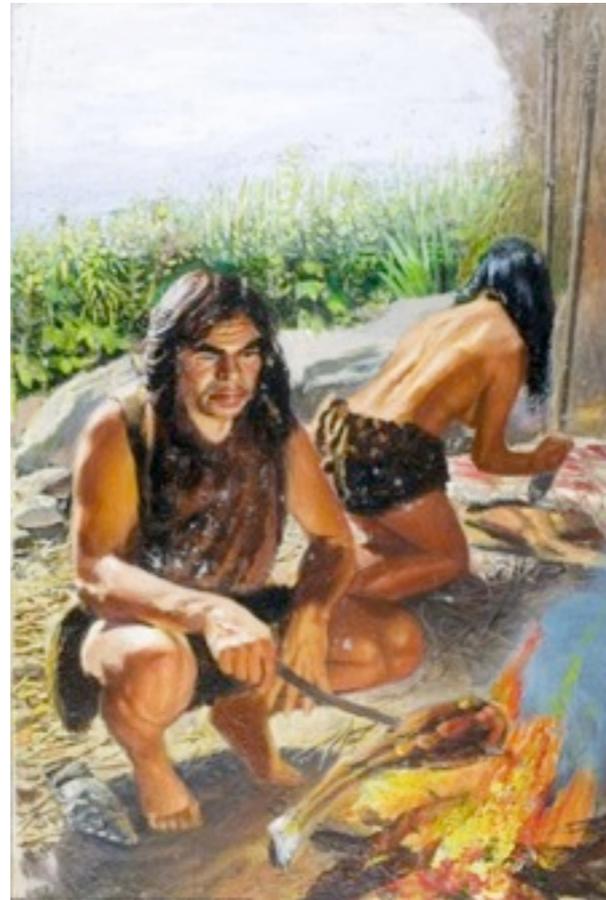


# 第一章：热力学系统的平 衡态及状态方程

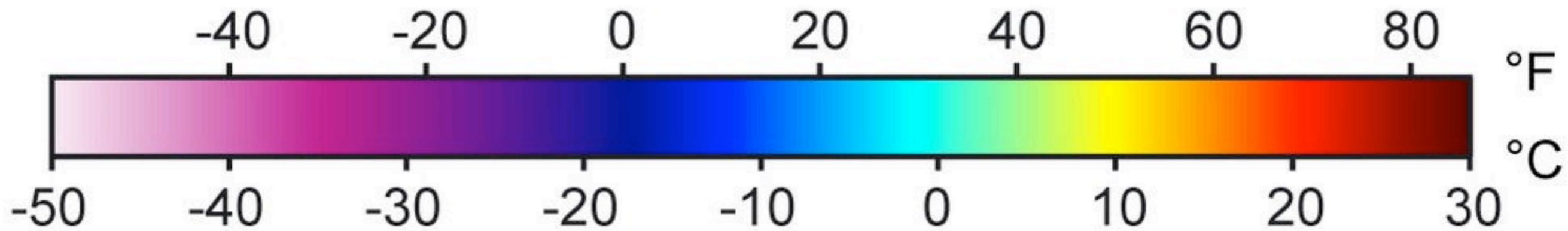
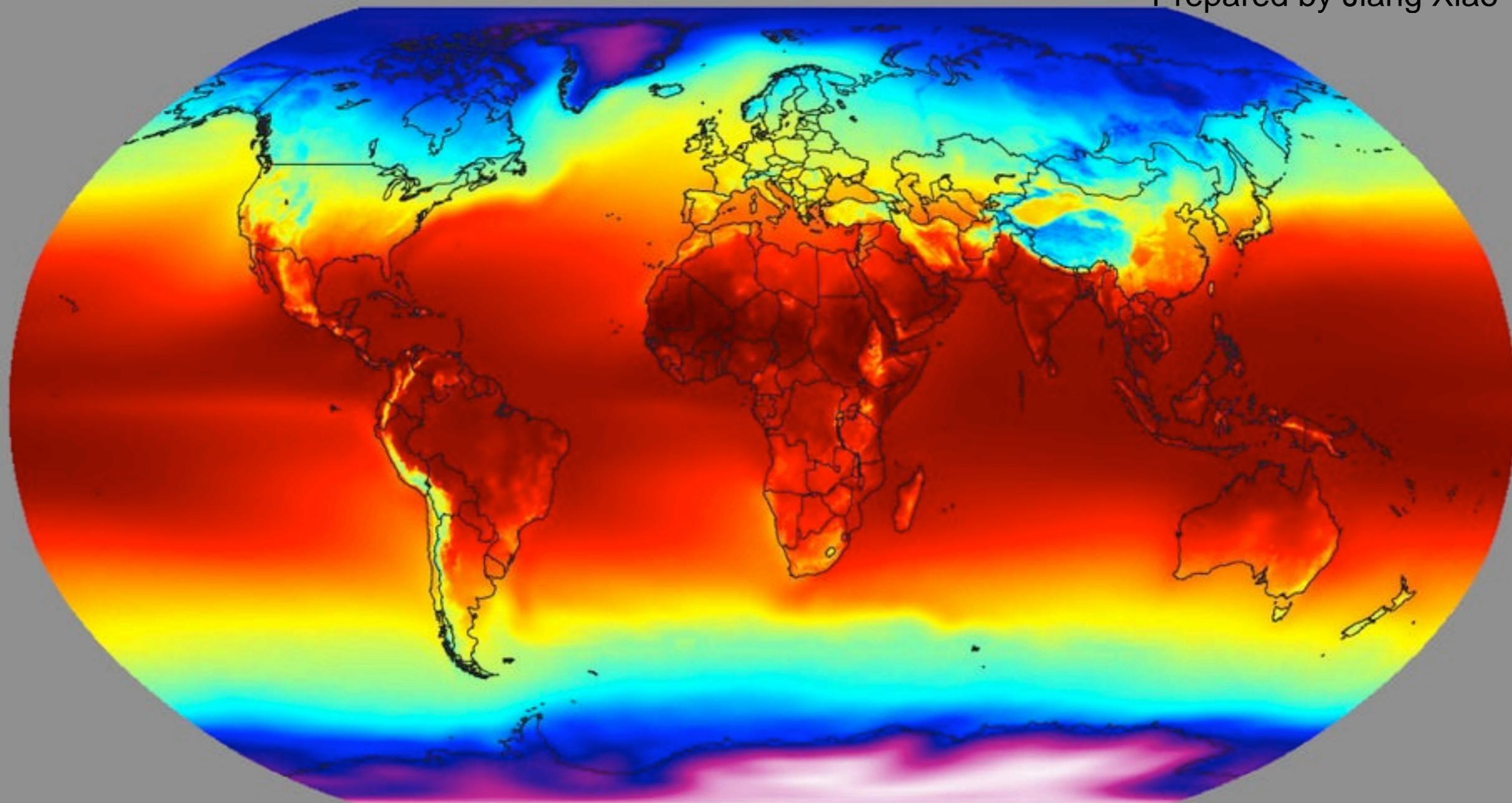
---

