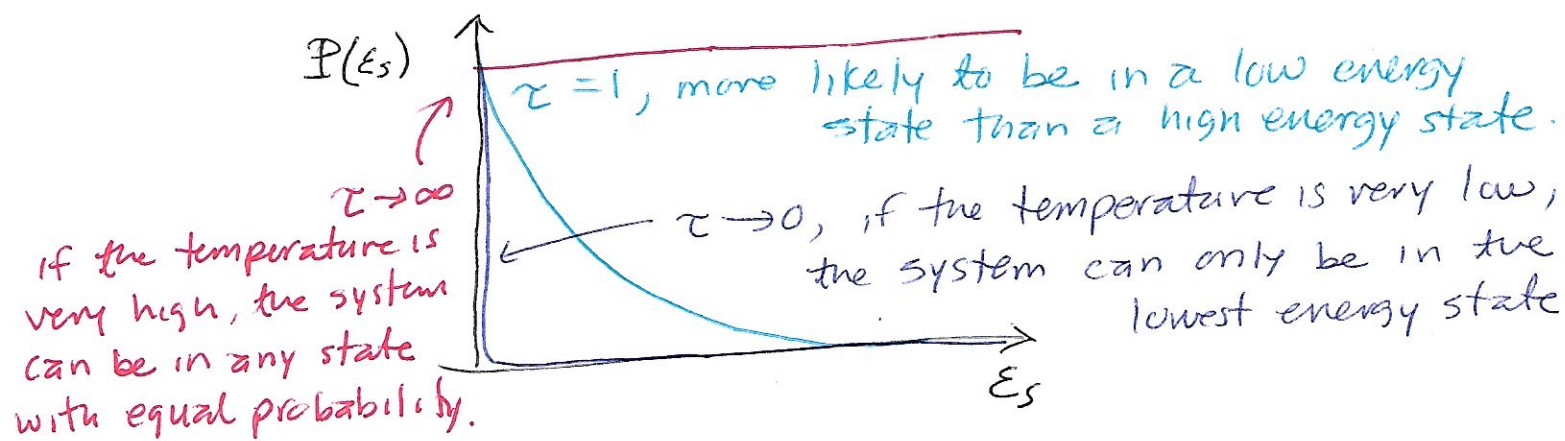**KK Eq. 3.9**

so

$$P(\varepsilon_s) \propto e^{-\varepsilon_s/\tau}$$

energy of the system

temperature of reservoir

This is fundamentally different result than for <u>closed</u> systems in which the fundamental assumption is that each state is equally likely. Not so in an <u>open</u> system.

Let $\tau = 1$, then $P(\varepsilon_s) \propto e^{-\varepsilon_s} = \dfrac{1}{e^{\varepsilon_s}}$

Let $\tau \rightarrow 0$, then $P(\varepsilon_s) \propto e^{-\varepsilon_s/0} = \dfrac{1}{e^{\infty}} = 0$

Let $\tau \rightarrow \infty$, then $P(\varepsilon_s) \propto e^{-\varepsilon_s/\infty} = \dfrac{1}{e^0} = 1$

$\tau = 1$, more likely to be in a low energy state than a high energy state.

$\tau \rightarrow 0$, if the temperature is very low, the system can only be in the lowest energy state

if the temperature is very high, the system can be in any state with equal probability.

Remember that the sum of all probabilities must be equal to 1 (the zeroth moment).

$$\sum_s \exp(-\varepsilon_s/\tau) = Z(\tau) \qquad KK \; Eq. \; 3.10$$

we call this sum the "partition function." The letter Z stands for "Zustandssumme" which means "sum over states"

Z is the proportionality factor between the Boltzmann factor $e^{-\varepsilon_s/\tau}$ and the probability $P(\varepsilon_s)$, so

$$P(\varepsilon_s) = e^{-\varepsilon_s/\tau}/Z$$

$$\sum_s P(\varepsilon_s) = \frac{1}{Z} \sum_s e^{-\varepsilon_s/\tau} = \frac{Z}{Z} = 1$$

The partition function is one of the most useful quantities in thermodynamics because it relates macroscopic and microscopic quantities.

