Show that $PV^\gamma = $ constant holds for an adiabatic process

$$PV = RT_o \text{ for isothermal process}$$

$$W = \int dW = -\int P dV = -c \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \left. -\frac{c V^{1-\gamma}}{1-\gamma} \right|_{V_1}^{V_2} = \left(\frac{1}{\gamma-1}\right)\left(P_2 V_2 - P_1 V_1\right)$$

$$\therefore C = PV^\gamma = P_2 V_2^\gamma = P_1 V_1^\gamma \text{ at any state}$$

$$S(n) = k \ln \Omega = k \ln\left(\frac{N!}{n!(N-n)!}\right)$$

$$= k\left[\ln N! - \ln n! - \ln(N-n)!\right] \quad N \text{ is big}$$

$$N >> 0 \quad \ln N! = N \ln N - N \quad \text{Stirlings}$$

under what conditions is Stirling's approximation true? $N > 10$
try it!

$$S(n) = k\left[\left(N(\ln N) - N\right) - \left(n \ln n - n\right) - \left((N-n)\ln(N-n) - (N-n)\right)\right]$$

$$= k\left[N \ln N - n \ln n - (N-n)\ln(N-n)\right]$$

$$\frac{1}{T} = \frac{1}{\varepsilon}\frac{\partial S(n)}{\partial n} = \frac{k}{\varepsilon}\left\{-\ln n - n\frac{1}{n} - (N-n)\left(\frac{-n}{N-n}\right) - \ln(N-n)\right]$$

$$\boxed{\frac{1}{T} = \frac{1}{\varepsilon}\frac{\partial S(n)}{\partial n} = \frac{k}{\varepsilon}\ln\left(\frac{N-n}{n}\right)} \quad \text{condition of entropy}$$

dimensionless $\ln\left(\frac{N-n}{n}\right) = \frac{\varepsilon}{kT}$

$$\frac{N-n}{n} = e^{\varepsilon/kT}$$

$$\frac{N}{n} = 1 + e^{\varepsilon/kT}$$

$$\frac{n}{N} = \frac{1}{1 + e^{\varepsilon/kT}} \quad n << N \quad \varepsilon \sim 1eV$$

$$kT = \left(\frac{1}{40}\right)eV \quad @ \; T = 300K$$

write as a power of 10

$$e^{-40} \sim 10^{-17}$$

$$\ln_e x = \log_{10} x \cdot \ln_e 10 = \frac{\ln x}{\ln_e 10} = \frac{\ln x}{2.302}$$

$$n = 10^{-17} \, 10^{23} = 10^6 \quad \text{a million atoms on the surface of a mole of crystal}$$

$T = 1000 K$

$$kT = \frac{1}{40}\left(\frac{1000}{300}\right) = \frac{1}{12} \text{ eV} \qquad \frac{\varepsilon}{kT} = \frac{1 \text{ eV}}{\frac{1}{12}\text{ eV}} = 12$$
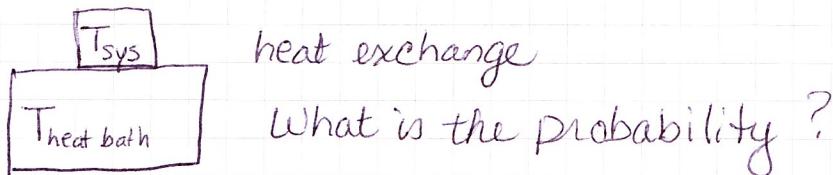
$$\therefore \frac{n}{N} \sim e^{-12} \sim 10^{-5} \qquad n = 10^{-5} \cdot 10^{23} = 10^{18} \text{ atoms on a}$$
$$\text{mole of crystal @ 1000 k}$$
$$\underline{\text{passivation}}$$

A system at equilibrium with a heat bath

heat capacity $\to \infty$ of heat bath compared to system
The system is infinitely small compared to heat bath

P_r = probability of finding the system in a
particular state $\quad r = 1, 2, 3, \ldots$ index of quantum state
of energy E_r

heat exchange

What is the probability ?

Fundamental Postulate: All microstates of same E_r are
equally probable

Total energy of the system $E_0 = E_r + E_{heat\,bath}$

$$P_r \propto e^{S_2(E_0 - E_r)/k} = {}^{1/k}[S_2(E_0) - E_r/T]$$

$$P_r \propto e^{S_2(E_0)/k} \, e^{-E_r/kT}$$

$$P_r = (\text{constant}) e^{-E_r/kT} \qquad \text{Boltzmann}$$

$\Big\}$ derivation

Can determine the constant by normalization

$$\sum_n P_n = 1 \qquad P_r = C e^{-E_r/kT} \qquad \therefore C = \frac{1}{\sum\limits_r e^{-E_r/kT}}$$

$$Z = \text{Canonical Equipartition Function} = \sum_r e^{-E_r/kT}$$

the trick is to find a system that is simple enough
to figure it out

$$\beta = \frac{1}{kT} \qquad Z = \sum_r e^{-\beta E_r} \qquad \boxed{P_r = \frac{1}{Z} e^{-E_r/kT}} \qquad *$$

Lecture 3 continued

Derivation

We can't get the exact energy of a system, therefore there is always an uncertainty in how many microstates are there.

