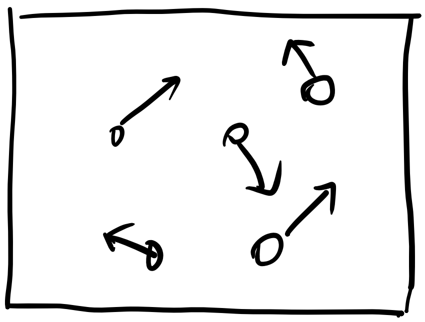
能量均分定理



collision

three dimension equivalent

$$m v_x \rightarrow -m v_x$$

$\Delta p = 2m v_x$ (momentum change)

$F \Delta t = \Delta p$ (前后两次碰

同一侧壁时间差)

(pressure) $p S \Delta t = \Delta p$

$\Delta t = \dfrac{2L_x}{v_x}$ (collision period)

$$p S \, 2L_x = 2 m v_x^2$$

volume $p V_v = m v_x^2$

(total pressure) $P_t V_v = m\left(\sum_i v_{ix}^2\right) = N m \overline{v_x^2}$

又 ∵ $P_t V_v = N k_B T = nRT$

$$\boxed{\begin{array}{c} N m \overline{v_x^2} \\ \parallel \text{ 各向同性} \\ \frac{1}{3} N m \overline{v^2} = N k_B T \end{array}}$$

$v^2 = v_x^2 + v_y^2 + v_z^2$

(如果所有分子都在 x 方向)

$$m \overline{v_x^2} = k_B T$$

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T$$

$$\frac{1}{2} m \overline{v^2} = 3 \times \frac{1}{2} k_B T$$

能量按自由度均分：

1° 质点自由度：$t=3$ (3d)

受限运动 $t=2$ (2d)

$t=1$ (1d)

2° 刚体自由度：$\overset{(t)}{3}$ + 转动自由度 $(3)^{(r)}$

转轴 2 + 转角 1

3° 分子自由度：

(1) 单原子分子： He，Ne，Ar

$t=3$

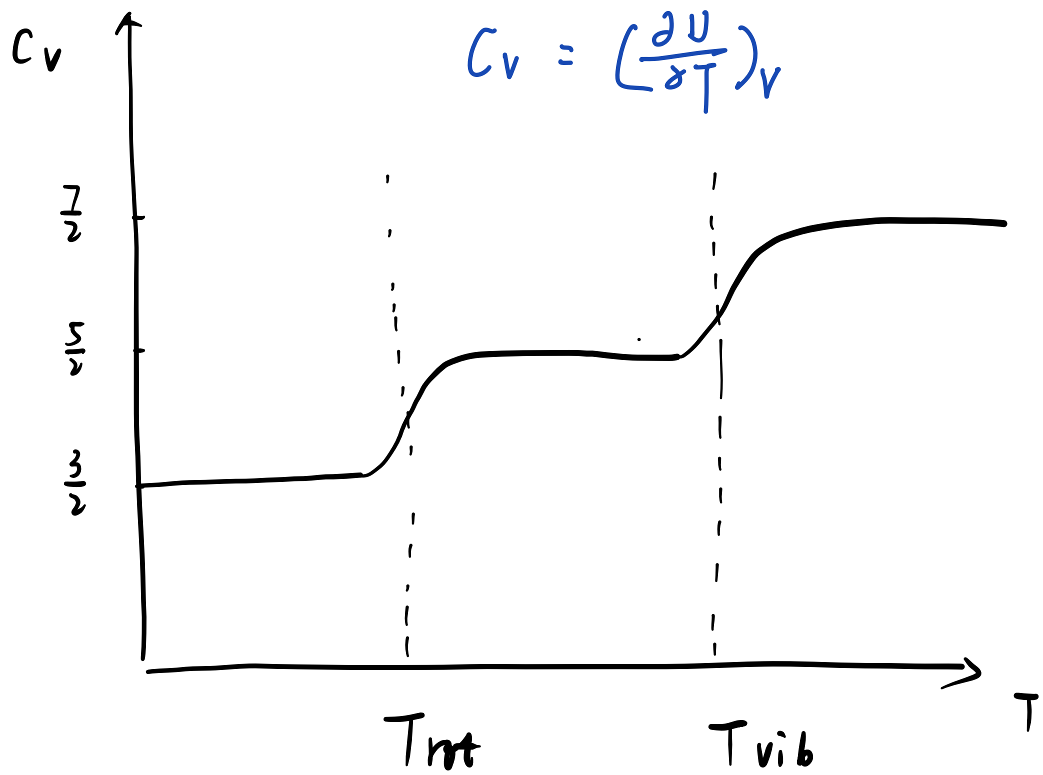
(2) 刚性双原子： O_2，H_2，CO

质心 $t=3$，$r=2$ (仅転轴)