Consider the average energy of a system $U = \langle \varepsilon \rangle$

$$\langle \varepsilon \rangle = \sum_s \varepsilon_s P(\varepsilon_s) \qquad \text{(first moment)}$$

$$U = \langle \varepsilon \rangle = \frac{\sum_s \varepsilon_s \exp(-\varepsilon_s/\tau)}{Z}$$

but $\dfrac{d}{d\tau} Z = \dfrac{d}{d\tau} \sum_s e^{-\varepsilon_s/\tau} = \sum_s \dfrac{d}{d\tau} e^{-\varepsilon_s/\tau}$

Let $u = -\varepsilon_s/\tau$, then $du = + \varepsilon_s/\tau^2$

$$\frac{d}{d\tau} Z = \sum_s \frac{\varepsilon_s}{\tau^2} e^{-\varepsilon_s/\tau} \implies \tau^2 \frac{d}{d\tau} Z = \sum_s \varepsilon_s \exp(-\varepsilon_s/\tau)$$
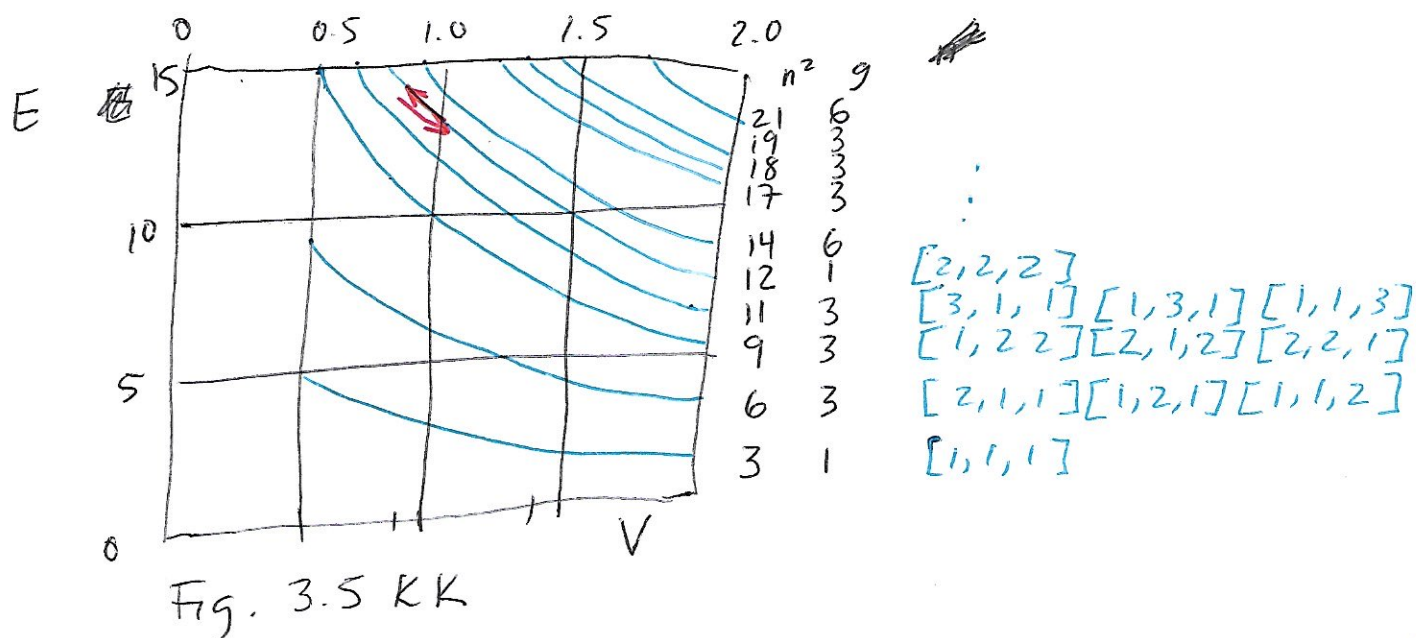
$$U = \langle \varepsilon \rangle \underset{\leftarrow \text{macroscopic}}{=} \frac{\tau^2}{Z} \frac{d}{d\tau} Z = \tau^2 \frac{d}{d\tau} \ln Z \underset{\leftarrow \text{microscopic}}{\overset{\leftarrow \text{macroscopic}}{}}$$

KK Eq. 3.12

Reversible process (pg. 64 KK)

Consider a particle in a box (from modern physics or quantum). We will see the details later, at this point we just need to remember that the ~~energy levels~~ states are given by $n^2 = n_x^2 + n_y^2 + n_z^2$

Fig. 3.5 KK

★ If you smash the box to change its volume violently, the particle will very likely change its state, but if you change the volume very slowly, then you can move along the same state. The change in entropy would be zero, so that means that you can move back and forth, you are not limited by "irreversibility/arrow of time."

A volume change that leaves the system in the same quantum state is called "isentropic." reversible process." it also implies that it is adiabatic (no heat transfer.)