# 火与热

---



火刑、炮烙之刑、火烧赤壁

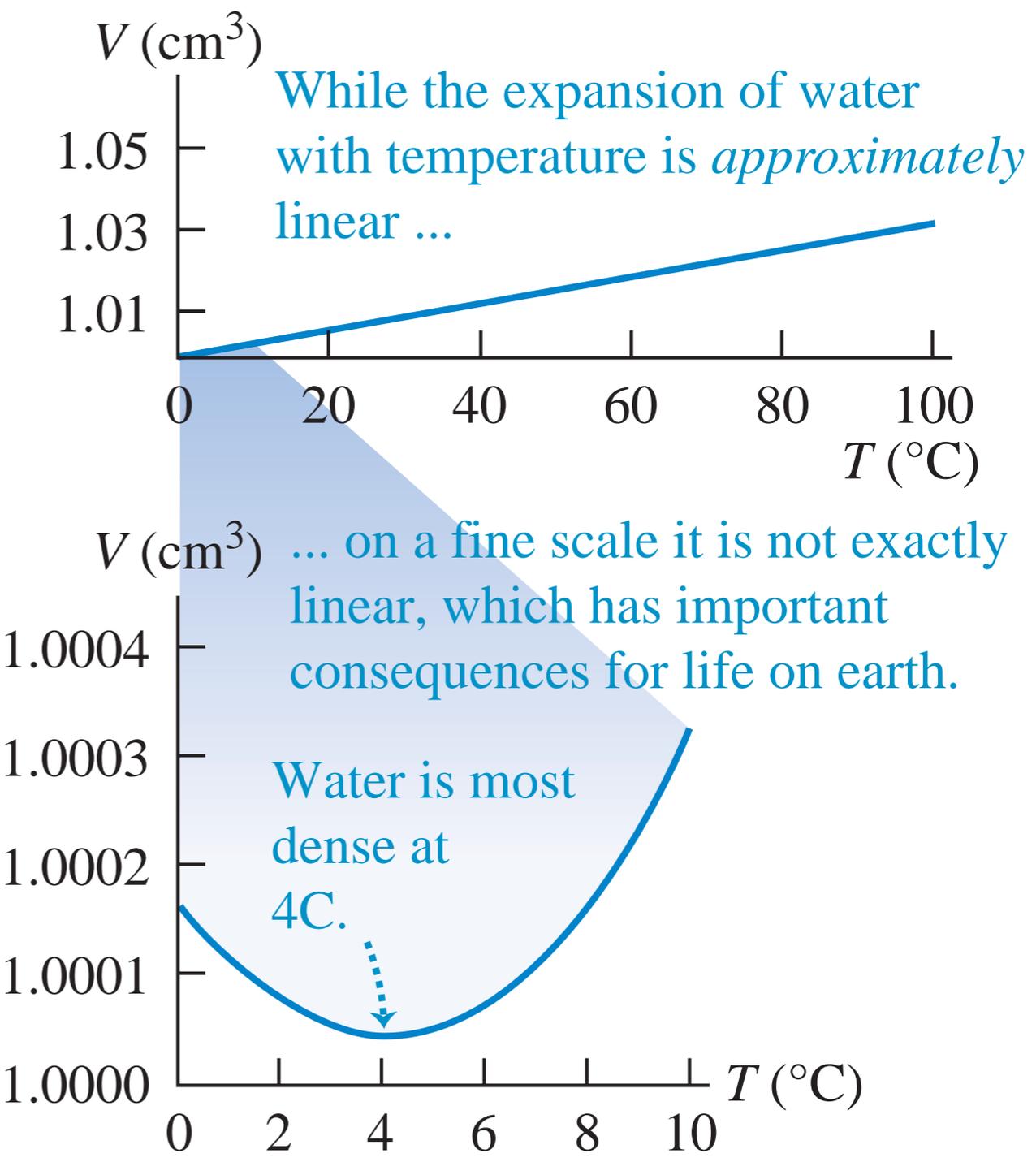


**Annual Mean Temperature**

# 热胀冷缩



### 液态水的热胀冷缩



# 热质说与分子运动说

---

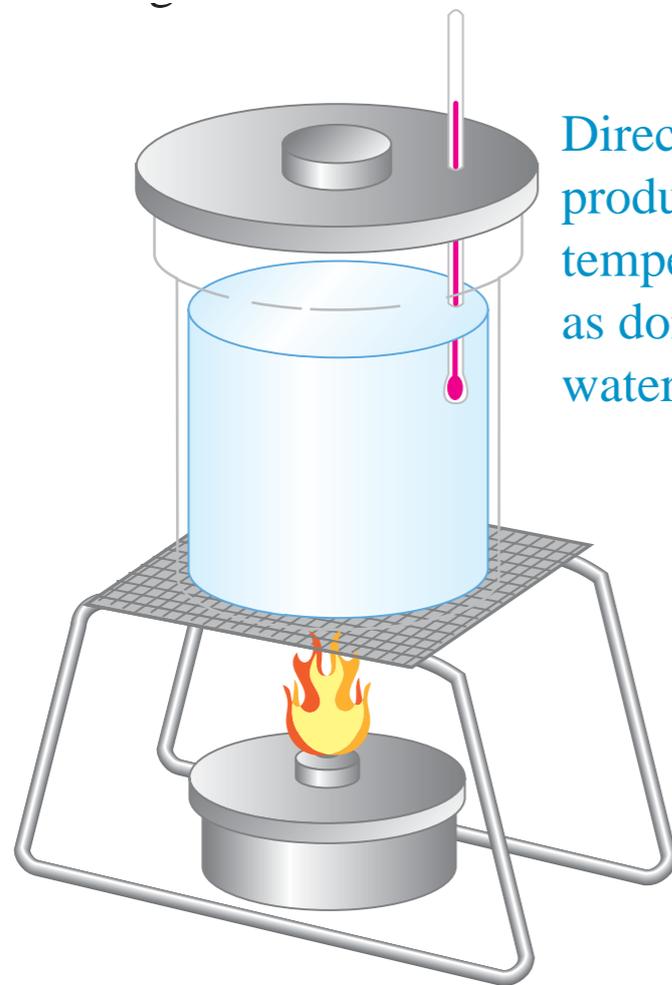
热质是以一种无质量的气体，可以从热的物体流向冷的物体。

摩擦生热、钻木取火表明热可以由机械功转化而来。

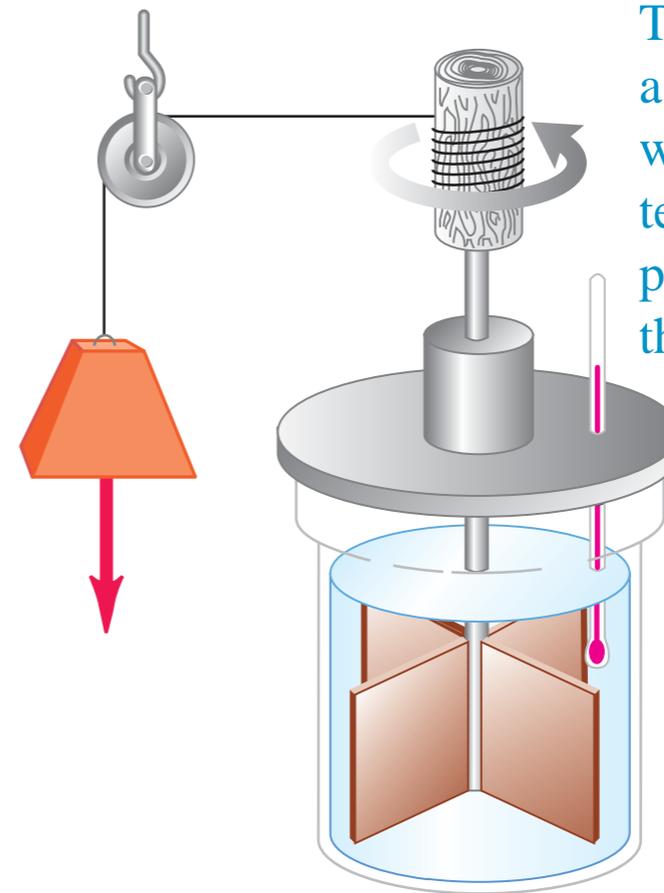
热是原子分子的无规则运动，热的物体分子运动剧烈，热量是分子无规则运动的能量。

热学基本概念：温度、热量

# 热和比热



Direct heating can produce the same temperature change as doing work on the water.



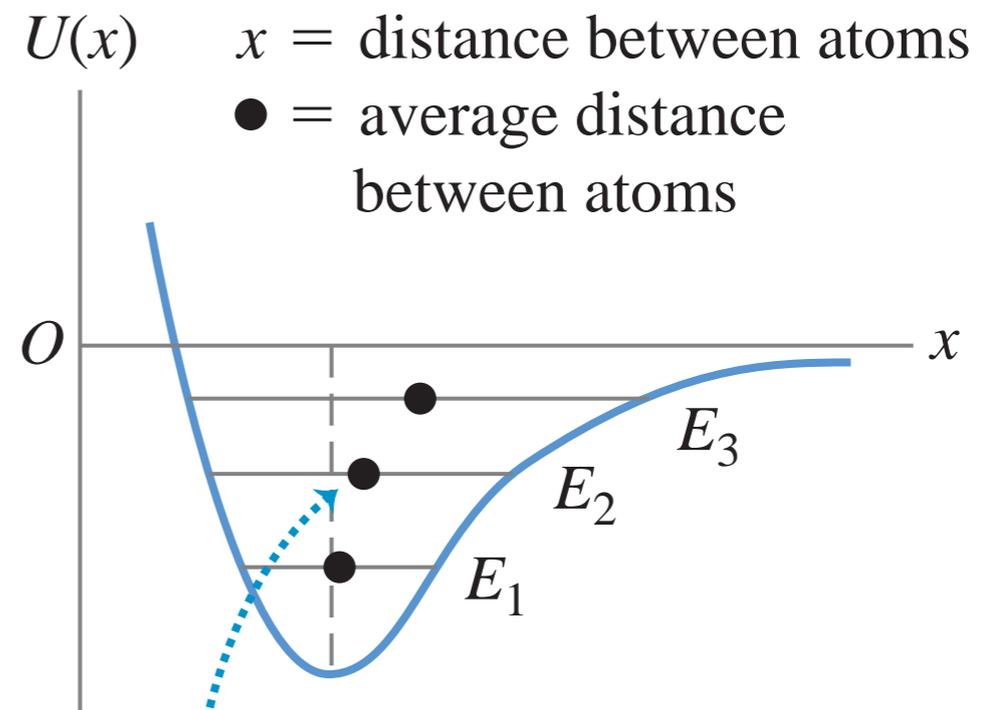
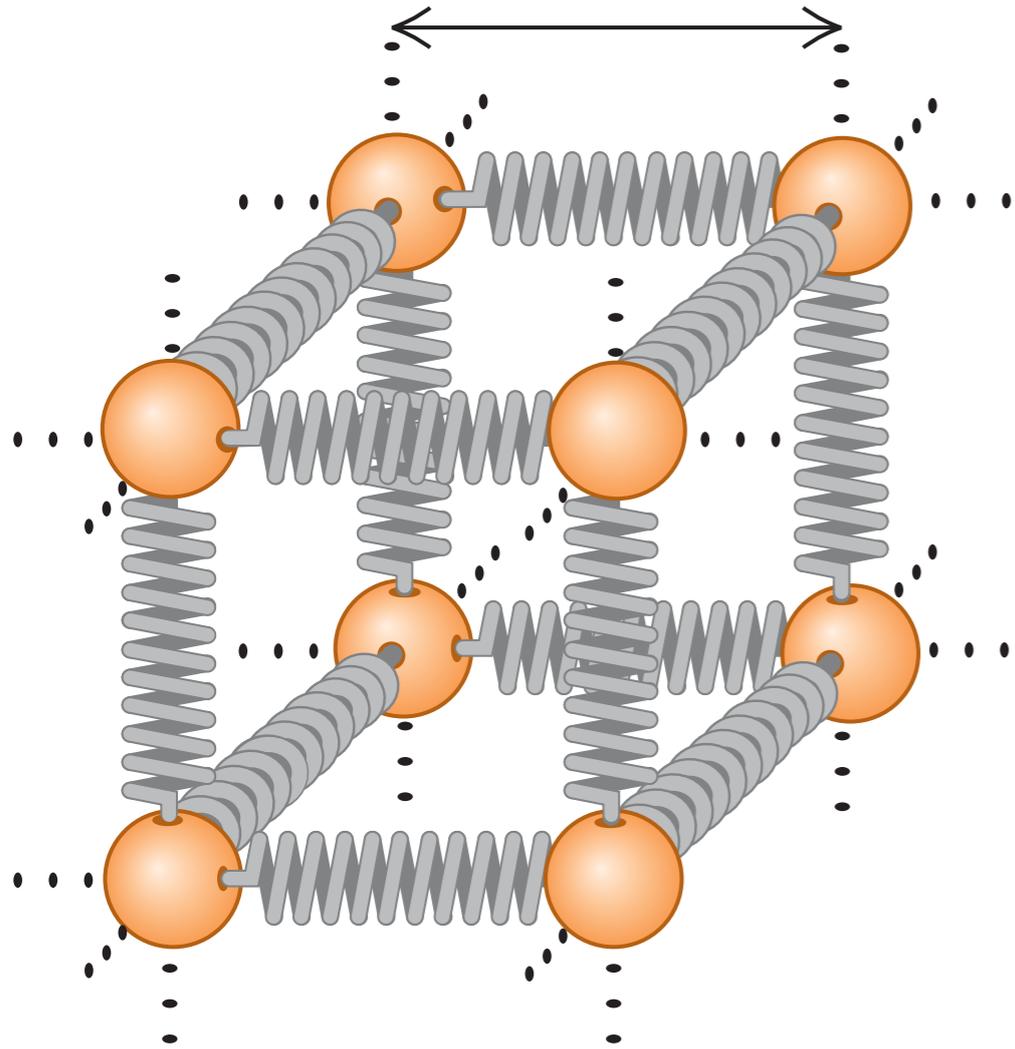
The water warms as the paddle does work on it; the temperature rise is proportional to the amount of work done.

$$\Delta Q = mc\Delta T \quad \Rightarrow \quad c = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

