On average,

each degree-of-freedom term in internal energy has value $\frac{1}{2} k_B T$

average over time $\rightarrow$ $\langle \frac{1}{2} m v_{5x}^2 \rangle = \frac{1}{2} k_B T$

$\langle \frac{1}{2} m v_{5 19, z}^2 \rangle = \frac{1}{2} k_B T$

} in equilibrium

Equipartition Theorem

$k_B = 1.38 \times 10^{-23}$ J/K

T : absolute temperature i.e. (in Kelvin)

Absolute Temperature

0°C arbitrary

0 K = −273°C : means no thermal energy
absolute zero

20 K is twice the temperature of 10 K

1 K = −272°C

°C + 273 → K

300 K = 27°C standard temperature
"room temperature"

use Kelvin ↓ T vs ΔT ↓ K or C°

$T_f - T_i = \Delta T$

300 K − 293 K = 7 K

27°C − 20°C = 7 C°

If particles are not points, may store thermal energy in other ways

- rotational energy $\frac{1}{2}I\omega^2$
- vibrational energy

$$U_{vib} = \frac{1}{2}mv_{rel}^2 + \frac{1}{2}k_s\Delta x^2$$

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Equipartition Theorem

"in thermal equilibrium, every quadratic degree-of-freedom term in the thermal energy has an average value of $\frac{1}{2}k_BT$."

quadratic: constant × (degree of freedom)^2

position or velocity

Liquids do not have quadratic terms and so do not obey equipartition theorem

Let f be the number of d.o.f. per particle

→ Each particle has average energy $\langle E_i \rangle = f\frac{1}{2}kT$

With N such particles,

$$\langle Energy \rangle = N\frac{f}{2}kT$$

if $N \gg 1$ fluctuations small $\boxed{U = N\frac{f}{2}kT}$

— —

Calculating f

1) translational $\vec{v}$

$v_{1x}, v_{1y}, v_{1z}, \ldots$

f_t = # dimensions particle can move in freely

$f_t = 0$ for a solid

2) rotational

f_r = # of perpendicular axes particle can rotate around... $f_r = 3$

...BUT don't count axes around which ~~sy~~ particle has continuous rotational symmetry.

surface $f_r = 1$

sphere $f_r = 0$ (points, too)

cylinder $f_r = 2$ H_2

— — — — —

3) Vibrational

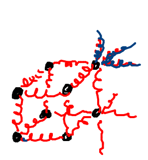
e.g. O_2

$$U_{vib} = \frac{1}{2}mv_{rel}^2 + \frac{1}{2}k_s(\Delta x)^2$$

two terms

$f_v = 2$/spring

e.g. 3D solid



3 springs/particle

$f_v = 6$

— — — — —

Freezing Out

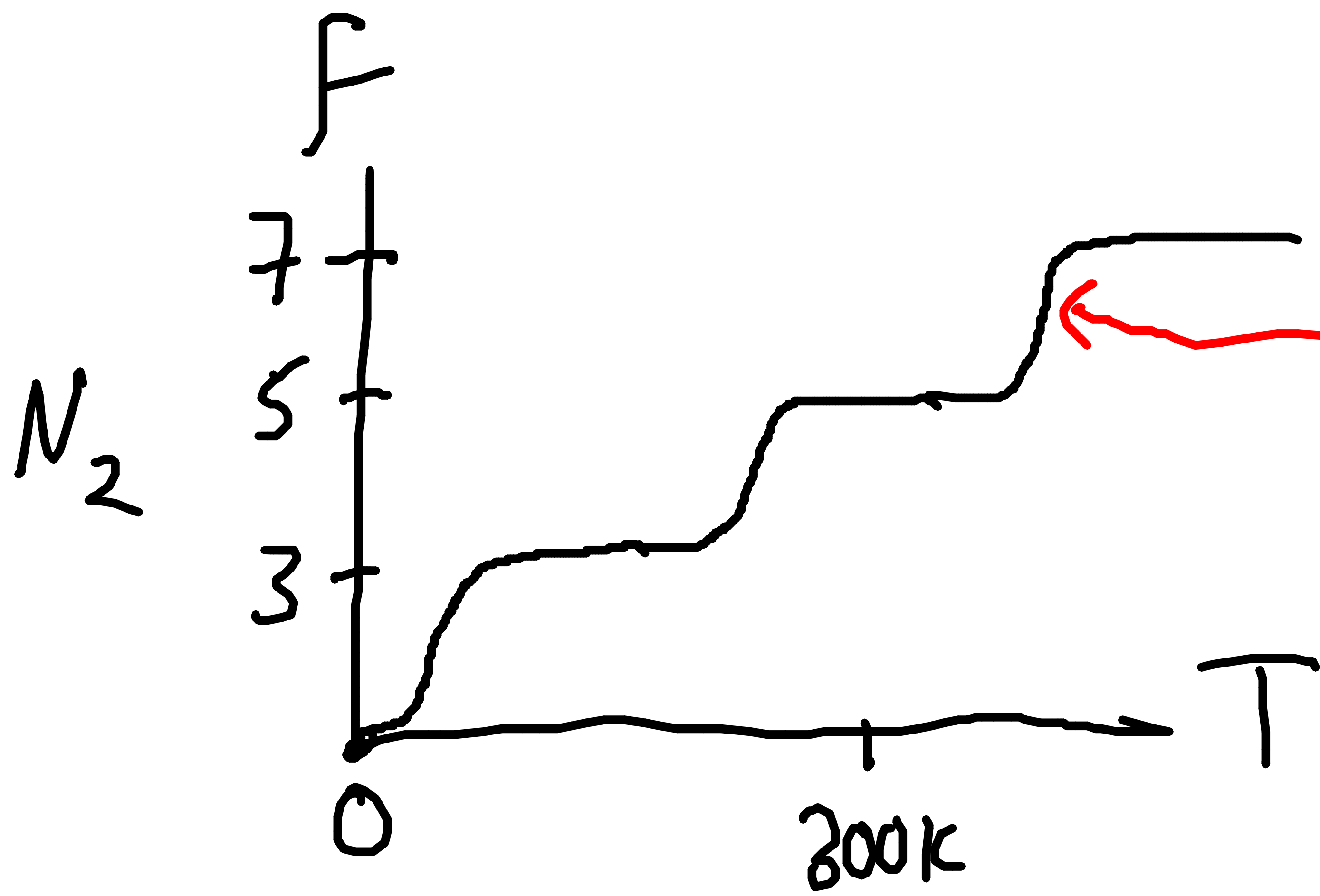
not all d.o.f. are "active" at every T

e.g. N_2 at room temperature

$f = 3 + 2 + 0$

because thermal energy isn't high enough to get the vibrations started

because thermal ene



f can be non-integer at some T

also f(T).