To first order, the change in the energy of state s after a reversible volume change is

$$\mathcal{E}_s(V - \Delta V) = \mathcal{E}_s(V) - \left(\frac{d\mathcal{E}_s}{dV}\right)\Delta V \qquad \text{KK. Eq. 3.21}$$

If the box is squeezed isotropically, then the work done by the pressure applied normal to all faces is

$$\Delta U = U(V - \Delta V) - U(V) = -\left(\frac{d\mathcal{E}_s}{dV}\right)\Delta V \qquad \text{KK Eq 3.22}$$

↳ since energy is conserved in an adiabatic process

$$\Delta V = A(\Delta x + \Delta y + \Delta z) \quad \text{and} \quad \Delta x = \Delta y = \Delta z \leftarrow \text{isotropic}$$

$$p = F/A \implies F = pA \implies \cancel{F = pA}$$

$$F_x \Delta x + F_y \Delta y + F_z \Delta z = p_s A(\Delta x + \Delta y + \Delta z) = p\Delta V$$

$$\implies \Delta U = p_s \Delta V = -\frac{d\mathcal{E}_s}{dV}\Delta V$$

$$\text{so} \quad p_s = -\frac{d\mathcal{E}_s}{dV}$$

$$\langle P_\sigma \rangle = -\frac{d}{dV}\langle \mathcal{E} \rangle = -\frac{dU}{dV}$$

More appropriately, $\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$ KK 3.26

Consider the differential of $\sigma(U,V)$

← isentropic

$$d\sigma(U,V) = \left(\frac{\partial\sigma}{\partial U}\right)_V dU + \left(\frac{\partial\sigma}{\partial V}\right)_U dV = 0$$

then

$$\left(\frac{\partial\sigma}{\partial U}\right)_V \frac{(\delta U)_\sigma}{(\delta V)_\sigma} + \left(\frac{\partial\sigma}{\partial V}\right)_U \frac{(\delta V)_\sigma}{(\delta V)_\sigma} = 0 \frac{1}{(\delta V)_\sigma}$$

$$\Rightarrow \left(\frac{\partial\sigma}{\partial U}\right)_V \left(\frac{\delta U}{\delta V}\right)_\sigma + \left(\frac{\partial\sigma}{\partial V}\right)_U = 0$$

$$\frac{(\delta U)_\sigma}{(\delta V)_\sigma} \equiv \left(\frac{\partial U}{\partial V}\right)_\sigma, \quad \text{also,} \quad \frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_V,$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_\sigma = -\tau \left(\frac{\partial\sigma}{\partial V}\right)_U}$$

$$\boxed{+ p = + \tau \left(\frac{\partial\sigma}{\partial V}\right)_U} \quad \text{KK Eq. 3.32}$$

Thermodynamic Identity

$$d\sigma(U,V) = \underbrace{\left(\frac{\partial\sigma}{\partial U}\right)_V}_{1/\tau} dU + \underbrace{\left(\frac{\partial\sigma}{\partial V}\right)_U}_{p/\tau} dV$$

KK Eq. 3.34a

$$d\sigma(U,V) = \frac{1}{\tau} dU + \frac{p}{\tau} dV \Rightarrow \boxed{\tau d\sigma = dU + p dV}$$

$$\tau d\sigma = dU + p dV \qquad \sigma(U, V)$$

- heat added to system ($\tau d\sigma$)
- change in internal energy (dU)
- work done by the system ($p dV$)

$$\left(\frac{\partial \sigma}{\partial U}\right)_V = \frac{1}{\tau}\left(\frac{\partial U}{\partial U}\right)_V = \frac{1}{\tau}$$

$$\left(\frac{\partial \sigma}{\partial V}\right)_U = \frac{p}{\tau}\left(\frac{\partial V}{\partial V}\right)_U = \frac{p}{\tau}$$

$$dU = \tau d\sigma - p dV \qquad U(\sigma, V)$$

- intensive — extensive ($\tau d\sigma$)
- intensive — extensive ($p dV$)

$$\left(\frac{\partial U}{\partial \sigma}\right)_V = \tau\left(\frac{\partial \sigma}{\partial \sigma}\right)_V = \tau$$

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -p\left(\frac{\partial V}{\partial V}\right)_\sigma = -p$$

$$p dV = \tau d\sigma - dU \qquad V(\sigma, U)$$

$$\left(\frac{\partial V}{\partial \sigma}\right)_U = \frac{\tau}{p}\left(\frac{\partial \sigma}{\partial \sigma}\right)_U = \tau/p$$

$$\left(\frac{\partial V}{\partial U}\right)_\sigma = -\frac{1}{p}\left(\frac{\partial U}{\partial U}\right)_\sigma = -1/p$$

Notice that conjugate variables (τ, σ), (p, V), (μ, N) are pairs of extensive/intensive variables and their product has units of energy