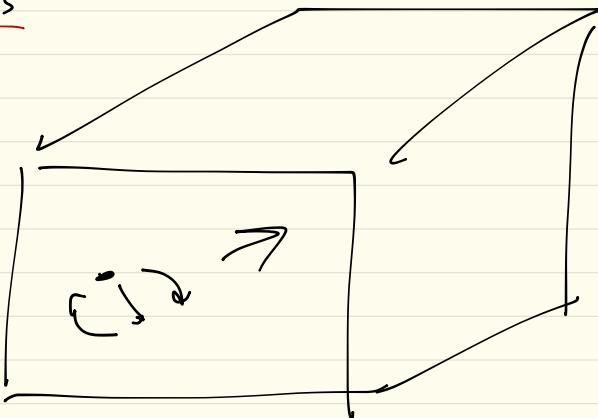


## Ideal gas



Molecules freely rotating, vibrating, . . .

$$\text{Separable: } E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

$$\begin{aligned}
 g &= \sum e^{-E\beta} \\
 &= \sum e^{-E_{\text{trans}}\beta} \sum e^{-E_{\text{rot}}\beta} \sum e^{-E_{\text{vib}}\beta} \\
 &= \underline{\underline{g_{\text{trans}} \cdot g_{\text{rot}} \cdot g_{\text{vib}}}}
 \end{aligned}$$

$$Q = \frac{g^N}{N!}$$

(2)

Show equations of canonical ensemble  
freely translating gas

$$\rightsquigarrow E_{\text{trans}} = \frac{U}{\Lambda^3} \quad \Lambda = \frac{\hbar}{\sqrt{2\pi mkT}}$$

$$\rightsquigarrow U(T, V, N) = \frac{3}{2} N k_B T$$

$$PV = N k_B T$$

$$S = R \ln \left[ \frac{e^{5/2} V}{N \Lambda^3} \right] \quad \begin{matrix} \text{exactly same} \\ \text{as we've seen} \end{matrix}$$

Sackur-Tetrode eq.

$$S^\circ(T)/R = \ln \left[ \frac{e^{5/2}}{\Lambda^3} V^\circ \right] = \ln \left[ \frac{e^{5/2}}{\Lambda^3} \frac{1}{C_0} \right] \\ = \ln \left[ \frac{e^{5/2}}{\Lambda^3} \frac{k_B T}{P^\circ} \right]$$

You choose the standard state!

rotating molecule

vibrating molecule

With these tools can get at the ideal gas heat capacity of any molecule  $C_p^{\text{ig}}(T)$

Apply stat. mech to our UOT models

(3) 1

(Many)

monatomic

Particles in a box  $\rightarrow$  ideal gts

Hole  $E_n = \frac{n^2 \pi^2 t^2}{2mL^2} = n^2 E_0$

$$q_{\text{trans}, 10} = \sum_{n=1}^{\infty} e^{-n^2 E_0 \beta}$$

Example Kr, 1dm<sup>3</sup> box 298 K

$$E_0 = 5.6 \times 10^{-22} \text{ eV}$$

(tiny!)

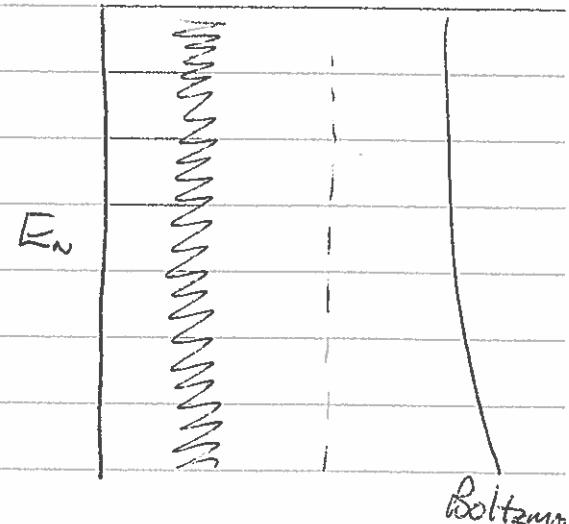
$$k_B T = 0.026 \text{ eV}$$

$$\Theta_{\text{trans}} = \frac{E_0}{k_B T} = \frac{5.6 \times 10^{-22}}{0.026} = 6 \times 10^{18} \text{ K}$$

but...