# 分子运动和物质状态

## Lennard-Jones potential

Average distance between atoms

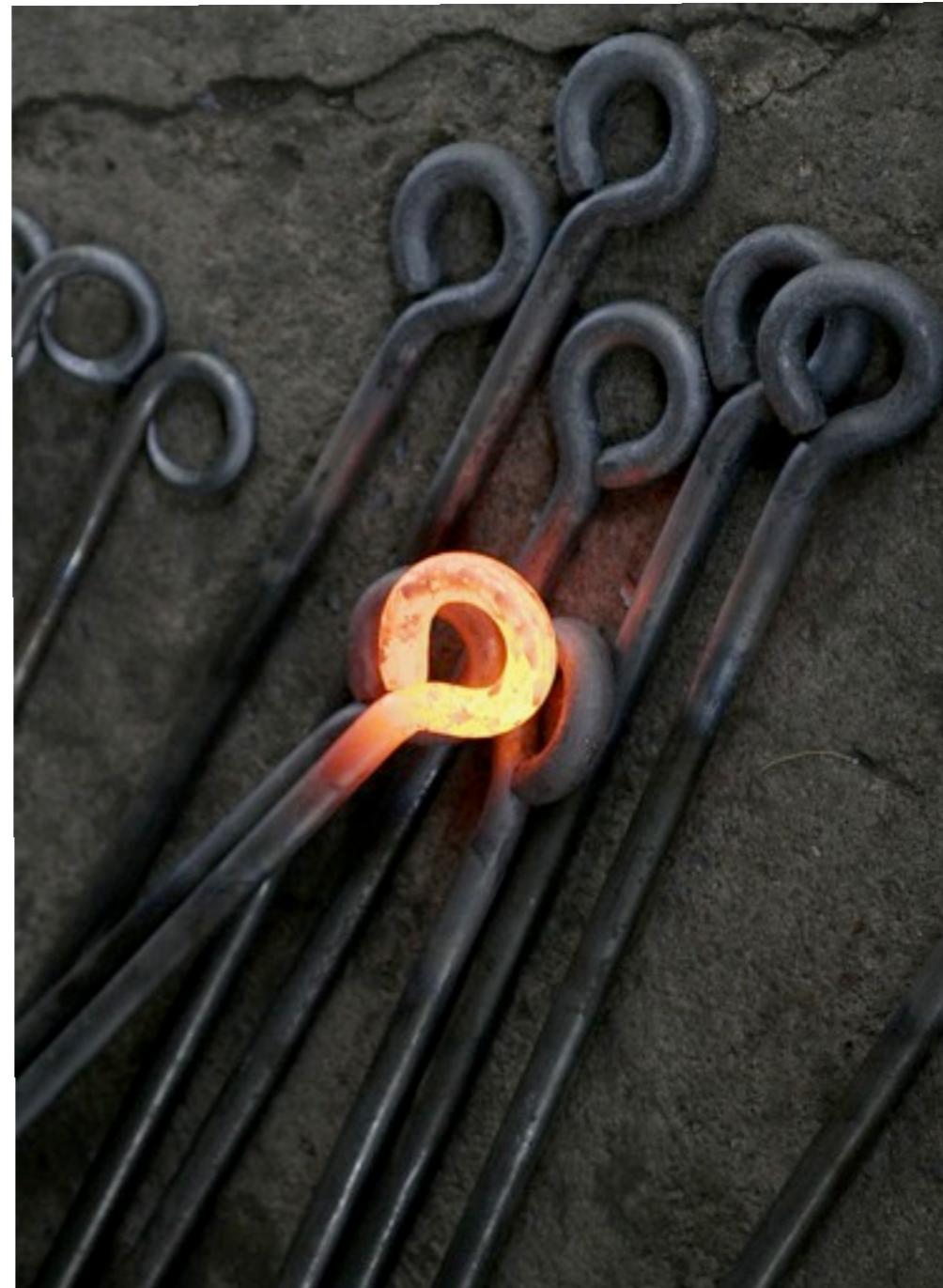
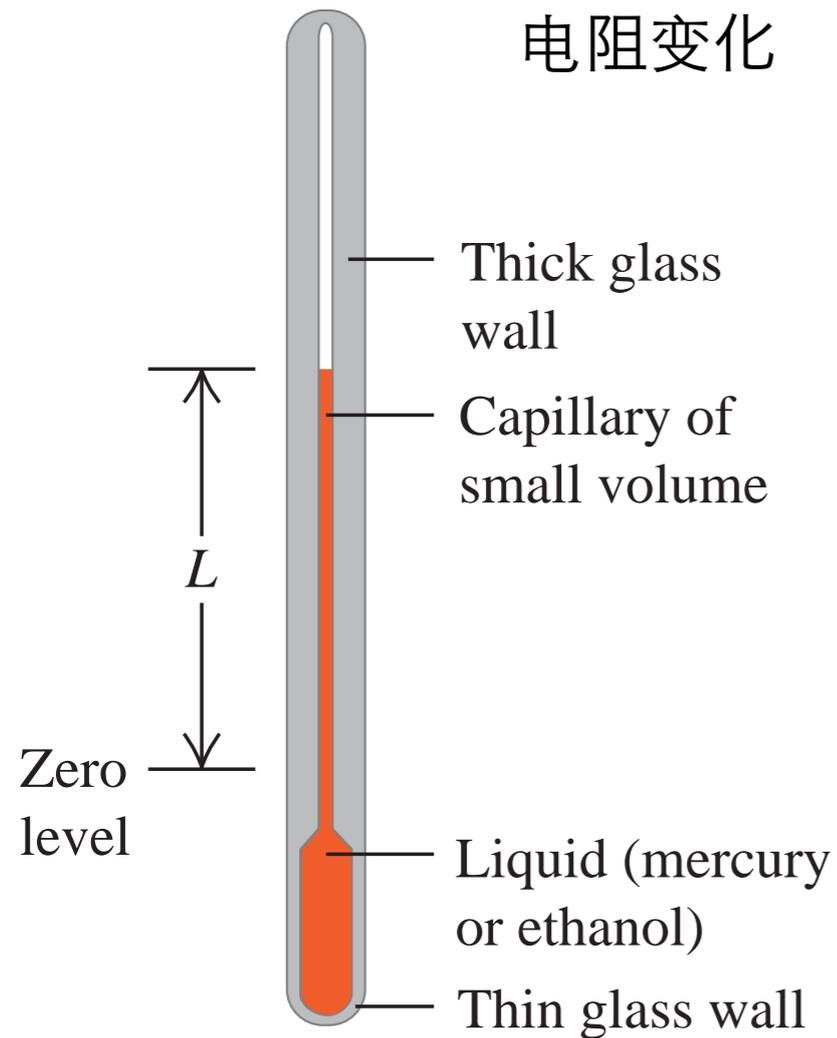


As energy increases from  $E_1$  to  $E_2$  to  $E_3$ , average distance between atoms increases.

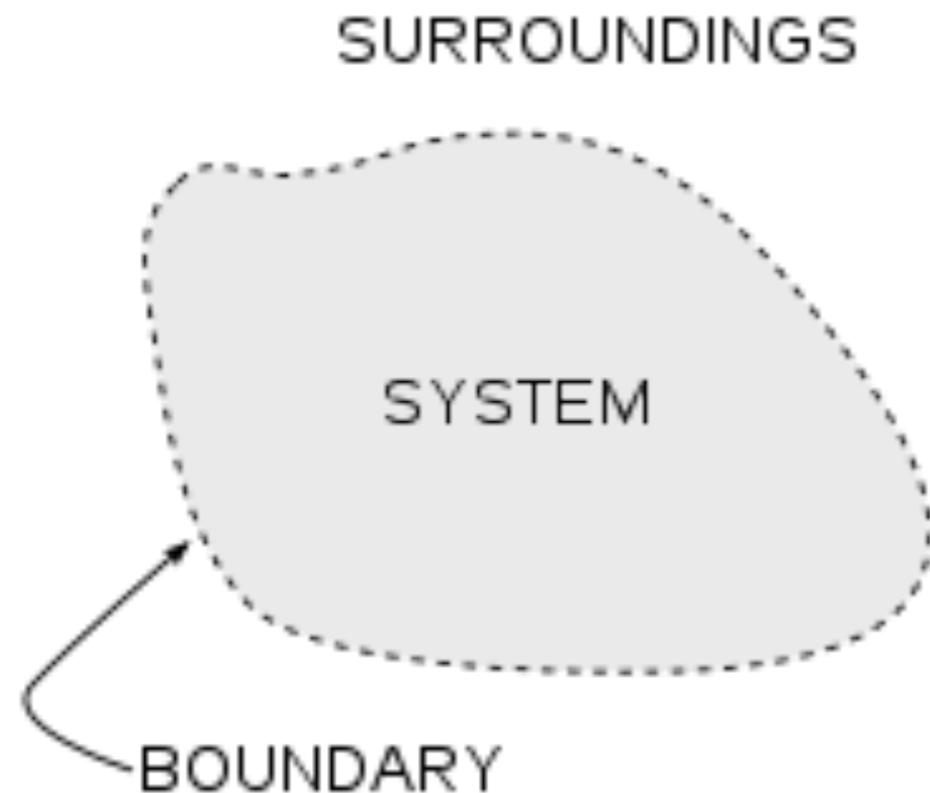
$$E = \frac{1}{2} m \bar{v}^2 \propto T$$

# 温度计

温度的影响：热胀冷缩  
蒸腾凝聚  
焰色变化  
电阻变化



# 热力学体系



阿佛加德罗常数： $N_A = 6 \times 10^{23}$

1摩尔 (1 mol) =  $N_A$

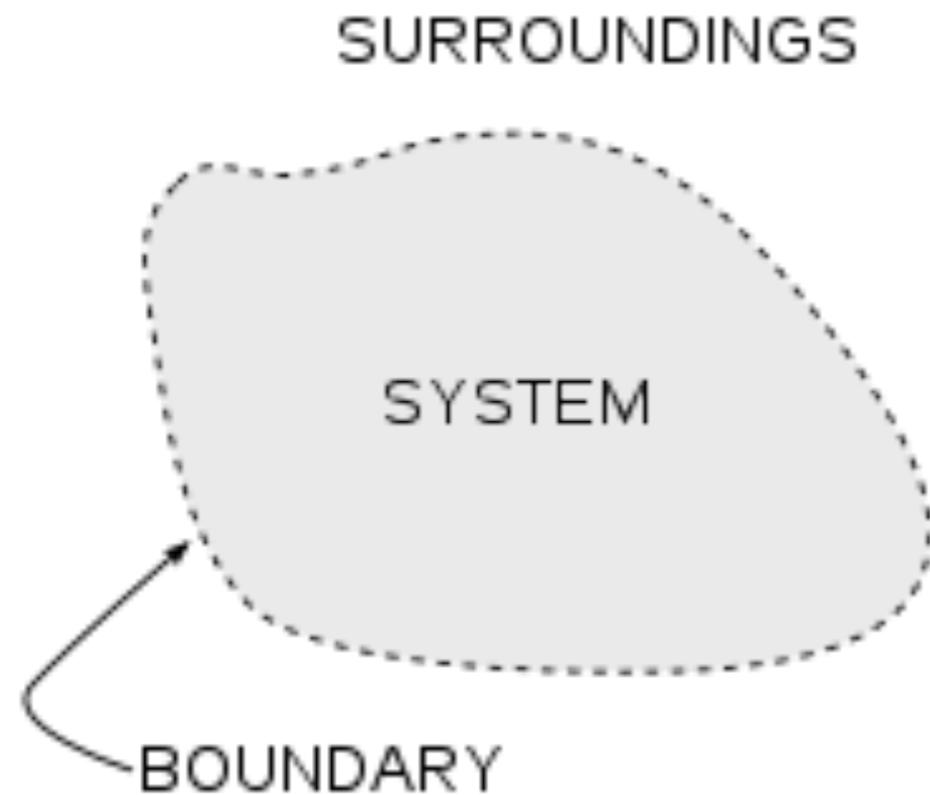
1 mol 水( $H_2O$ ) = 18 g

1 mol 空气( $O_2, N_2$ ) = 29 g

估算地球上空气的总质量、总摩尔数。

系统类别	物质交换	能量交换	做功	例子
孤立体系	无	无	无	刚性绝热容器内的气体
封闭体系	无	有	有	封闭气球内的气体
开放体系	有	有	有	开口容器

# 平衡态和非平衡态



**宏观物理量：**

**微观物理量：**

**广延量**

质量( $M$ )

分子质量( $m$ )

体积( $V$ )

直径( $d$ )

热容量( $C_V, C_p$ )

速度( $v$ )

**强度量**

温度( $T$ )

动量( $p$ )

压强( $p$ )

