Chap 3 is about relationship between thermodynamic params

3.1 Temperature

In Chap 2, I did the example of ideal gas and found $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$. This is true in general!!!

To see logic, remember that two objects in thermal equilibrium have same temperature.

Also, remember that two objects, a and b, are in thermal equilibrium when $\Omega_a \cdot \Omega_b = \max$

$$S_{TOT} = S_a + S_b = \ln(\Omega_a \Omega_b) = \max$$

Suppose you have the two systems interact so only U_A can change ($U_a + U_b = U$ = constant from cons. of energy)

$$\left(\frac{\partial S_{TOT}}{\partial U_A}\right) \underset{\substack{\uparrow \\ \text{definition} \\ \text{of maximum}}}{=} 0 = \left(\frac{\partial S_A}{\partial U_a}\right)_{N_a V_a} + \left(\frac{\partial S_b}{\partial U_a}\right)_{N_b V_b} = \left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} \underset{\substack{\uparrow \\ \text{uses } dU_a = -dU_b}}{-} \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b, V_b}$$

$$\Rightarrow \left(\frac{\partial S_a}{\partial U_a}\right)_{N_a, V_a} = \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b, V_b} \text{ at thermal equilibrium}$$

Unit of $S = J/K \Rightarrow \frac{\partial S}{\partial U}$ has units $\frac{1}{K}$

But, but, but... hold on. We showed $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$ for ideal gas. This means we can say system a is an ideal gas and system b is any other system.

$$\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a, V_a} = \frac{1}{T_a} = \frac{1}{T_b} = \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b, V_b}$$

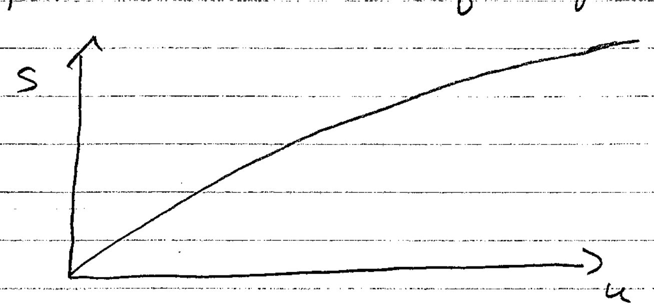
thermal equil

thermal equil.

This means $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$ in general.

This gives a firm definition of temperature in terms of underlying microscopic properties of the system!

Temperature = 1/(rate of change of entropy with respect to internal E)



typical case

$\frac{\partial S}{\partial U}$ decreases as U increases

T increases as U increases

(sec. 3.3 exception when only looking at part of a system)

All physical systems in full thermal equil. look like typical case

How to reach thermal equil.? Suppose a and b start so $\left(\partial S_a/\partial U_a\right)_{N_a V_a} > \left(\partial S_b/\partial U_b\right)_{N_b V_b}$

further — If U_a decreases, then $\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a}$ increases, U_b increases, $\left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b}$ decreases

closer — If U_a increases, then $\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a}$ decreases, U_b decreases, $\left(\partial S_b/\partial U_b\right)_{N_b V_b}$ increases

Can also write $T = \left(\frac{\partial U}{\partial S}\right)_{N,V}$ but typically have S in terms of U, N, V and not U in terms of S, N, V

From section 2.6 on entropy we found S for Einstein model

$$S = N k_B \ln\left[\left(\frac{q}{N}+1\right)\left(1+\frac{N}{q}\right)^{q/N}\right]$$

high T — When $T \gg \hbar\omega$ $\quad q/N \gg 1$

Remember $\left(1+\frac{1}{x}\right)^x \to e$ when x is large

$$\Rightarrow S = N k_B \ln\left[\frac{q}{N} e\right] = N k_B\left[\ln q + 1 - \ln N\right]$$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial q}\right)_{N,V} = \frac{N k_B}{\hbar\omega q} = \frac{N k_B}{U} = \frac{1}{T} \Rightarrow U = N k_B T$$