Try to construct sum

	$q_{\text{cont'n}}$
$n = 1$	$\frac{1}{1}$
$= 2$	$\frac{1}{1}$
$= 3$	$\frac{1}{1}$
$\dots$	
$10^5$	$0.999999\dots$
$\dots$	
$10^{10}$	$0.1\dots$
$\dots$	



Lots of terms contribute — from perspective of Boltzmann factor, energy spectrum is continuous

Integral approximation, ok when  $\Theta_{\text{trans}} \ll T$

$$Q_{\text{trans},1D} = \sum_{n=1}^{\infty} e^{-n^2 \epsilon_0 \beta} \approx \int_0^{\infty} e^{-x^2 \epsilon_0 \beta} dx \\ = \left( \frac{2\pi m}{\hbar^2 \beta} \right)^{1/2} L = \frac{1}{2} \left( \frac{\pi T}{\Theta_{\text{trans}}} \right)^{1/2}$$

"thermal wavelength"  $\lambda = \left( \frac{\hbar^2 \beta}{2\pi m} \right)^{1/2}$

$$Q_{1D} = L/\lambda \quad \text{dimension @ which quantization is evident}$$

Kr 1 dm<sup>3</sup> 298 K 1.104

$$\lambda = 1.7 \times 10^{-11} \text{ m}$$

$$Q_{1D}(298, 1 \text{ dm}) = 5.9 \times 10^9 \text{ states occupied}$$

Assuming all three directions (x, y, z) independent and cubic box

$$Q_{\text{trans},3D} = Q_{\text{trans},1D}^3 = V/\lambda^3$$

$$\text{Kr, } 1 \text{ dm}^3, 298 \text{ K} \rightarrow 2 \times 10^{29} \text{ states/atom}$$

$$Q_{\text{Kr}} = Q_{\text{trans}} / n! = \frac{1}{n!} \left( \frac{V}{\lambda^3} \right)^n$$

$$\ln Q = n \ln(V/\lambda^3) - \ln n!$$

- What's  $U$  for an ideal monatomic gas?

$$U = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = -n \left( \frac{\partial \ln \xi}{\partial \beta} \right)_{N,V}$$

$$\ln \xi = \ln V - 3 \ln \lambda$$

$$= \ln V - \frac{3}{2} \left( \ln \beta + \ln \frac{\hbar^2}{2m\pi} \right)$$

$$\left( \frac{\partial \ln \xi}{\partial \beta} \right)_{V,T} = \frac{3}{2} \cdot \frac{1}{\beta} - \frac{3}{2} \cdot \frac{1}{\beta}$$

$$U = \frac{3}{2} N \beta^{-1} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

$\bar{U} = \frac{3}{2} RT$

per mole

Just what we found from <sup>QFT</sup> kinetic theory

- What's  $C_v$ ?

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} R$$

$$= 12.47 \text{ J/mol K} \quad \text{independent of } T$$

Pretty good # for noble g<sub>s</sub>

- What's  $p$ ?

$$p = \frac{N}{V} \left( \frac{\partial \ln \xi}{\partial V} \right)_{N,P}$$

$$= \frac{N}{V} \cdot \frac{1}{V}$$

$PV = N k_B T = n R T$

wow! EOS  
of ideal g<sub>s</sub>  
from QM + stat  
mech

6

4

$$-nRT \left[ \ln v - \frac{3}{2} \ln A + 1 \right]$$

• What's  $A$ ?  $-nRT \left[ \ln v + \frac{3}{2} \ln T + \text{const} \right]$

$$A = -\frac{N}{\beta} \left[ \ln \left( \frac{v}{N} \right) + 1 \right]$$

so...?

$$= -nRT \left[ \ln \left( \frac{V}{NA^3} \right) + 1 \right]$$

$$= -nRT \left[ \ln \left( \frac{RT}{P} \right) - 3 \ln A + 1 \right]$$

$$A \propto RT \ln P$$

- What's  $S$ ?

$$S = k_B (U_B + \ln Q)$$

$$\ln Q = N \ln \left( \frac{V}{A^3} \right) - \ln N!$$

$$\approx N \ln \left( \frac{V}{A^3} \right) - (N \ln N - N)$$

Stirling's approx

$$S = Nk_B \left( \frac{3}{2} + \ln \left( \frac{V}{A^3} \right) - \ln N + 1 \right)$$

$$= Nk_B \left( \ln e^{5/2} + \ln \left( \frac{V}{A^3} \right) - \ln N \right)$$

$$= Nk_B \ln \left[ \frac{e^{5/2} V}{N A^3} \right]$$

$$= Nk_B \ln \left[ \frac{e^{5/2} V}{N A^3} \right]$$

$$\boxed{\bar{S} = R \ln \left[ \frac{e^{5/2} V}{N A^3} \right] = R \ln \left[ \frac{e^{5/2} k_B T}{P A^3} \right]}$$

Sackur-Tetrode equation

Unlike energy, entropy depends on density/pressure AND mass

# Asides:

Using stat. mech., can show that

$$S_0 = \frac{3}{2} k \left( \frac{5}{3} + \ln \frac{4\pi m}{3h^2} \right)$$

where  $m$  is the molecular mass and  $h$  Planck's constant.

