For classical gas (ideal)
in d (space) dimensions,
would find $U = \frac{d}{2} N\tau$

or $\frac{1}{2} N\tau$ per "degree of freedom"

Equipartition Theorem
in ideal gas, each independent mode of motion that's accessible to an ideal gas molecule (in the sense that the mode is not too costly in energy @ $\tau = k_B T$) gives a "degree of freedom" and an energy $\frac{1}{2} N\tau$

$\Rightarrow$ for F degrees of freedom
Internal energy $U = \frac{F}{2} N\tau$

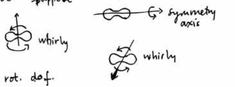
What other degrees of freedom can a gas molecule have?

That depends on the molecule.

"Usual suspects" list
- translation
- rotation
- vibration
- electronic/nuclear spin..

- Any kind of molecule possesses translational d.o.f. in $d=3$ there are precisely 3.

- How many rotational d.o.f. there are depends on the symmetry of the molecule !!
  - monatomic : model as sphere rotate it any of 3 ways & it looks same $\Rightarrow$ no rotational (rot.) d.o.f.
  - diatomic - suppose



$\Rightarrow$ 2 rot. d.o.f.

  - polyatomic with no special symmetry $\Rightarrow$ 3 rot. d.o.f.

- Vibrational degrees of freedom?
  - depends on how many bonds there are (and symmetry considerations ..)

e.g. diatomic 

one vib. d.o.f.

We can encode some of this in the specific heat!

$U = \frac{f}{2} N\tau$

and at certain temperatures various d.o.f. come into play. Pick diatomic, say

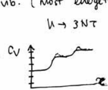
At lowest $\tau$, $U = \frac{3}{2} N\tau$ translational.

Then come rot. (like microwave = rot. mode of $H_2O$!)

$U \to \frac{5}{2} N\tau$

then vib. (most energetically expensive)

$U \to 3N\tau$

$\Rightarrow$ 

More quantitatively

$$\varepsilon = \varepsilon_{trans} + \underset{\uparrow \text{ rot, vib, etc...}}{\varepsilon_{int}}$$

$$\equiv \varepsilon_{\vec{n}} + \varepsilon_{int}$$

Now, $\mathfrak{z}_{\vec{n}} = \sum_{N,s} e^{-(\varepsilon_{s(N)} - \mu N)/\tau}$

Classically, only the zero energy one matters and the next level...

in other words, the probability of occupancy of an orbital being $>1$ is vanishingly small & we can neglect it (for classical gas only!)

$$\Rightarrow \quad \mathfrak{z}_{\vec{n}} = 1 + \sum_{int} e^{-(\varepsilon_{\vec{n}} + \varepsilon_{int} - \mu)/\tau}$$

↑ "setting" the zero of the energy at zero – recall that no particles means no energies (trans. or vib/rot.)

i.e. $$\mathfrak{z}_{\vec{n}} = 1 + e^{\mu/\tau} e^{-\varepsilon_{\vec{n}}/\tau} \underbrace{\sum_{int} e^{-\varepsilon_{int}/\tau}}_{\equiv Z_{int}}$$

i.e. $$\mathfrak{z}_{\vec{n}} = 1 + e^{\mu/\tau} e^{-\varepsilon_{\vec{n}}/\tau} . Z_{int} = 1 + \lambda Z_{int} e^{-\varepsilon_{\vec{n}}/\tau}$$

Probability of occupying the orbital $\vec{n}$?

$$f(\epsilon_{\vec{n}}) = \frac{\lambda Z_{int}\, e^{-\epsilon_{\vec{n}}/\tau}}{1 + \underbrace{\lambda Z_{int}\, e^{-\epsilon_{\vec{n}}/\tau}}_{\text{small in}}} \qquad \frac{\text{Gibbs factor}}{\text{partition fn}}$$

Classical régime

For the monatomic gas we had

$$f(\epsilon_{\vec{n}}) = \lambda\, e^{-\epsilon_{\vec{n}}/\tau}$$

so effectively $\lambda \to \lambda Z_{int}$ for internal d.o.f

In particular, since $\lambda_{monatomic} = \frac{n}{n_Q(\tau)}$,

for $\left\{\begin{matrix}\text{system with} \\ \text{internal d.o.f.}\end{matrix}\right\}$

$$\underset{\overset{\uparrow}{e^{\mu/\tau}}}{\lambda} Z_{int} = \frac{n}{n_Q(\tau)}$$

$$\Rightarrow \boxed{\mu = \tau\left[\log\left(n/n_Q(\tau)\right) - \log Z_{int}\right]}$$

Now recall that

$$\left(\frac{\partial F}{\partial N}\right)_{\tau, V} = \mu$$

(Partially) integrating w.r.t. $N$ gives $F = \int_0^N \mu \, dN'$

i.e. $\boxed{F = F_{monatomic} - N\tau \log Z_{int}}$

Then, since

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V ,$$

$$\sigma = \sigma_{\text{monatomic}} + N \frac{\partial}{\partial \tau}\left(\tau \log Z_{\text{int}}\right)_V$$