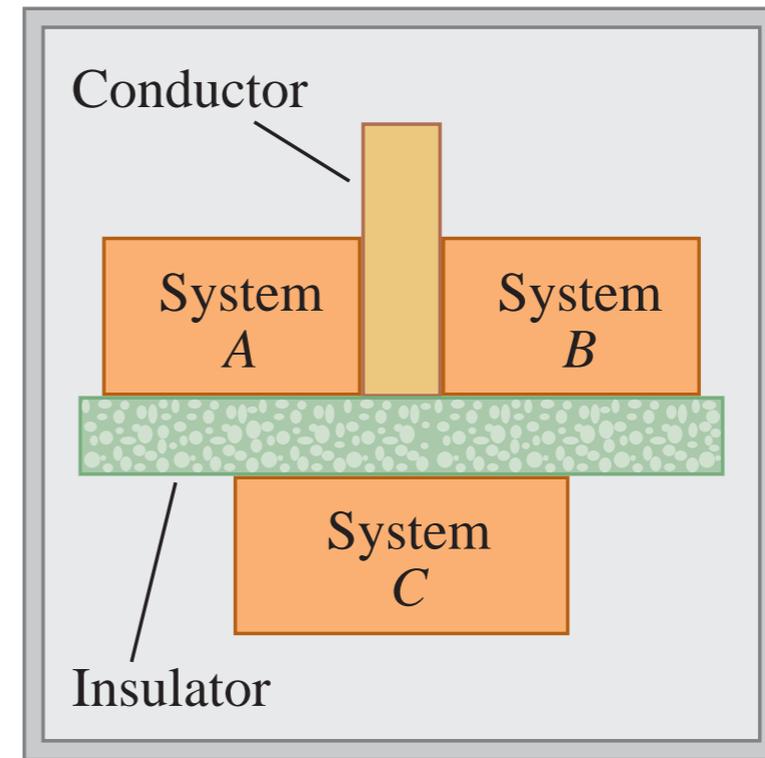
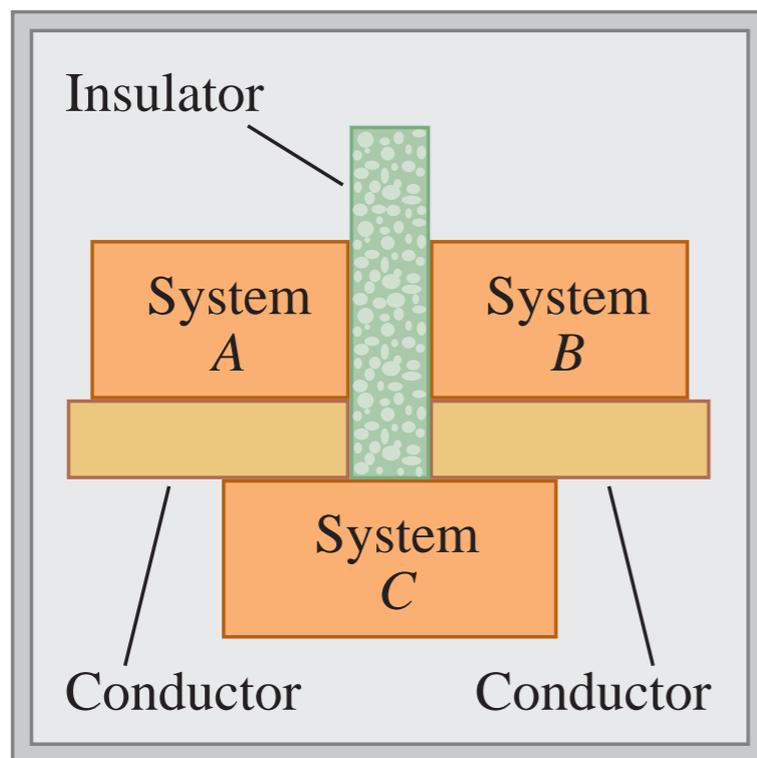
能量( $E$ )

平衡态：体系的宏观性质不随时间变化。

非平衡态：反之。

# 热力学第零定律

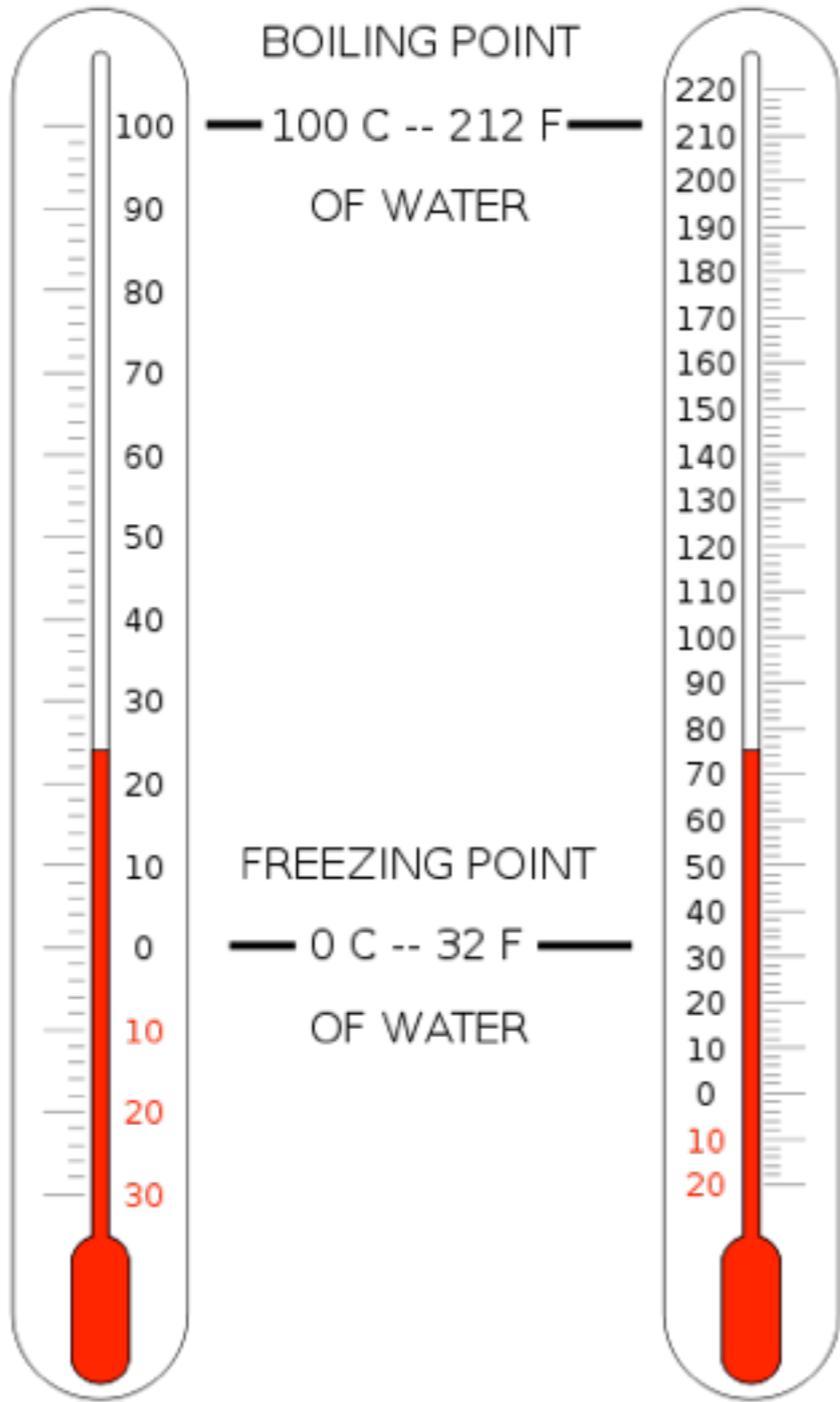
**热力学第零定律**：如果两个热力系的每一个都与第三个热力系处于热平衡，则它们彼此也处于热平衡。



两个系统处于热平衡当且仅当它们具有相同的温度。

# 温度计和温标

摄氏温标 (°C, Celsius, 1742)



CENTIGRADE

FAHRENHEIT

华氏温标 (°F, Fahrenheit, 1714)

	K	C	F
Water boils	373	100°	212°
	↑ 100 K	↑ 100 C°	↑ 180 F°
Water freezes	273	0°	32°
CO <sub>2</sub> solidifies	195	-78°	-109°
Oxygen liquefies	90	-183°	-298°
Absolute zero	0	-273°	-460°

绝对温度 (K, Kelvin)