Sackur-Tetrode eqn

$$S(T, V, N) = cNR \ln \frac{T}{T_0} + NR \ln \frac{V}{Nv_0} + Ns_0$$



momentum  
DOFs



position  
DOFs

$S = k \ln \Omega$ . What are the "microstates"

to count in an ideal gas?

For molecules specified by  
 $\{\vec{r}, \vec{p}\}$  pos, position (scals w/V)  
 And momentums (scals w/T)

The two EOS's above could have been inferred from gas kinetic theory + the Boltzmann distribution, and  $S$  from stat. mech.

8

5

$$S = R \left[ \ln \frac{e^{5/2} k_B}{N^3} + \ln T - \ln P \right]$$

Kr, 298 K, 1 bar

$$N = 1.104 \times 10^{-11} \text{ m}^{-3}$$

$$\Rightarrow \bar{S}^\circ = 164.085 \text{ J/mol K}$$

Look it up! Exactly right

Note dependence of  $S$  on  $P$  (or  $N/V$ ) is why we have to specify "standard state".

Sackur-Tetrode diverges as  $T \rightarrow 0$ . Why?  
 $\Theta_{trans} \cancel{\rightarrow} 0 \rightarrow$  integral approx fails

Standard state - since  $\Theta_{trans}$  depends strongly on concentration, conventionally to define a standard state, typically

$$N/V^\circ = c^\circ \text{ mol/l}$$

$$\bar{S}^\circ = R \ln \left[ \frac{e^{5/2}}{c^\circ N^3} \right]$$

Alternatively a standard state pressure (eq 1 bar), so  $\frac{N}{V} = \frac{P^\circ}{k_B T}$

$$\bar{S}^\circ = R \ln \left[ \frac{e^{5/2} k_B T}{P^\circ N^3} \right]$$

## Diatomic

$$q_{\text{KS}} \quad Q_{\text{total}} = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}}$$

$$Q = \tilde{Q}_{\text{total}} / n!$$

- rotational partition function

have to recall rotational energy states

$$\epsilon_l = \frac{\hbar^2}{2I} l(l+1) = hcB l(l+1) = \epsilon_{\text{rot}} l(l+1)$$

$$l=0, 1, 2, \dots \quad g(l) = 2l+1$$

degeneracy!!

$$g_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1)$$

Convenient to define rotational temperature

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2I} \frac{\epsilon_{\text{rot}}}{k_B}$$

$$Q_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\epsilon_{\text{rot}} l(l+1) / \Theta_{\text{rot}}}$$

$$= \sum_{l=0}^{\infty} (2l+1) \left( e^{-\Theta_{\text{rot}} / T} \right)^{l(l+1)}$$

Can't be summed in closed form.

example CO 300 K

$$B = 1.93 \text{ cm}^{-1} \quad \epsilon = hcB = 3.8 \times 10^{-23} \text{ J}$$

$$\Theta_{\text{rot}} = 2.78 \text{ K}$$

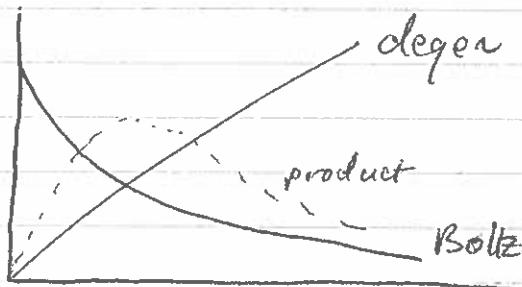
$$e^{-\Theta_{\text{rot}} / T} = 0.991$$

degen.      Boltz.

<u><math>l</math></u>	<u><math>2l+1</math></u>	<u><math>(e^{-\Theta_{\text{rot}}/T})^{l(l+1)}</math></u>	<u>product</u>
0	1	1	1
1	3	0.981	2.94
2	5	0.946	4.73
3	7	0.895	6.26
4	9	0.831	7.48
10	21	0.361	7.58
20	41	0.020	0.84
:	:	:	:
30	61	<u>0.011</u> $1.8 \times 10^{-4}$	<u>0.011</u>
:	:	:	:

$Q = \Sigma$

Lots of energy states contribute,  
summing can be tedious.