KK gives example of spin states.
With spin angular momentum J,
there are 2J+1 possible configurations

$$( J_z = -J, -J+1, \ldots, +J-1, +J )$$

and pretending that all these have same energy
gives

$$Z_{\text{int}} = \sum_{\text{int}} e^{-\varepsilon_{\text{int}}/\tau}$$

$$\equiv \sum_{J} (1) = 2J+1$$

Then $F_{\text{int}} = -N\tau \log(2J+1)$

and $\sigma_{\text{int}} = N \log(2J+1)$

can be measured experimentally?

$$\boxed{C_p}$$

We had $C_V = \left(\frac{\partial U}{\partial \tau}\right)_V$

or equivalently

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

(see this using $dU = \tau d\sigma - p dV$)

What if we did not find it convenient to hold $V$ fixed, but rather $p$ fixed?

$$\Rightarrow \boxed{C_p \equiv \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p}$$

Now use $\tau d\sigma - p dV = dU$

$$\Rightarrow \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = p\left(\frac{\partial V}{\partial \tau}\right)_p + \underset{\uparrow}{\left(\frac{\partial U}{\partial \tau}\right)_p}$$

Recall $U = \frac{F}{2}N\tau$, indep. of $p$, for ideal gas

$$\Rightarrow \left(\frac{\partial U}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_V \equiv C_V$$

Also, $pV = N\tau$ so $\left(\frac{\partial V}{\partial \tau}\right)_p = \frac{N}{p}$

$$\Rightarrow \underset{\text{ideal gas}}{\boxed{C_p = N + C_V}} \qquad C_p = \overset{\swarrow\,\text{d.o.f. "active" @ }\tau.}{\frac{F}{2}}N + N$$

Experimental
Use of $\quad C_p \equiv \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_p$

$$\Rightarrow \quad \sigma(\tau) - \sigma(\tau_0) = \int_{\tau_0}^{\tau} d\tau' \left\{ \frac{C_p(\tau')}{\tau'} \right\} \Bigg|_{p = \text{constant}}$$

this can be integrated numerically
by measuring in the lab !!

Common things to do with a classical ideal gas-

1) Keep $\tau$ constant, expand $V$, reversibly
(isothermal)

2) Keep $\sigma$ constant, expand $V$, reversibly
(isentropic/
adiabatic)

3) Expand into vacuum, suddenly (irreversibly)

① $\tau$ = const, $V \uparrow$ ($N$ = const. too)

In this case, find pressure from $pV = N\tau$

Reservoir keeps $\tau$ constant

so if $V_2 = 2V_1$
$p_2 = \frac{1}{2} p_1$

Entropy?

Sackur-Tetrode: $\sigma = N \log\left(\frac{n_Q(\tau)}{n}\right) + \frac{5}{2}N$
$\uparrow$ for monatomic

Here, $\tau$ = const. so $\frac{n_Q(\tau)}{N}$ = const

& $\sigma = N \log V$ + const (isothermal)

$$\Rightarrow \sigma_2 - \sigma_1 = N\log(V_2) - N\log(V_1) = N\log\left(\frac{V_2}{V_1}\right) = N\log 2$$

② $\sigma = \text{const}, \; V \uparrow$ (N = const. too)

In full, Sackur-Tetrode says for MONATOMIC gas:-

$$\sigma = N \log\left(\frac{n_Q(\tau)}{n}\right) + \frac{5N}{2} \quad \text{where} \quad n_Q(\tau) = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$$

$n = N/V$

i.e. $\sigma(\tau, V) = N \log\left(\tau^{3/2} V\right) + \text{constant}$

So if $\sigma$ = constant during reversible process then

$$\tau^{3/2} V = \text{const}$$

Using $pV = N\tau$, find

$$\tau^{5/2} p^{-1} = \text{const}$$

and/or

$$p^{3/2} V^{5/2} = \text{const}.$$

So if $V_2 = 2V_1$,

$$\tau_1^{3/2} V_1 = \tau_2^{3/2} V_2$$

$$\left(\frac{\tau_1}{\tau_2}\right)^{3/2} = \frac{V_2}{V_1} \Rightarrow \tau_2 = 2^{-2/3}\tau_1 \cong 0.63\,\tau_1$$

$$\Rightarrow U_2 - U_1 = \tfrac{3}{2}N(\tau_2 - \tau_1) < 0$$

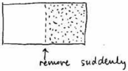
Also if $V_2 = 2V_1$,

$$p_1^{3/2} V_1^{5/2} = p_2^{3/2} V_2^{5/2}$$

$$\therefore \left(\frac{p_2}{p_1}\right)^{3/2} = \left(\frac{V_1}{V_2}\right)^{5/2} \quad \text{i.e.} \quad p_2 = 2^{-5/3} p_1 \cong 0.31\, p_1$$

## 3) Sudden Expansion into vacuum

e.g.
$V_2 = 2V_1$



- No work done — no pressure for the "boundary" layer to push against
- No heat flow — sudden approximation (adiabatic)

$\Rightarrow \quad \Delta U = 0$

$\Rightarrow \quad \Delta \tau = 0$

**But** — what about entropy?

**We** had from (1) $\quad \sigma_2 - \sigma_1 = N \log\left(\frac{V_2}{V_1}\right) = N \log 2$

Extra entropy $\because$ molecules have more available states

$\because$ box is bigger