所有原子均在轴上

(3) 刚性多原子： H_2O，NH_3

(不共线) $t(3)+r(3)=6$



CO： $T_{rot}\approx 2.8\,K$

$T_{vib} \approx 3103\,K$

(appeal to quantum physics)

vibration degree of freedom

(今后学习)

$\frac{1}{2} k_B T$, 位力定理,

kinetic, potential

$\frac{1}{2} k_B T \times 2$

Q: 不同 molecule 热运动造成了什么的不同?

$\frac{1}{2} m \overline{v^2} \propto \frac{1}{2} k_B T$

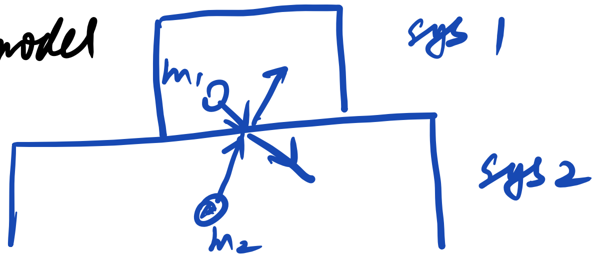
单个分子, 越重对内能贡献越大

$m \uparrow$, $\Delta p = 2mv$

$F \uparrow$, pressure $\uparrow$

弹性碰撞

toy model



For simplicity → 1D

动量守恒：$m_1 v_1 + m_2 v_2 = m_1 v_1' + m_2 v_2'$

动能守恒：$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} m_1 v_1'^2 + \frac{1}{2} m_2 v_2'^2$

(v, v' 自带符号)

$$v_1' = \frac{m_1 - m_2}{m_1 + m_2} v_1 + \frac{2m_2}{m_1 + m_2} v_2$$

$$v_2' = \frac{m_2 - m_1}{m_1 + m_2} v_2 + \frac{2m_1}{m_1 + m_2} v_1$$

(同种物体碰撞，交换速度，nothing change!)

$$\Delta U_1 = \frac{1}{2} m_1 v_1'^2 - \frac{1}{2} m_1 v_1^2$$

$$= \frac{4 m_1 m_2}{(m_1 + m_2)^2} \left[\frac{1}{2} m_2 v_2^2 - \frac{1}{2} m_1 v_1^2 + \frac{1}{2}(m_1 - m_2) v_1 v_2 \right]$$

有时正，有时负，做平均

each collision leads to different ΔU_1,

on average

$$\langle \Delta U_1 \rangle = \frac{4 m_1 m_2}{(m_1+m_2)^2} \left[\langle \tfrac{1}{2} m_2 v_2^2 \rangle - \langle \tfrac{1}{2} m_1 v_1^2 \rangle \right]$$

here, $\langle \frac{1}{2} (m_1 - m_2) v_1 v_2 \rangle = 0$

两个独立事件，简单地看有正有负

$$\langle v_1 v_2 \rangle = \langle v_1 \rangle \langle v_2 \rangle = 0 \quad !$$

When equilibrium is reached, we expect the average energy exchange vanishes,

能量 flow $= 0$ $\quad \langle \Delta U_1 \rangle = 0$ @ equilibrium

$\Longrightarrow$ 每个气体分子的平均动能相等

$$\langle \tfrac{1}{2} m_2 v_2^2 \rangle = \langle \tfrac{1}{2} m_1 v_1^2 \rangle$$

Thus, it is tempting to define the temperature this way,

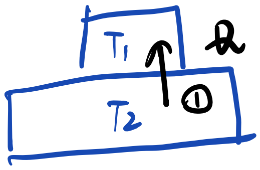
吸引人的
诱惑人的

$$\langle \frac{1}{2} m_i v_i^2 \rangle = \frac{1}{2} k_B T_i \quad (i = 1, 2)$$

$$\Downarrow$$

$$T_1 = T_2$$

$\boxed{\text{equilibrium criterion}}$



① $T_2 > T_1 \rightarrow$ $\langle \Delta u_1 \rangle > 0$

② $T_2 < T_1$, $\langle \Delta u_1 \rangle < 0$

③ $T_2 = T_1$, $\langle \Delta u_1 \rangle = 0 \rightarrow$ in thermal equilibrium