As long as  $\Theta_{\text{rot}} \ll T$ , can again make integral approx

$$\sum_{l=0}^{\infty} (2l+1)(e^{-\epsilon_0 \beta})^{l(l+1)} \approx \int_0^{\infty} (2l+1)(e^{-\epsilon_0 \beta})^{l(l+1)} dl$$

$$= T / \Theta_{\text{rot}}$$

$$\text{CO, } 300 \text{ K, } T/\Theta_{\text{rot}} \approx 108$$

If molecule is symmetric ( $D_{\infty h}$ ), one little glitch, even  $\lambda$  become indistinguishable + don't count (pure QC effect)

$$g_{\text{rot}} = \frac{1}{2} T/\Theta_{\text{rot}}$$

Thermo contributions are easy.

$$U_{\text{rot}}(T) = -N \left( \frac{\partial \ln g_{\text{rot}}}{\partial \beta} \right) = \frac{N}{\beta} = Nk_B T \quad T \gg \Theta_{\text{rot}}$$

equipartition

$$C_V = \frac{\partial U}{\partial T} = Nk_B$$

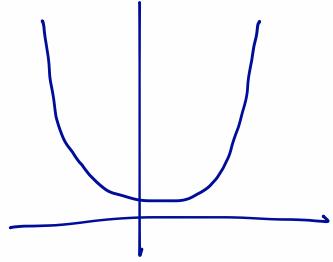
$$\begin{aligned} S_{\text{rot}} &= \frac{U_{\text{rot}}}{T} + Nk_B \ln g \\ &= Nk_B (1 + \ln g_{\text{rot}}) \quad \} \\ &= Nk_B (1 + \ln T - \ln \Theta_{\text{rot}}) \end{aligned}$$

$$\begin{aligned}
 q &= V/\lambda^3 \quad \mu = -k_B T \ln\left(\frac{e}{N}\right) \\
 &= -k_B T \ln\left(\frac{1}{N^3} \frac{RT}{P}\right) \\
 &= -k_B T \ln\left(\frac{1}{N^3} \frac{RT}{P_0}\right) + k_B T \ln P/P_0
 \end{aligned}$$

$$\boxed{\mu(T, P) = \mu^\circ(T, P_0) + k_B T \ln P/P_0}$$

$$= -k_B T \ln \underline{q^\circ(T, P)} + k_B T \ln P/P_0$$

harmonic oscillator



- vibrational partition function

- energy states of a harmonic oscillator!

$$E_v = (v + \frac{1}{2}) \hbar c \tilde{\omega}$$

$v = 0, 1, 2, \dots$

If we let  $\frac{1}{2} \hbar c \tilde{\omega}$  be the zero of energy, then

$$q_{\text{vib}} = \sum_{v=0}^{\infty} (e^{-\frac{1}{2} \hbar c \tilde{\omega} \beta})^v$$

geometric series

$$q_{\text{vib}} = \frac{1}{1 - e^{-\frac{1}{2} \hbar c \tilde{\omega} \beta}}$$

$$\sum a^n = \frac{1}{1-a} \quad a < 1$$

partition function for a harmonic oscillator

4-24-06

ex I<sub>2</sub>,  $\tilde{\omega} = 214.6 \text{ cm}^{-1}$  at 298 K

$$\theta_v = \frac{\hbar c \tilde{\omega}}{k_B}$$

$$= 310 \text{ K}$$

(CO)

$2157 \text{ cm}^{-1}$

↓

3100 K

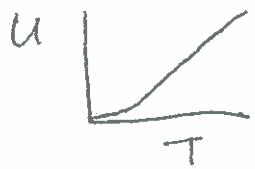
$$\hbar c \tilde{\omega} = 4.26 \times 10^{-21} \text{ J}$$

$$\hbar c \tilde{\omega} \beta = 1.036$$

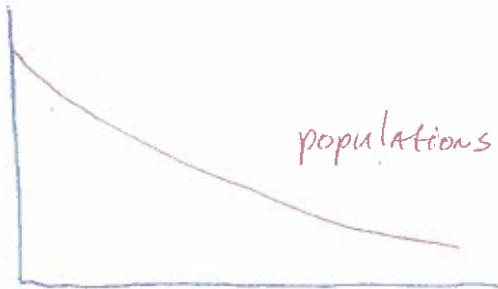
$$e^{-\hbar c \tilde{\omega} \beta} = 0.355$$