$$T_K = T_C + 273.15$$

# 温度计

$10^{39}\text{K}$  : 大爆炸后宇宙温度

$10^9\text{K}$  : 宇宙He合成

$10^7\text{K}$  : 热核聚变温度

$10^4\text{K}$  : 太阳表面温度

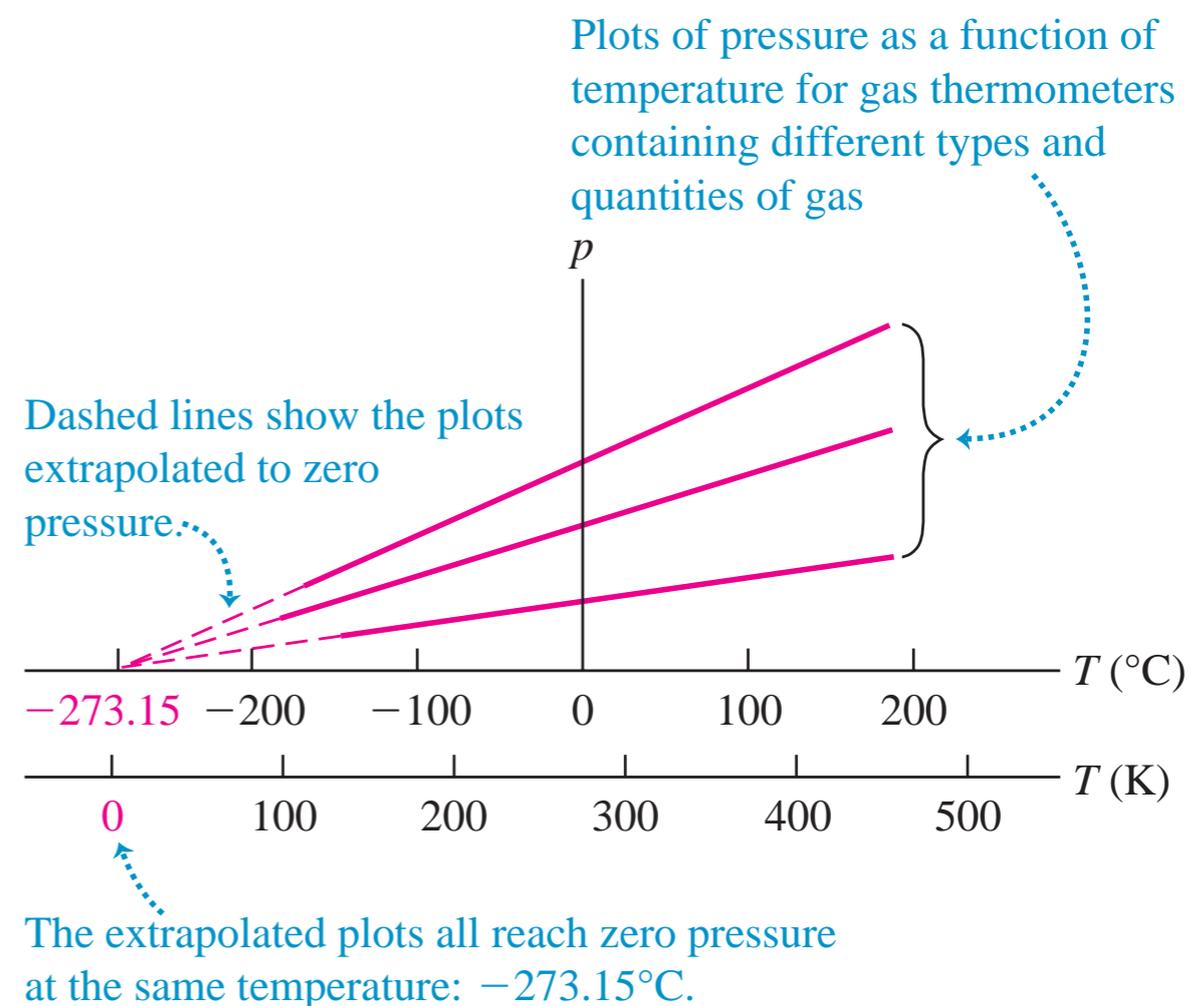
$10^2\text{K}$  : 室温

$10\text{K}$  : 氢的液化

$3\text{K}$  : 微波背景辐射

$10^{-3}\text{K}$  : 稀释致冷

$10^{-8}\text{K}$  : 核自旋致冷

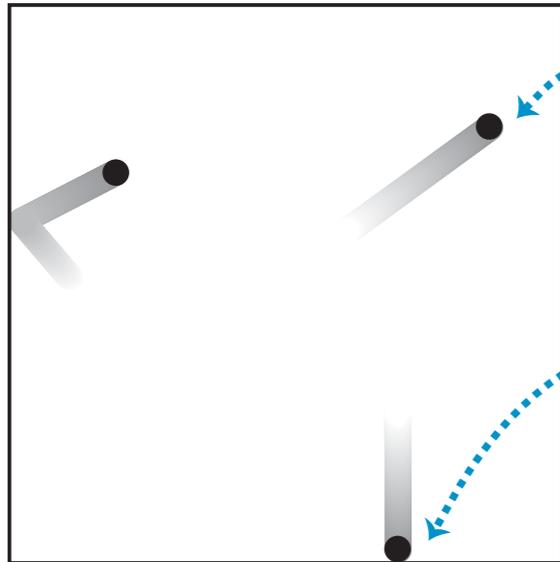


$$p = p_0(1 + \alpha_p T_C) = p_0 T_K$$

绝对温度 (K, Kelvin)  $T_K = T_C + 273.15$

# 理想气体和实际气体

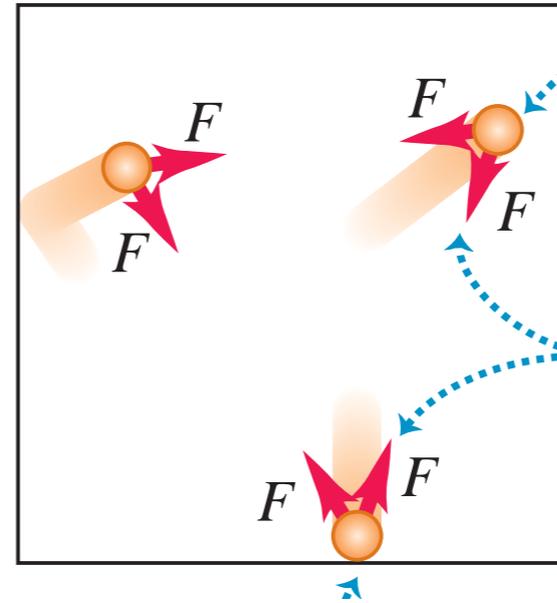
理想气体



Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

实际气体



Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

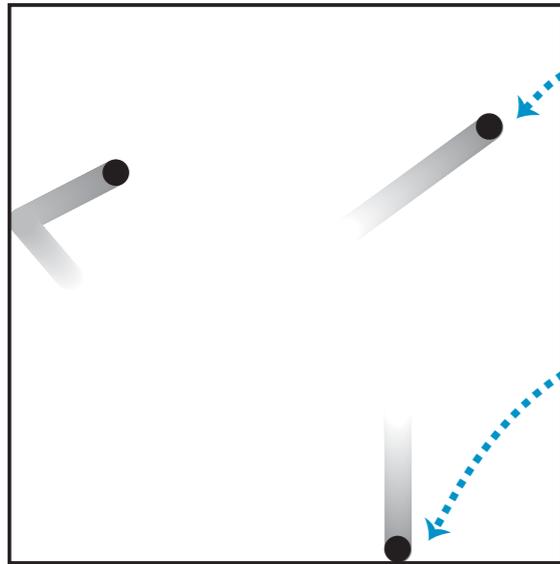
理想气体假设：

1. 分子本身占有空间体积可忽略不计
2. 分子之间及分子与容器壁之间不断弹性碰撞
3. 除在碰撞瞬间外，分子之间、分子与容器壁之间无相互作用
4. 分子运动遵守经典牛顿力学规律

$$d = \left( \frac{1 \text{ m}^3}{\frac{\rho_{\text{air}}}{29 \text{ g/mol}} N_A} \right)^{1/3} \sim 3.4 \text{ nm} \gg r_{\text{O}_2} \sim 0.3 \text{ nm}$$

# 理想气体和实际气体

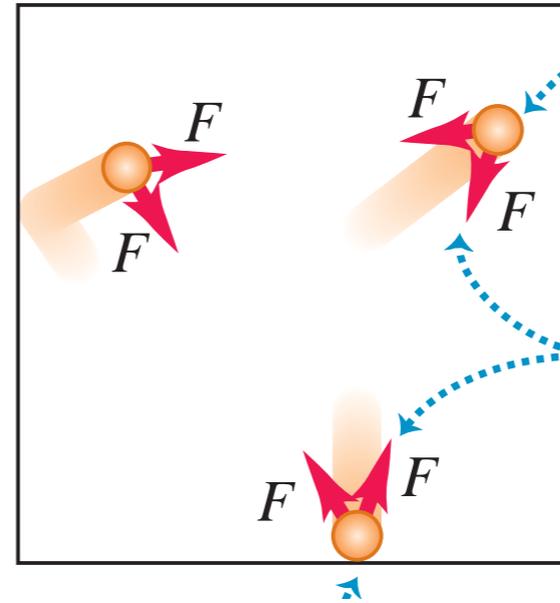
理想气体



Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

实际气体



Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

状态参量：压强( $p$ ), 体积( $V$ ), 温度( $T$ )

状态方程： $f(p, V, T) = 0$

理想气体： $pV = \nu RT$

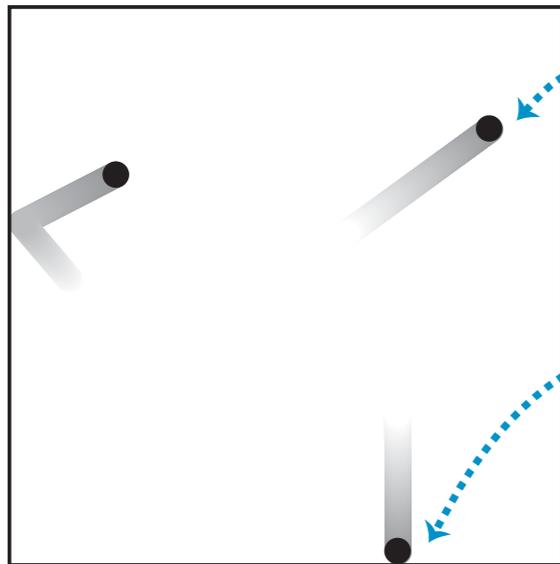
摩尔数： $\nu = \frac{N}{N_A}$  mol

普适气体常数： $R = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$

阿佛加德罗常数： $N_A = 6 \times 10^{23}$

# 理想气体和实际气体

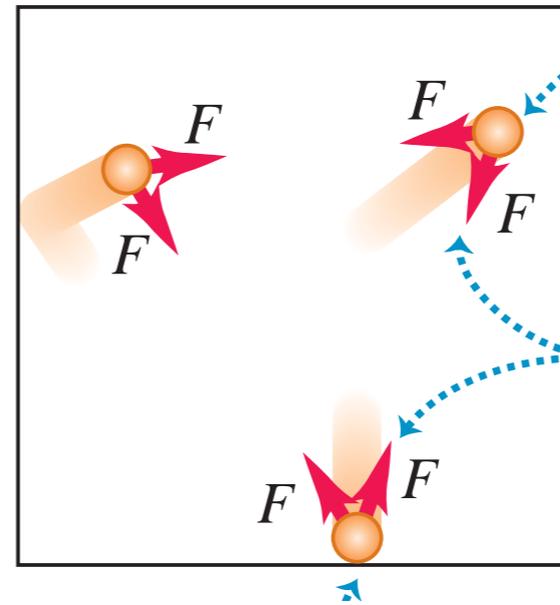
理想气体



Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

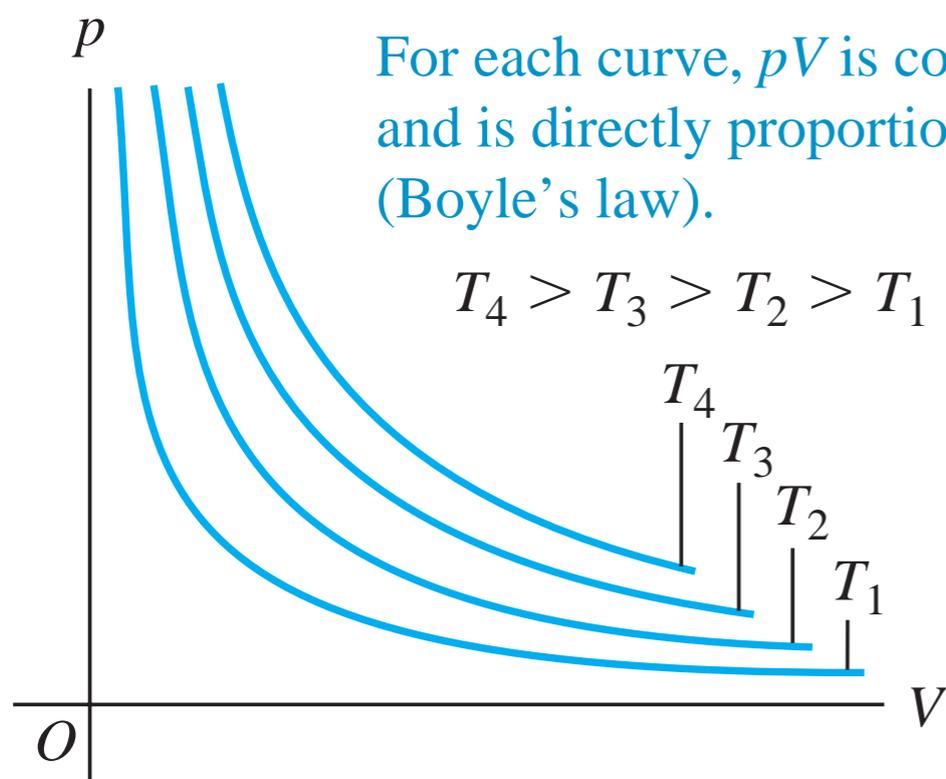
实际气体



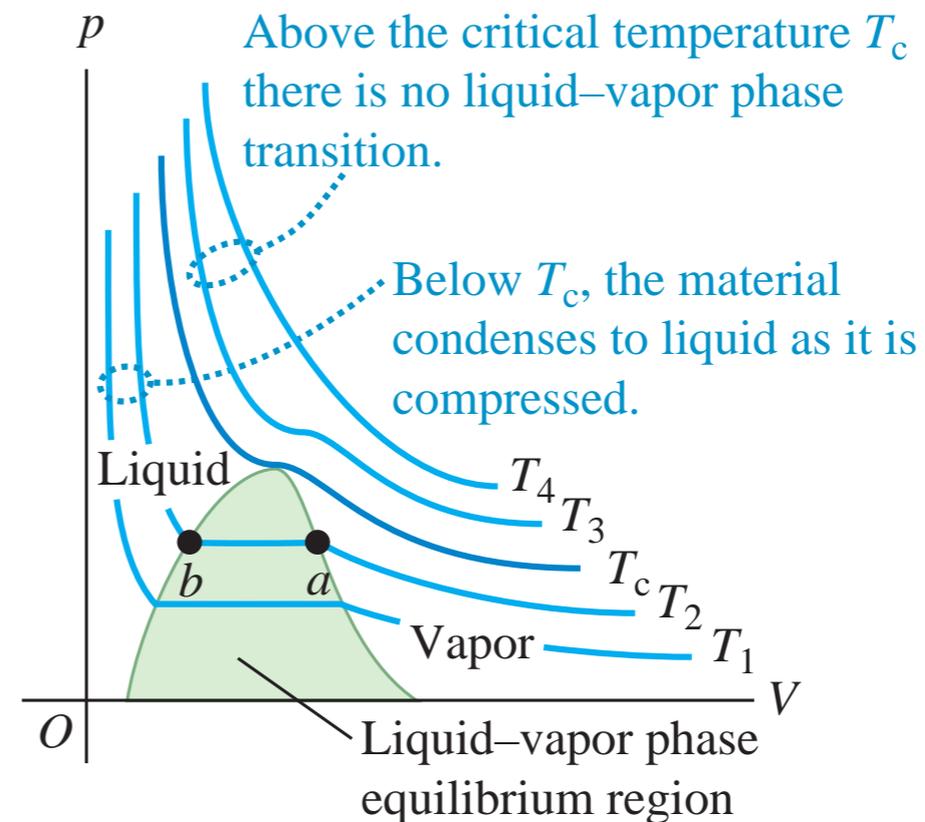
Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