$\Omega_2(E_0 - E_r) =$ The number of microstates of the heat bath

But the system is in an exact state Ω_1

$\Omega = \Omega_1 \Omega_2 = \Omega_2(E_0 - E_r)$

$p_r \propto \Omega_2(E_0 - E_r)$ useful fundamental postulate

$\nearrow S_2(E_0 - E_r) = k \ln \Omega_2(E_0 - E_r)$

heat bath

$$\Omega_2(E_0 - E_r) = e^{S_2(E_0 - E_r)/k}$$

do a Taylor Series expansion

$$S_2(E_0 - E_r) = S_2(E_0) - E_r \frac{\partial S_2}{\partial E_2}\bigg|_{E_2 = E_0} - \frac{E_r^2}{2!} \frac{\partial^2 S_2}{\partial E_2^2}\bigg|_{E_2 = E_0}$$

$E_0 \gg E_r$

$\left|\dfrac{\text{Third Term}}{\text{Second Term}}\right| \sim \dfrac{E_r \frac{1}{T}}{\frac{E_r^2}{2!} \frac{\partial}{\partial E_2}\left(\frac{1}{T}\right)\frac{\partial T}{\partial E_2}}$ $\dfrac{\frac{E_r^2}{T} \frac{\partial}{\partial T}\left(\frac{1}{T}\right)\frac{\partial T}{\partial E_2}}{E_r \frac{1}{T}} \sim \dfrac{\frac{1}{T^2} \frac{\partial T}{\partial E_r} E_r}{\frac{1}{T}}$ $\Bigg\}$

                                                             change in T
                           $\sim \dfrac{(\Delta T)_{E_r}}{T} \ll 0$ the third term   of heat bath
                                              can be   if you add E_r
                                              eliminated!

$\lim E_0 \gg E_r$

$$S_2(E_0 - E_r) = S_2(E_0) - E_r \frac{\partial S_2}{\partial E_2}\bigg|_{E = E_0} = S_2(E_0) - \frac{E_r}{T} /\!/$$

Useful Result: $P_r = \frac{1}{Z} e^{-E_r/kT}$

What is the energy of the system?

Statistical average over all microstates

$$\langle E \rangle = \sum_r E_r P_r = \sum_r E_r \frac{1}{Z} e^{-E_r/kT} = \sum_r E_r \frac{1}{Z} e^{-\beta E_r}$$

Z depends on β $\qquad \frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\sum_r \frac{E_r}{Z} e^{-\beta E_r}$

$$\boxed{Z = \sum_r e^{-\beta E_r} \qquad \frac{\partial Z}{\partial \beta} = \sum_r e^{-\beta E_r}(-E_r)}$$

$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$ if you can calculate the partition function then you can get the average energy

Can't use $S = k \ln(\ )$ to get entropy, but we can also get the entropy.

It will appear to have a definite energy

$$(\Delta E)^2 = \overline{(E - \overline{E})^2} = \overline{E^2 - 2E\overline{E} + \overline{E}^2} = \overline{E^2} - 2\overline{E}\overline{E} + \overline{E}^2 = \overline{E^2} - (\overline{E})^2$$

$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} \qquad \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \rightarrow \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{-\partial \langle E \rangle}{\partial \beta} \leftarrow \langle E \rangle = \sum_r E_r P_r$

$$= -\frac{\partial}{\partial \beta} \sum_r E_r P_r$$

$$= -\frac{\partial}{\partial \beta} \sum_r E_r \frac{1}{Z} e^{-\beta E_r}$$

$\frac{\partial^2 \ln Z}{\partial \beta^2} = -\sum_r E_r \left[\frac{1}{Z} e^{-\beta E_r}(-E_r) + e^{-\beta E_r}\left(-\frac{1}{Z^2} \frac{\partial Z}{\partial \beta}\right) \right]$ ~~$\sum_r E_r \left[\frac{e^{-\beta E_r}}{Z}\right]$~~

$$-\frac{1}{Z^2} \sum_{r'} E_{r'} e^{-\beta E_{r'}}$$

$$= \sum_r E_r^2 P_r - \left(\sum_{r'} E_{r'} P_{r'}\right)\left(\sum_{r} E_r P_r\right) = \langle E^2 \rangle - \langle E_r \rangle^2 = (\Delta E)^2$$

with $\frac{\partial \ln Z}{\partial \beta} = -\langle E \rangle \qquad (\Delta E)^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial \langle E \rangle}{\partial T}\frac{\partial T}{\partial \beta} = \frac{\partial E}{\partial T}\frac{1}{k} + k^2 T^2$

$\beta = \frac{1}{kT} \quad \frac{\partial T}{\partial \beta} = \frac{-1}{k\beta^2} \qquad\qquad\qquad\qquad = kT^2 \frac{\partial \langle E \rangle}{\partial T}$

$\Delta E = \sqrt{k} \, T \sqrt{C_V} \qquad \boxed{(\Delta E)^2 = kT^2 C_V}$ heat capacity

$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{\langle E \rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$