<u>v</u>	<u><math>(e^{-\hbar c \tilde{\omega} \beta})^v</math></u>	<u><math>\theta_v</math></u>
0	1	64.5
1	0.355	22.9
2	0.126	8.1
3	0.045	2.9
4	0.016	1.0
	<u>1.542</u>	<u>99.5 %</u>
		$q = 1.55$

unstable



For harmonic oscillator,  
pops decrease monotonically  
with  $E$



4-16-07

Again can calculate  $\bar{E}$ ,  $\bar{S}$ , etc.

$$\bar{E} = \frac{N\epsilon}{e^{\epsilon/\beta} - 1} \quad \epsilon = hc\tilde{\nu}$$

Used to  
describe a  
photon gas!

$$\bar{S} = Nk_B \left\{ \frac{\beta\epsilon}{e^{\beta\epsilon} - 1} - \ln(1 - e^{-\beta\epsilon}) \right\}$$

For typical molecules,  $\tilde{\nu}$  is fairly large compared to  $k_B T$ , And  $g_{\text{vib}} \approx 1$

For polyatomics, each vibration is treated independently, And  $g_{\text{vib}} = g_1^{v_1} \cdot g_2^{v_2} \cdots g_n^{v_n}$

To calculate the partition function for a molecule, then, we do

$$q_{\text{total}} = q_{\text{trans}} * q_{\text{rot}} * q_{\text{vib}}$$

$$Q = \frac{q_{\text{total}}^n}{n!}$$

And then get whatever we want!

Anharmonicity

• electronic partition functions

In principle we should sum over the electronic energy states of the atom / molecule as well.

$$\text{Eq H atom } E_n = -R_H \cdot \frac{1}{n^2} \quad n=1, 2, \dots \quad R_H = 13.6 \text{ eV}$$

$\approx 11000 \text{ cm}^{-1}$

$$g(n) = 2n^2$$

1

$$\text{Shift zero: } E_n = R_H \left(1 - \frac{1}{n^2}\right)$$

count

spin

degeneracy

$$q = \sum_{n=1}^{\infty} g(n) e^{-E_n \beta}$$

$T = 300 \text{ K}$

$n=1$	$g(n)$	$e^{-E_n \beta}$	$\frac{g}{\sum g}$	%
1	2	$\frac{1}{e^{127}}$	$\frac{1}{2}$	100
2	8	$4 \times 10^{-127}$	0	-

At most temperatures of interest, only the lowest electronic state contributes, and

$$Z_{\text{elec}} = \text{ground state degeneracy}$$

Fermi-Dire statistics  
really apply

GFS,  
HW $U_{\text{internal energy}} \rightarrow$  average energy of states $S_{\text{entropy}} \rightarrow$  # available / accessible states $C_V, \text{internal heat capacity} \rightarrow$  ~~4 states~~<sup>well</sup> / AT

	$\frac{\epsilon_{\text{trans}}}{\frac{\hbar^2}{2mL^2}}$	$\frac{\theta_{\text{trans}}}{\sim 10^{-21} \text{ cm}^{-1}}$	$\# \text{states @ RT}$
<u>translational</u>	$\sim 10^{-21} \text{ cm}^{-1}$	$\sim 10^{30}$	

classical limit,  $U = \frac{3}{2} RT$

<u>rotational</u>	$\frac{\epsilon_{\text{rot}}}{\sim 1 \text{ cm}^{-1}}$	$\theta_{\text{rot}} \sim 1 \text{ K}$	$\# \text{states @ RT} \sim 100's$
			semi-classical, $U \sim \# \text{DOF. } \frac{1}{2} RT$

<u>vibrational</u>	$\frac{\epsilon_{\text{vib}}}{\sim 1000 \text{ cm}^{-1}}$	$\theta_{\text{vib}} \sim 1000 \text{ K}$	$\# \text{states @ RT} \sim 1$
			non-classical

<u>electronic</u>	$\frac{\epsilon_{\text{elec}}}{\sim 10000 \text{ cm}^{-1}}$	$\theta_{\text{elec}} \sim 10000 \text{ K}$	$\# \text{states @ RT} \sim 1$

In summary  
for ideal gases

$$Q = (q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elec}})^n / n!$$

$$U = U_{\text{trans}} + U_{\text{rot}} + \dots$$

...