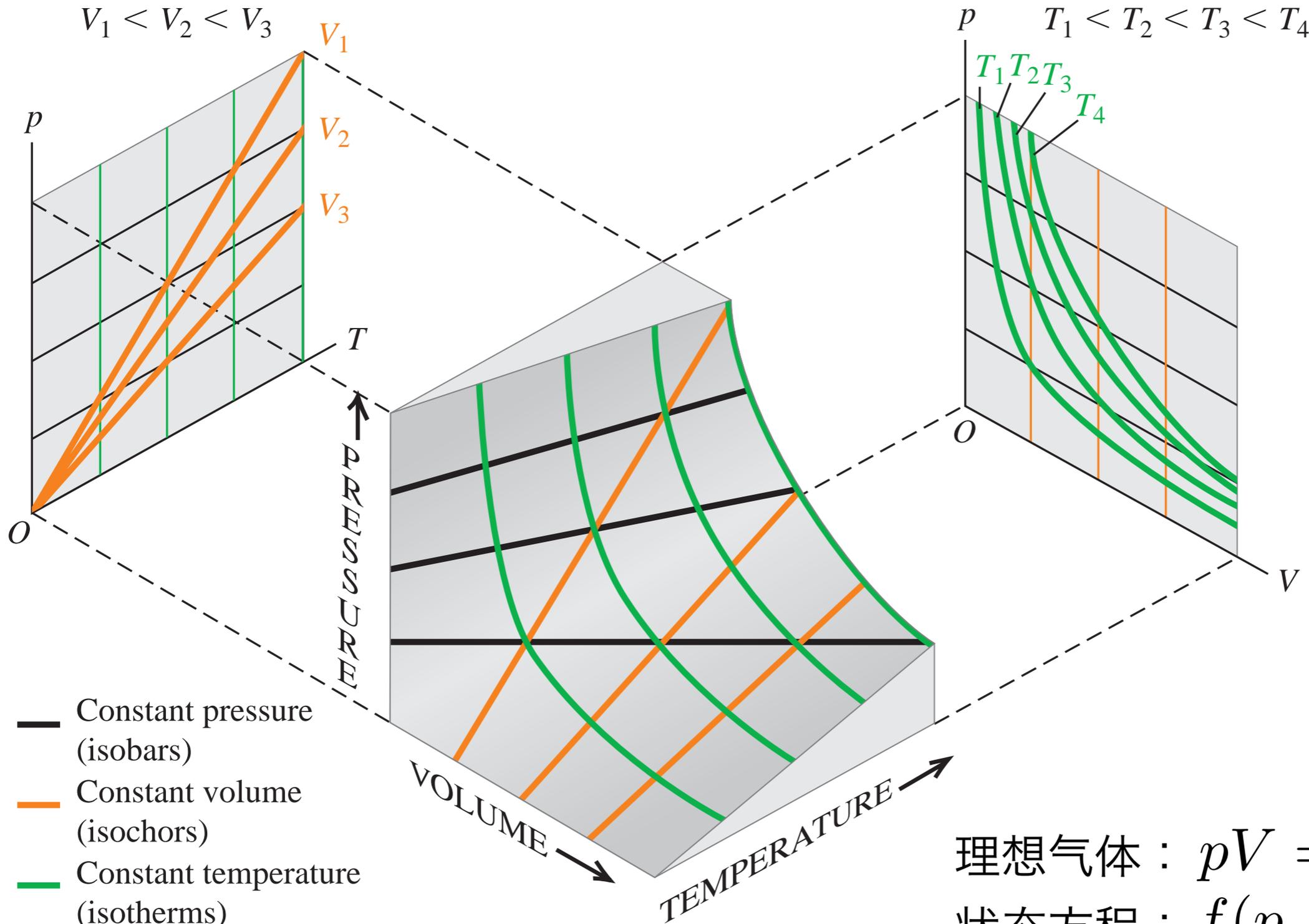
理想气体： $pV = \nu RT$



$T_4 > T_3 > T_c > T_2 > T_1$

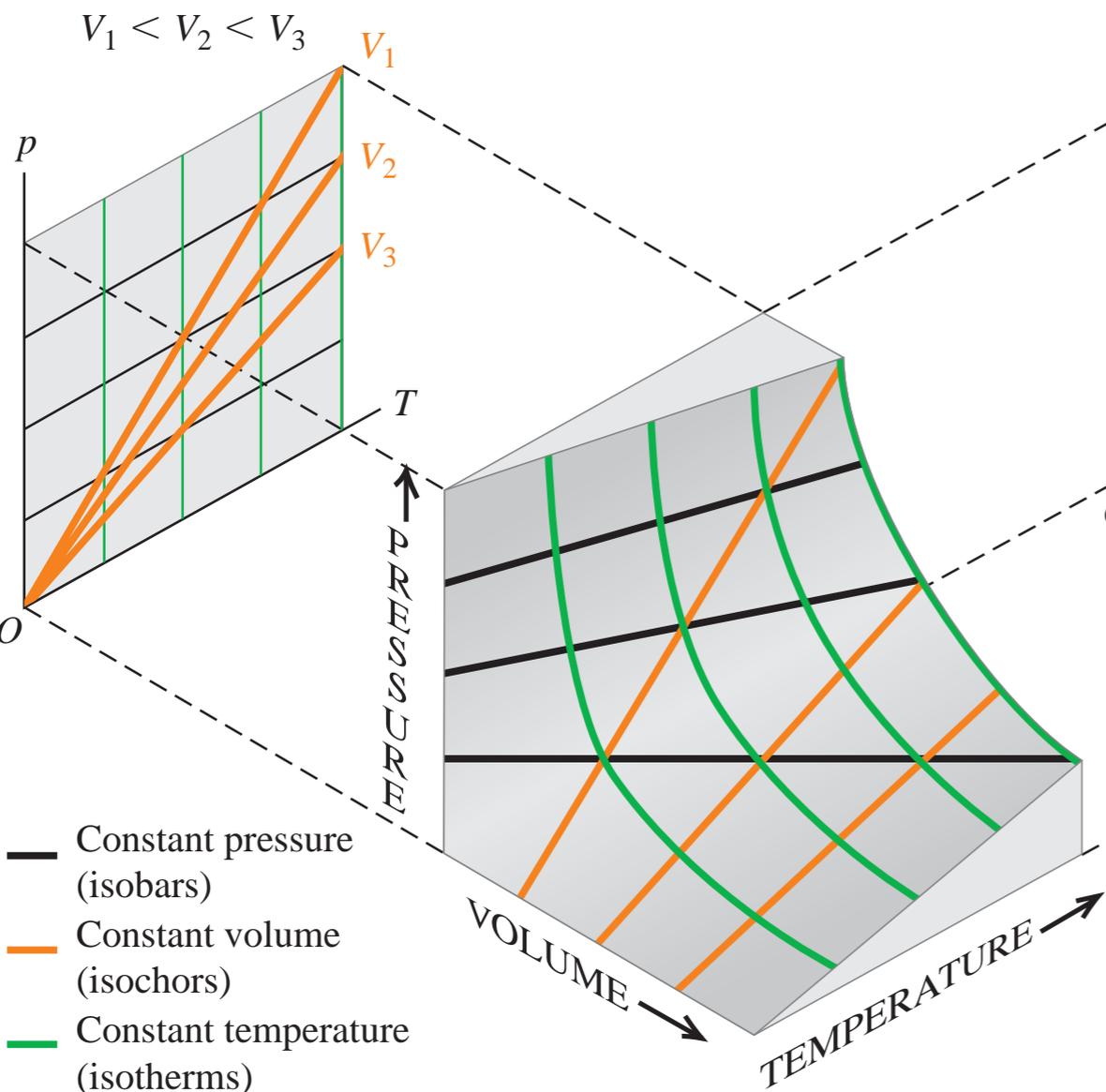


# 理想气体状态图



理想气体： $pV = \nu RT$   
状态方程： $f(p, V, T) = 0$

# 理想气体状态方程



玻意耳-马略特定律： $pV = k_1$

查理定律： $\frac{V}{T} = k_2$

盖-吕萨克定律： $\frac{p}{T} = k_3$

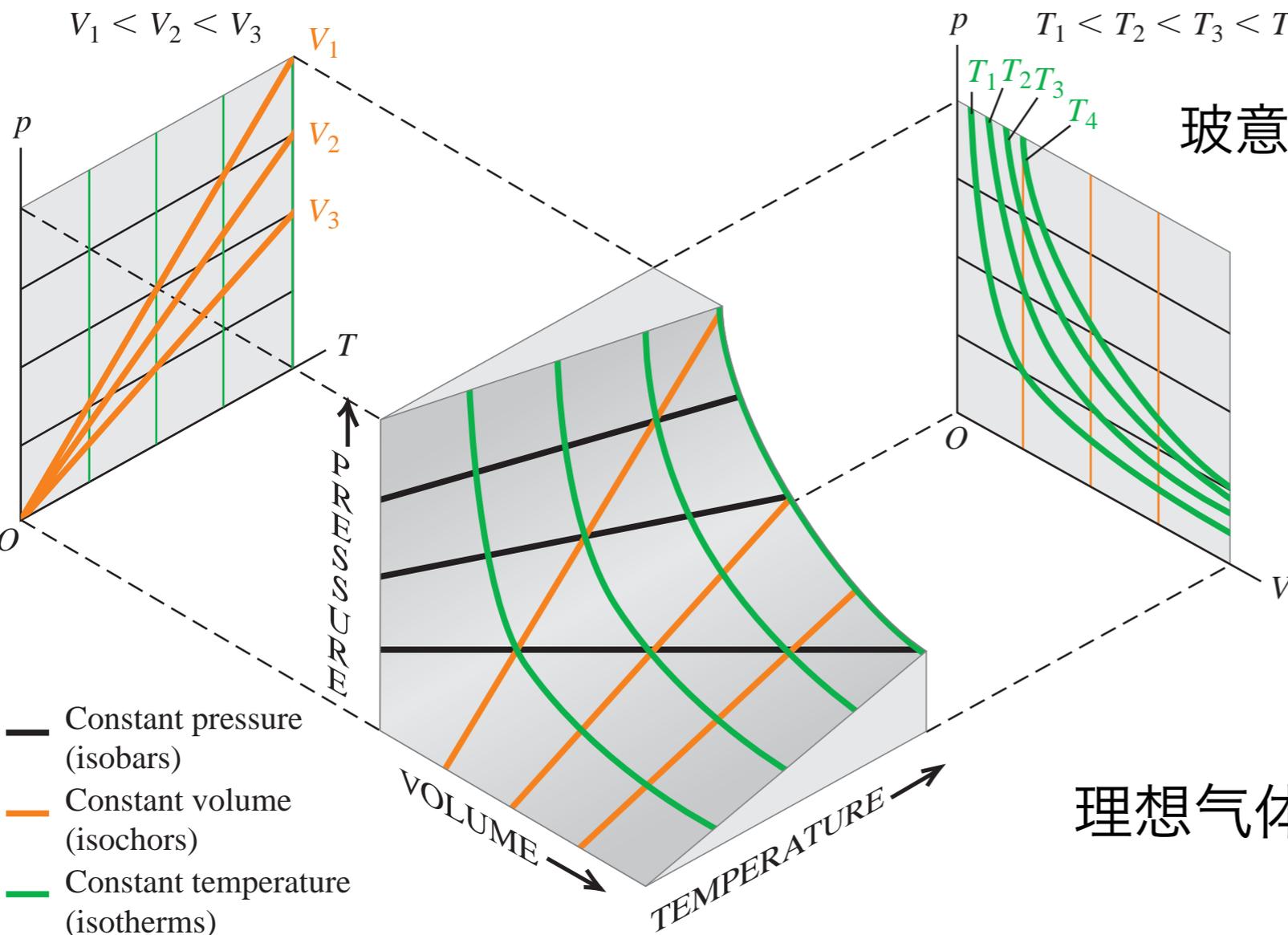
理想气体状态方程： $pV = \nu RT$

摩尔数： $\nu = \frac{N}{N_A} \text{ mol}$

阿佛加德罗常数： $N_A = 6 \times 10^{23}$

普适气体常数： $R = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$

# 理想气体状态方程



玻意耳-马略特定律： $pV = k_1$

查理定律： $\frac{V}{T} = k_2$

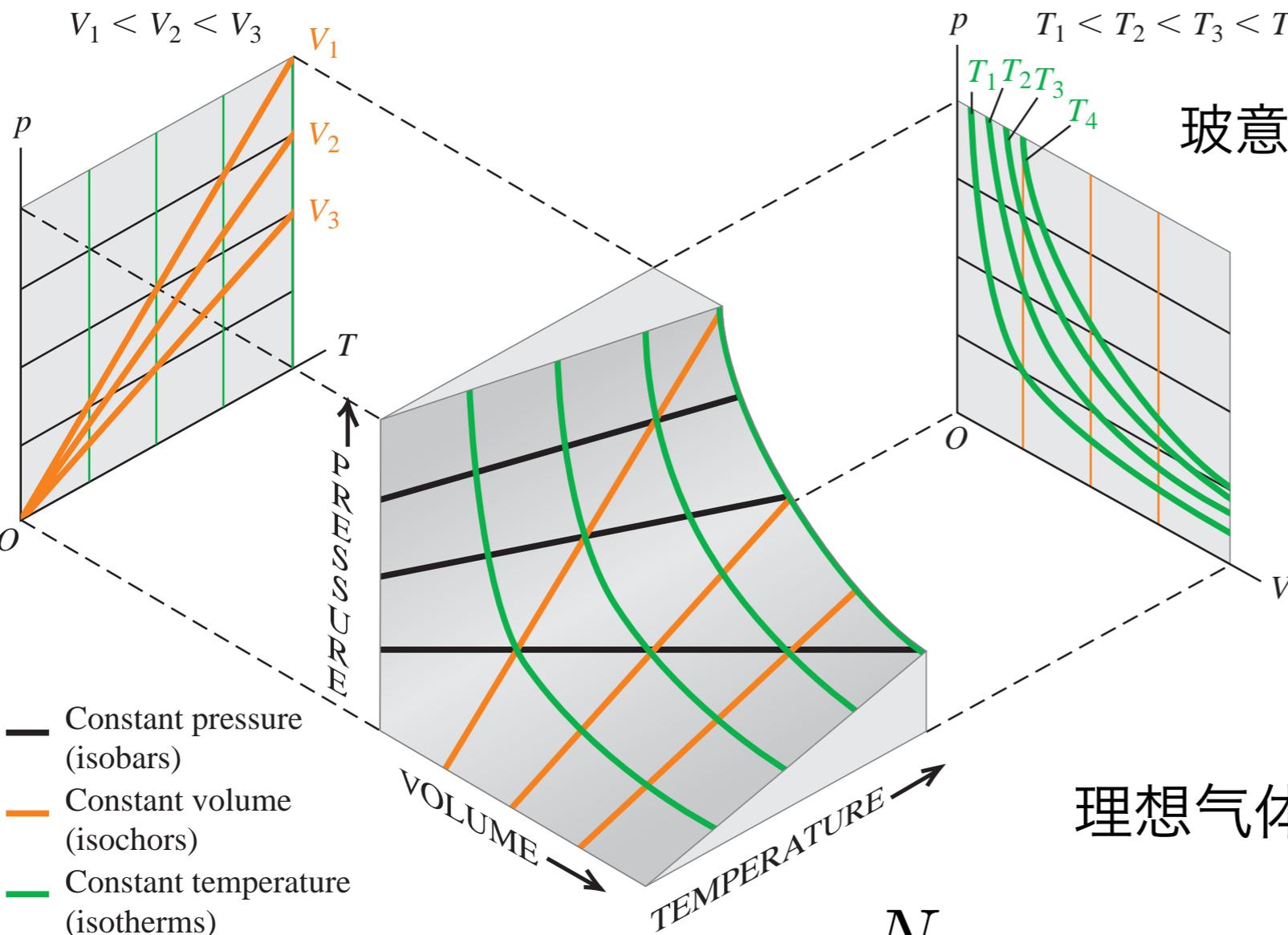
盖-吕萨克定律： $\frac{p}{T} = k_3$

理想气体状态方程： $pV = \nu RT$

- Constant pressure (isobars)
- Constant volume (isochors)