Remember from Equipartition theorem $KE + PE = N k_B T$ for harmonic oscillator

Suppose don't have the case $T >> \hbar\omega$

$S = Nk_B \ln\left(\frac{\varepsilon}{N}+1\right) + \varepsilon k_B \ln\left(1+\frac{N}{\varepsilon}\right)$

$$\frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial \varepsilon}\right)_{NV} = \frac{1}{\hbar\omega}\left[Nk_B \frac{1}{N}\frac{1}{\left(\frac{\varepsilon}{N}+1\right)} + k_B \ln\left(1+\frac{N}{\varepsilon}\right) - \frac{k_B}{\varepsilon}\frac{1}{\left(1+\frac{N}{\varepsilon}\right)}\right]$$

$$= \frac{k_B}{\hbar\omega}\left[\cancel{\frac{1}{\varepsilon+N}} + \ln\left(1+\frac{N}{\varepsilon}\right) - \cancel{\frac{1}{\varepsilon+N}}\right] = \frac{k_B}{\hbar\omega}\ln\left(1+\frac{N}{\varepsilon}\right) = \frac{1}{T}$$

Solve for ε $\quad \ln\left(1+\frac{N}{\varepsilon}\right) = \frac{\hbar\omega}{k_B T} \Rightarrow \left(1+\frac{N}{\varepsilon}\right) = e^{\frac{\hbar\omega}{k_B T}}$

$$\Rightarrow \varepsilon = \frac{N}{e^{\frac{\hbar\omega}{k_B T}}-1} \qquad U = \hbar\omega\varepsilon = \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}}-1}$$

Does this behave correctly when $\frac{\hbar\omega}{k_B T} << 1$? $\quad e^{\frac{\hbar\omega}{k_B T}} \doteq 1 + \frac{\hbar\omega}{k_B T}$

$U = N\hbar\omega / (\hbar\omega/k_B T) \overset{\checkmark}{=} Nk_B T$

How does it behave as $T \to 0$? $\quad U \to N\hbar\omega\, e^{-\frac{\hbar\omega}{k_B T}}$

Goes to 0 much faster than T.

Compute $\quad S = Nk_B \ln\left(\frac{\varepsilon}{N}+1\right) + \varepsilon k_B \ln\left(1+\frac{N}{\varepsilon}\right)$

$\left(1+N/\varepsilon\right) = e^{\hbar\omega/k_B T}$

$\left(1+\varepsilon/N\right) = e^{\hbar\omega/k_B T} \Big/ \left(e^{\frac{\hbar\omega}{k_B T}}-1\right) = \frac{U}{N\hbar\omega}\, e^{\frac{\hbar\omega}{k_B T}}$

$$\Rightarrow \varepsilon k_B \ln\left(1+\frac{N}{\varepsilon}\right) = \varepsilon k_B \frac{\hbar\omega}{k_B T} = \frac{U}{T}$$

$$Nk_B \ln\left(\varepsilon/N+1\right) = Nk_B \ln\left[\frac{U}{N\hbar\omega}e^{\hbar\omega/k_B T}\right] = \frac{N\hbar\omega}{T} + Nk_B \ln\left(\frac{U}{N\hbar\omega}\right)$$

$$S = \frac{U}{T} + \frac{N\hbar\omega}{T} - Nk_B \ln\left(e^{\frac{\hbar\omega}{k_B T}}-1\right)$$

$$= \frac{N\hbar\omega}{T}\left[1 + \frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1}\right] - Nk_B\frac{\hbar\omega}{k_B T} - Nk_B \ln\left(1-e^{-\frac{\hbar\omega}{k_B T}}\right)$$

$$= \frac{N\hbar\omega}{T}\frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1} - Nk_B \ln\left(1-e^{-\frac{\hbar\omega}{k_B T}}\right)$$

How does S behave as $T \to 0$?

$$S \doteq \frac{N\hbar\omega}{T}e^{-\frac{\hbar\omega}{k_B T}} + Nk_B e^{-\hbar\omega/k_B T}$$

$\Rightarrow S \to 0$ as $T \to 0$ (faster than any power)

Reverse prob 3.6 For an ideal gas with f degrees of freedom we had $U = \frac{f}{2} N k_B T$. What must the multiplicity be?

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T} = \frac{\frac{f}{2} N k_B}{U} \Rightarrow S = \frac{f}{2} N k_B \ln U + \text{const.}$$

$$\Omega = e^{S/k_B} = \underbrace{C}_{\text{constant}} e^{\frac{f}{2} N \ln U} = C\, U^{\frac{f}{2} N}$$

Note: This can't be correct as $U \to 0$ because $\Omega \to 0$ $S \to -\infty$ in this limit.