4/16/08

Gottschall  
dies

C

**Table 1:** Statistical Thermodynamics of an Ideal Gas**Translational DOFs** 3-D particle in a box model

$$\theta_{\text{trans}} = \frac{\pi^2 \hbar^2}{2mL^2 k_B}, \quad \Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2}$$

For  $T \gg \Theta_{\text{trans}}$ ,  $\Lambda \ll L$ ,  $q_{\text{trans}} = V/\Lambda^3$  (essentially always true)

$$U_{\text{trans}} = \frac{3}{2}RT \quad C_{v,\text{trans}} = \frac{3}{2}R \quad S_{\text{trans}}^\circ = R \ln \left( \frac{e^{5/2}V^\circ}{N^\circ \Lambda^3} \right) = R \ln \left( \frac{e^{5/2}k_B T}{P^\circ \Lambda^3} \right)$$

**Rotational DOFs** Rigid rotor model**Linear molecule**  $\theta_{\text{rot}} = hcB/k_B$ 

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\theta_{\text{rot}}/T}, \approx \frac{1}{\sigma} \frac{T}{\theta_{\text{rot}}}, \quad T \gg \theta_{\text{rot}} \quad \sigma = \begin{cases} 1, & \text{unsymmetric} \\ 2, & \text{symmetric} \end{cases}$$

$$U_{\text{rot}} = RT \quad C_{v,\text{rot}} = R \quad S_{\text{rot}}^\circ = R(1 - \ln(\sigma\theta_{\text{rot}}/T))$$

**Non-linear molecule**  $\theta_{\text{rot},\alpha} = hcB_\alpha/k_B$ 

$$q_{\text{rot}} \approx \frac{1}{\sigma} \left( \frac{\pi T^3}{\theta_{\text{rot},\alpha} \theta_{\text{rot},\beta} \theta_{\text{rot},\gamma}} \right)^{1/2}, \quad T \gg \theta_{\text{rot},\alpha,\beta,\gamma} \quad \sigma = \text{rotational symmetry number}$$

$$U_{\text{rot}} = \frac{3}{2}RT \quad C_{v,\text{rot}} = \frac{3}{2}R \quad S_{\text{rot}}^\circ = \frac{R}{2} \left( 3 - \ln \frac{\sigma \theta_{\text{rot},\alpha} \theta_{\text{rot},\beta} \theta_{\text{rot},\gamma}}{\pi T^3} \right)$$

**Vibrational DOFs** Harmonic oscillator model**Single harmonic mode**  $\theta_{\text{vib}} = h\nu/k_B$ 

$$q_{\text{vib}} = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \approx \frac{T}{\theta_{\text{vib}}}, \quad T \gg \theta_{\text{vib}}$$

$$U_{\text{vib}} = R \frac{\theta_{\text{vib}}}{e^{\theta_{\text{vib}}/T} - 1} \quad C_{v,\text{vib}} = R \left( \frac{\theta_{\text{vib}}}{T} \frac{e^{\theta_{\text{vib}}/2T}}{e^{\theta_{\text{vib}}/T} - 1} \right)^2 \quad S_{\text{vib},i}^\circ = R \left( \frac{\theta_{\text{vib}}/T}{e^{\theta_{\text{vib}}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib}}/T}) \right)$$

**Multiple harmonic modes**  $\theta_{\text{vib},i} = h\nu_i/k_B$ 

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-\theta_{\text{vib},i}/T}}$$

$$U_{\text{vib}} = R \sum_i \frac{\theta_{\text{vib},i}}{e^{\theta_{\text{vib},i}/T} - 1} \quad C_{v,\text{vib}} = R \sum_i \left( \frac{\theta_{\text{vib},i}}{T} \frac{e^{\theta_{\text{vib},i}/2T}}{e^{\theta_{\text{vib},i}/T} - 1} \right)^2 \quad S_{\text{vib},i}^\circ = R \left( \frac{\theta_{\text{vib},i}/T}{e^{\theta_{\text{vib},i}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib},i}/T}) \right)$$

**Electronic DOFs**  $q_{\text{elec}} = \text{spin multiplicity}$

Note that in high T limit, each DOF contributes some factor of RT to total energy

In classical limit that energies are continuous, can write

$$U = \frac{\sum_{\text{an}} \epsilon_{\xi} e^{-\epsilon_{\xi} \beta}}{\sum_{\text{an}} e^{-\epsilon_{\xi} \beta}} \rightarrow \frac{\int_r \int_{\xi} \epsilon(r, \xi) e^{-\epsilon(r, \xi) \beta} dp dq}{\int_r \int_{\xi} e^{-\epsilon(r, \xi) \beta} dp dq}$$