辐射：交换光子也是一种碰撞

go back to

平均动能大的会给能量到平均动能小的系统

$$\langle \Delta u_1 \rangle = \frac{4 m_1 m_2}{(m_1 + m_2)^2} \left(\langle \frac{1}{2} m_2 v_2^2 \rangle - \langle \frac{1}{2} m_1 v_1^2 \rangle \right)$$

$$\propto (T_2 - T_1)$$

Let us find the dynamical equation for $T_1(t)$

(a) according to the definition

$$\langle u_1 \rangle = \langle \frac{1}{2} m_1 v_1^2 \rangle = \frac{1}{2} k_B T_1$$

$$\langle \frac{d u_1}{dt} \rangle = \frac{1}{2} k_B \frac{d T_1}{dt} \propto \frac{d T_1}{dt}$$

$\boxed{\text{energy flow \& temperature changing rate}}$

(b) From the above discussion

$$\langle \Delta U_1 \rangle \propto (T_2 - T_1)$$

$\Downarrow$ ΔT drives the energy flow

$$\left\langle \frac{dU_1}{dt} \right\rangle = \underline{f_{col}} \cdot \langle \Delta U_1 \rangle \propto (T_2 - T_1)$$

$\downarrow$

视为 const，当 ΔT 不太大时

suppose system 2 is HUGE $\Rightarrow$ $\boxed{T_2 = \text{const}}$

(reservior)

$$\left\langle \frac{dU_1}{dt} \right\rangle \propto \frac{dT_1}{dt} = \gamma (T_2 - T_1)$$

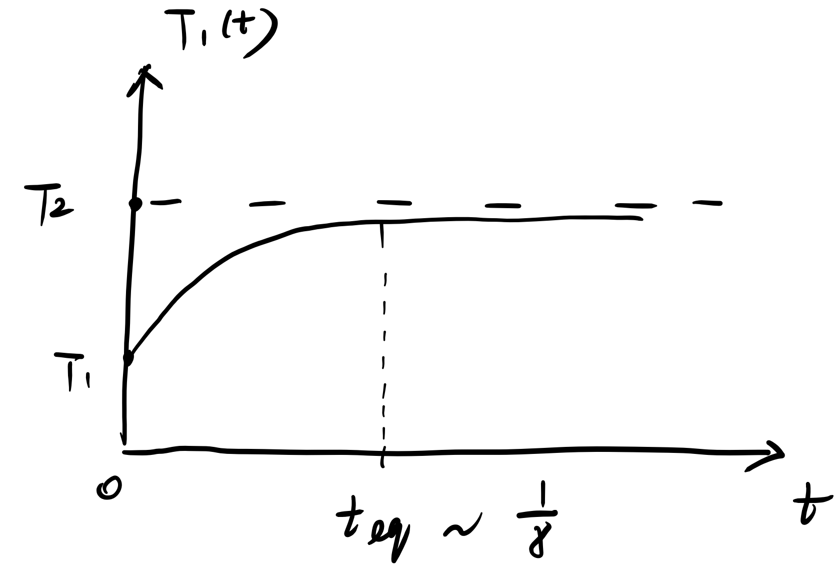
$\Downarrow$ $x = T_1 - T_2$

$$\frac{dx}{dt} = -\gamma x$$

It is straightforward to find the solution $X(t)$

$$X(t) = X(0)\, e^{-\gamma t} = -(T_2 - T_1)\, e^{-\gamma t}$$

$$T_1(t) = T_2 - (T_2 - T_1)^{-\gamma t}$$



It is easy to check

$$\begin{cases} T_1(0) = T_1 \\ T_1(\infty) = T_2 \end{cases}$$

女：有能量交换（two body collision），
并且不是互换能量，m，M
两组分的碰撞，$\Delta E_1 = -\Delta E_2$，
这样能定成 Boltzmann distribution e^{-E/k_BT}
吗？

or Boltzmann distribution's
key point ?

wiki：遍历性需求
均分定律只对处于热平衡的遍历系统有效，这意味着同一能量的态被选择的可能性必然一样。系统要让它所有各能量的形态的能量能够互相交换，或在遍历系统中跟一热库一起。