- Constant temperature (isotherms)

道尔顿分压定律 (n种气体混合)： $\nu = \sum_i \nu_i, \quad p = \sum_i p_i$

# 理想气体状态方程



玻意耳-马略特定律： $pV = k_1$

查理定律： $\frac{V}{T} = k_2$

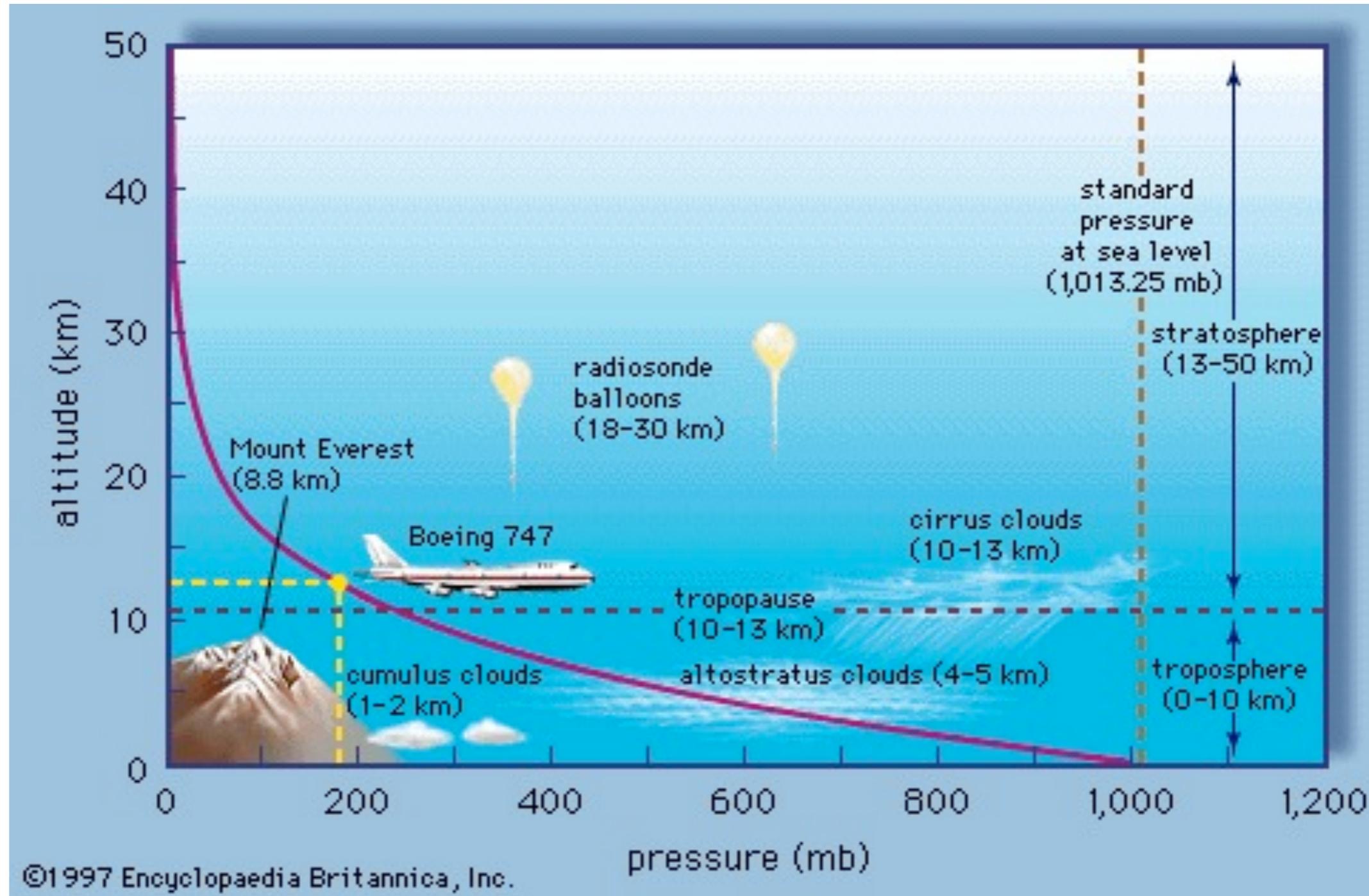
盖-吕萨克定律： $\frac{p}{T} = k_3$

理想气体状态方程： $pV = \nu RT$

$$pV = \frac{N}{N_A} RT \quad \Rightarrow \quad p = \frac{N}{V} \frac{R}{N_A} T = nkT$$

玻尔兹曼常数： $k = 1.38 \times 10^{-23} \text{ J/K}$

# 大气压强随高度变化



# 大气压强随高度变化

压强随高度变化： $p(y)$

假设空气组分**不**随高度变化

密度随高度变化： $\rho(y)$

$$dp(y) = -\rho(y)gdy \quad \Rightarrow \quad \frac{dp(y)}{dy} = -\rho(y)g$$

$$p = nkT = \frac{\rho}{M}kT \quad \Rightarrow \quad \rho(y) = \frac{M}{kT}p(y)$$

空气分子平均质量

$$\frac{dp(y)}{dy} = -\frac{Mg}{kT}p(y) \quad \Rightarrow \quad p(y) = p_0 e^{-Mgy/kT}$$