$\xi \rightarrow$  position  $p \rightarrow$  momentum

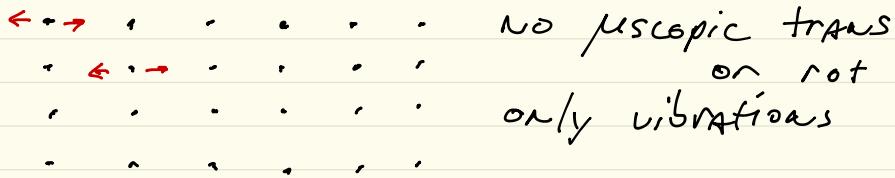
Can show if energy depends quadratically on  $p$  and/or  $\xi$ , each such DOF contributes  $\frac{1}{2}RT$  to  $U$ .

$$\text{translational : } \frac{p_x^2}{2m} \xrightarrow{x \quad y \quad z} \frac{1}{2}RT = \frac{3}{2}RT$$

$$\text{vibrational : } \frac{p_x^2}{2m} + \frac{1}{2}kx^2 \approx RT$$

Called law of equipartition, was very well known pre-QM

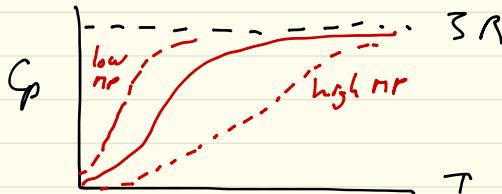
Apply ideas to a solid



NO microscopic trans  
or rot  
only vibrations

Assume each atom is a harmonic oscillator w/ same spring constant. Each contributes  $3RT$  to energy ( $3$  vib DOFs).  $\zeta_p \rightarrow 3R$

Known as law of Dulong & Petitt.



Works @ high  $T$ , fails @ low

Einstein realized that if these are QM oscillators, then must use

$$\zeta_{\text{vib}} = \frac{1}{1 + e^{-\Theta_{\text{vib}}/T}}$$

$Q_{\text{tot}} = (\zeta_{\text{vib}})^{3N}$ , assuming  $\Theta_{\text{vib}}$  same for all.

Note these are distinguishable

really should model as bosons

$$\varepsilon_{vib} = \frac{R\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} \quad C_v = 3R \left( \frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{(1 - e^{-\Theta_{vib}/T})^2}$$

$$U = 3N\varepsilon_{vib}$$

Much closer to observation

Properly gives  $C_v \rightarrow 0$  as  $T \rightarrow 0$

Not quite right functional form at low T though. Why?

Shouldn't think of these as individual oscillators. Think of as waves of different wavelength / frequency

  need to calculate density of these,  $g(v)$ .

$$g(v)dv \sim v^2 dv$$

Consider all frequencies  $0 \rightarrow v_{\text{deby}}$

such that  $\int_0^{v_{\text{deby}}} g(v)dv = 3N$

$$\Theta_0 = \frac{hv_0}{k_B} \quad \Rightarrow \quad C_v \sim \left( \frac{T}{\Theta_0} \right)^3 \int \dots$$

## Other ensembles

$$\underline{U \text{ } V \text{ } N} \quad p_j = 1 / Q(U, V, N)$$

microcanonical

$$\underline{T \text{ } V \text{ } N} \quad p_j = e^{-U_j \beta} / Q(T, V, N)$$

canonical/  
Helmholtz

$$\underline{T \text{ } P \text{ } N} \quad p_j(U_j, V) = e^{-U_j \beta} e^{-PV\beta} / \Delta(T, P, N)$$

Gibbs

$$G(T, P, N) = -kT \ln(\Delta(T, P, N))$$

isobaric/  
isothermal

$$\Delta(T, P, N) = \int_V Q(T, V, N) e^{-PV\beta} dV$$

$$\underline{T \text{ } V \mu} \quad p_j(U_j, N) = e^{-U_j \beta} e^{\mu N \beta} / \Xi(T, V, \mu)$$

grand  
canonical

$$\Psi(T, V, \mu) = -kT \ln \Xi$$

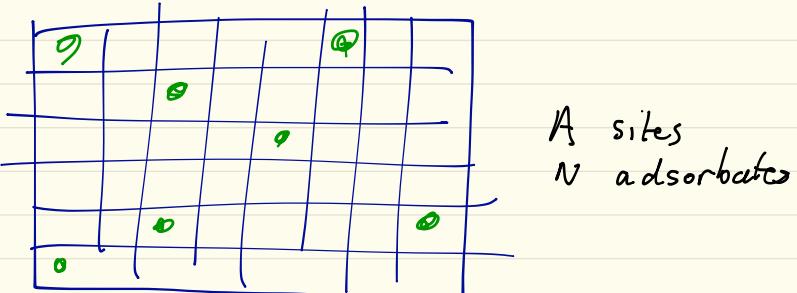
$$\Xi = \sum_N Q(T, V, N) e^{\mu N \beta}$$

## Langmuir adsorption

21

Adsorbates at a surface  
occupy "sites"

How many adsorbates  
at a given  $T + \mu$ ?



$$\Xi_{\text{site}} = \sum \text{internal DOFs of } A$$

$$\begin{aligned} Q(T, A, N) &= \Xi_{\text{site}}^N \cdot A^C_N \quad \xleftarrow{\text{"translation"}} \\ &= \Xi_{\text{site}}^N \cdot \frac{A!}{N! (A-N)!} \end{aligned}$$

Often want to know  $N(\mu, T)$  - grand canonical

$$\Xi(T, A, \mu) = \sum_{N=0}^A Q(T, A, N) e^{N\mu\beta}$$

$$\begin{aligned} &= \sum_{N=0}^A \Xi_{\text{site}}^N e^{N\mu\beta} \frac{A!}{N! (A-N)!} \\ &= (1 + \Xi_{\text{site}} e^{\mu\beta})^A \end{aligned}$$

binomial

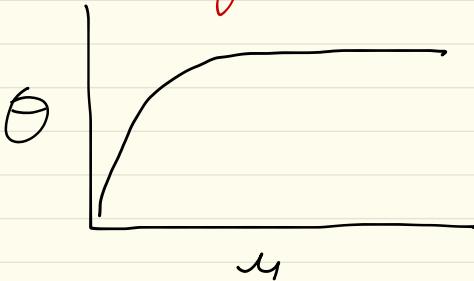
$$\Phi(T, A, \mu) = -Ak_B T \ln(1 + \Xi_{\text{site}} e^{\mu\beta})$$

$$N = - \left( \frac{\partial \Psi}{\partial \mu} \right)_{T, P} = + A k_B T \cdot \frac{1}{1 + \xi_{\text{site}} e^{\mu \beta}} \cdot \beta \xi_{\text{site}} e^{\mu \beta}$$

$$\frac{N}{A} = \Theta = \frac{\xi_{\text{site}}(\tau) e^{\mu \beta}}{1 + \xi_{\text{site}}(\tau) e^{\mu \beta}}$$

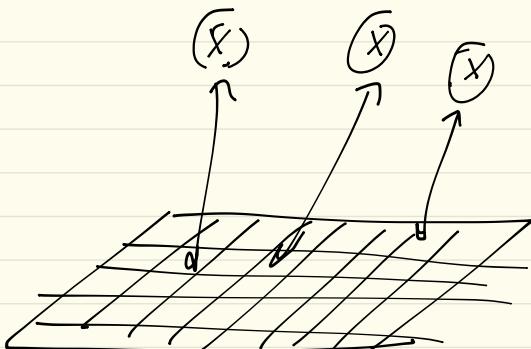
Langmuir isotherms

$$\begin{array}{ll} \mu \rightarrow -\infty & \Theta \rightarrow 0 \\ \mu \rightarrow \infty & \Theta \rightarrow 1 \end{array}$$



ideal gas reservoir - what if we want to relate  $\mu$  to some external reservoir?

$$\mu(T, P) = \mu^\circ(T, P^\circ) + k T \ln \frac{P}{P^\circ} - \Delta \bar{E}$$



$$\begin{aligned} \Delta \bar{E} &= E_{\text{ads}} - E_{\text{gas}} \\ &= \beta \cdot \bar{E} \end{aligned}$$

puts two systems  
on same energy  
scale

23

$$e^{\mu\beta} = e^{\mu_0\beta} \left(\frac{P}{P_0}\right) e^{-\Delta E\beta}$$

$$= \frac{1}{Z^\circ(T)} \left(\frac{P}{P_0}\right) e^{-\Delta E\beta}$$

Define  $K(T) = \frac{Z_{site}(T)}{Z^\circ(T)} e^{-\Delta E/k_b T} \quad X \equiv X^+$

$$\Theta = \frac{K(T) P/P_0}{1 + K(T) P/P_0}$$

Equilibrium constant is ratio of standard partition functions times a factor to account for energy offset.