# 理想气体微观模型

平衡态概率假设：

1. 分子在容器内空间任一点出现的概率相同

2. 分子运动速度按方向分布概率相同（各项同性）

$$n = \frac{dN}{dV} = \frac{N}{V}$$

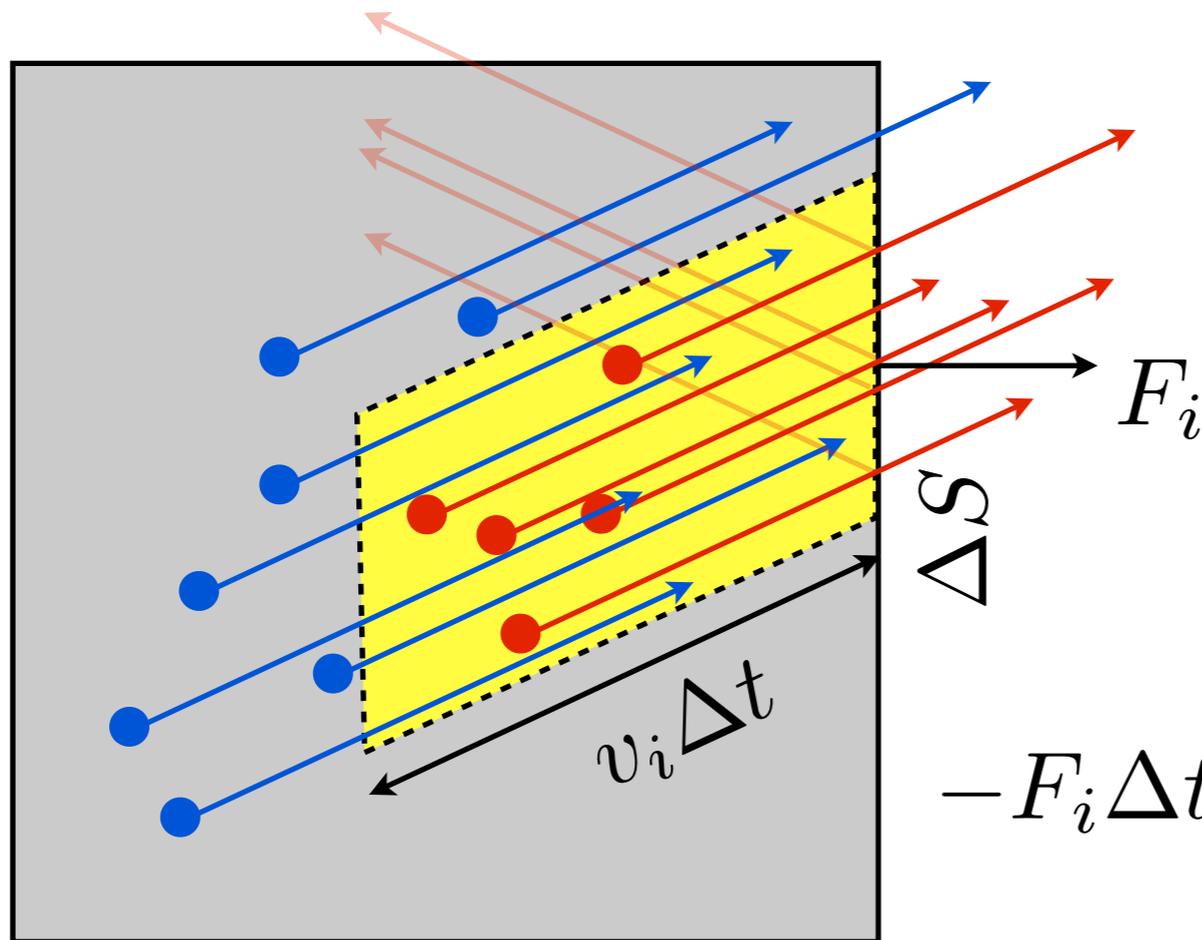
$$\mathbf{v}_i = v_{ix}\hat{\mathbf{x}} + v_{iy}\hat{\mathbf{y}} + v_{iz}\hat{\mathbf{z}}$$

$$\bar{\mathbf{v}} = \frac{1}{N} \sum_i \mathbf{v}_i = 0 \quad \Rightarrow \quad \bar{v}_{x,y,z} = \frac{1}{N} \sum_i v_{ix, iy, iz} = 0$$

$$\bar{v}^2 = \frac{1}{N} \sum_i v_i^2 = \frac{1}{N} \sum_i (v_{ix}^2 + v_{iy}^2 + v_{iz}^2) = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$$

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{1}{3} \bar{v}^2$$

# 理想气体的压强公式



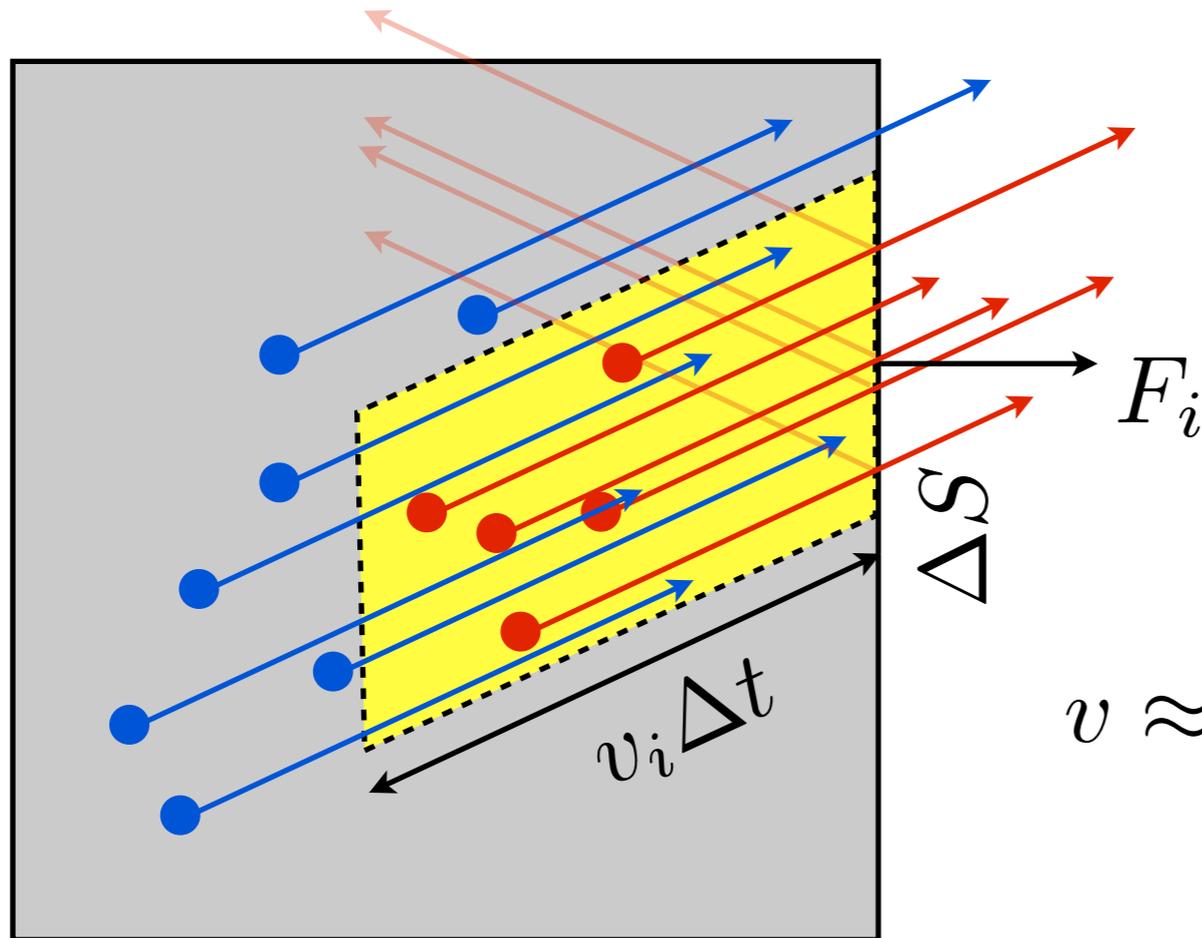
$$\mathbf{v}_i : n_i$$

$$\sum_i n_i = n$$

$$-F_i \Delta t = \Delta P_i = n_i (v_{ix} \Delta t \Delta S) (-2p_{ix})$$

$$\begin{aligned}
 p &= \frac{F}{\Delta S} = \sum_{i, v_{ix} > 0} \frac{F_i}{\Delta S} = 2 \sum_{i, v_{ix} > 0} n_i p_{ix} v_{ix} \\
 &= \sum_i n_i p_{ix} v_{ix} = n \overline{p_x v_x} = \frac{1}{3} n \overline{\mathbf{p} \cdot \mathbf{v}}
 \end{aligned}$$

# 理想气体的压强公式



1、非相对论情形

$$\mathbf{p} = m\mathbf{v} \Rightarrow \mathbf{p} \cdot \mathbf{v} = mv^2 = 2\varepsilon$$

$$p = \frac{1}{3}nm\overline{v^2} = \frac{2}{3}n\overline{\varepsilon}$$

2、极端相对论情形

$$v \approx c \Rightarrow \mathbf{p} \approx (\mathbf{v}/v)\varepsilon/c \Rightarrow \mathbf{p} \cdot \mathbf{v} \approx \varepsilon$$

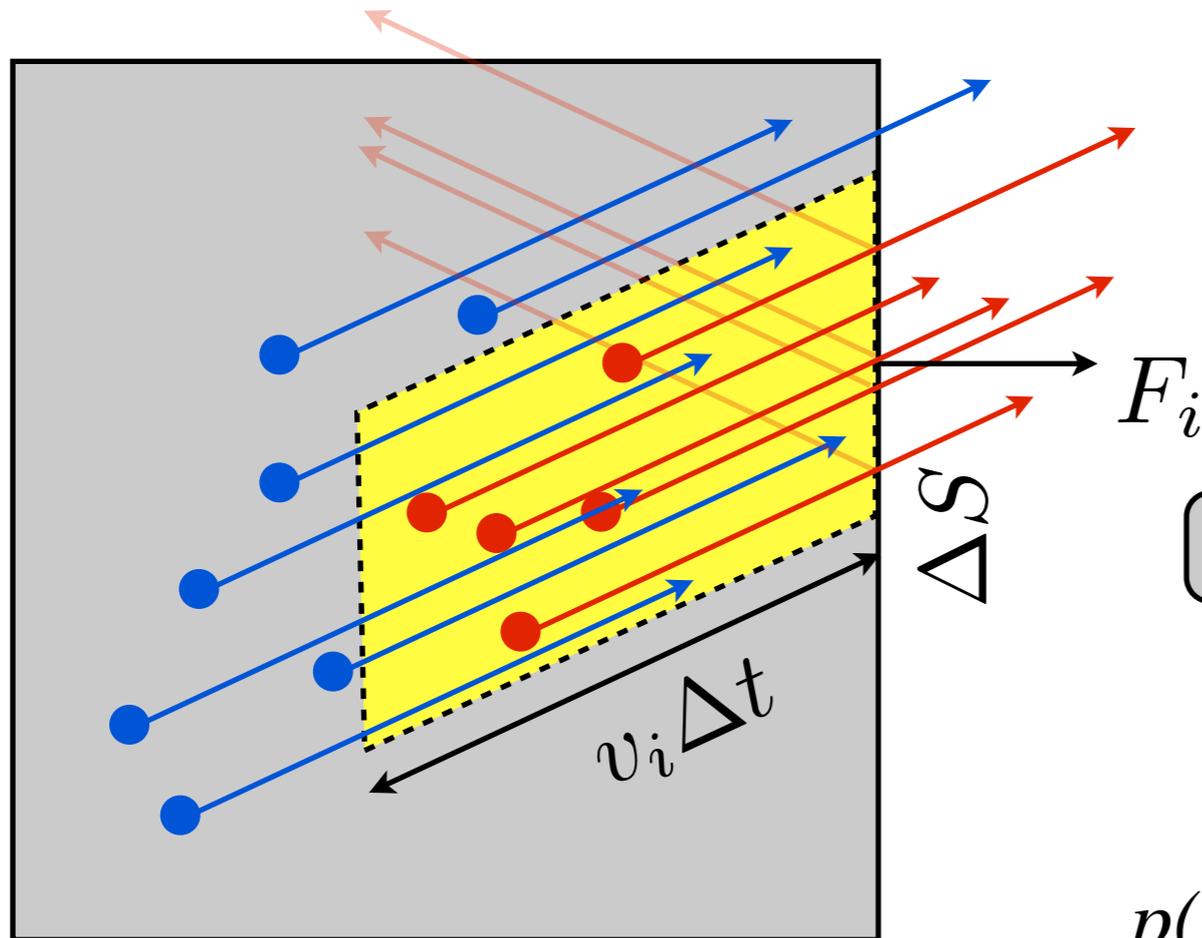
$$p = \frac{1}{3}n\overline{\varepsilon}$$

$$p = \frac{F}{\Delta S} = \sum_{i, v_{ix} > 0} \frac{F_i}{\Delta S} = 2 \sum_{i, v_{ix} > 0} n_i p_{ix} v_{ix}$$

$$= \sum_i n_i p_{ix} v_{ix} = n \overline{p_x v_x} = \frac{1}{3} n \overline{\mathbf{p} \cdot \mathbf{v}}$$

# 理想气体的压强公式

## 1、非相对论情形



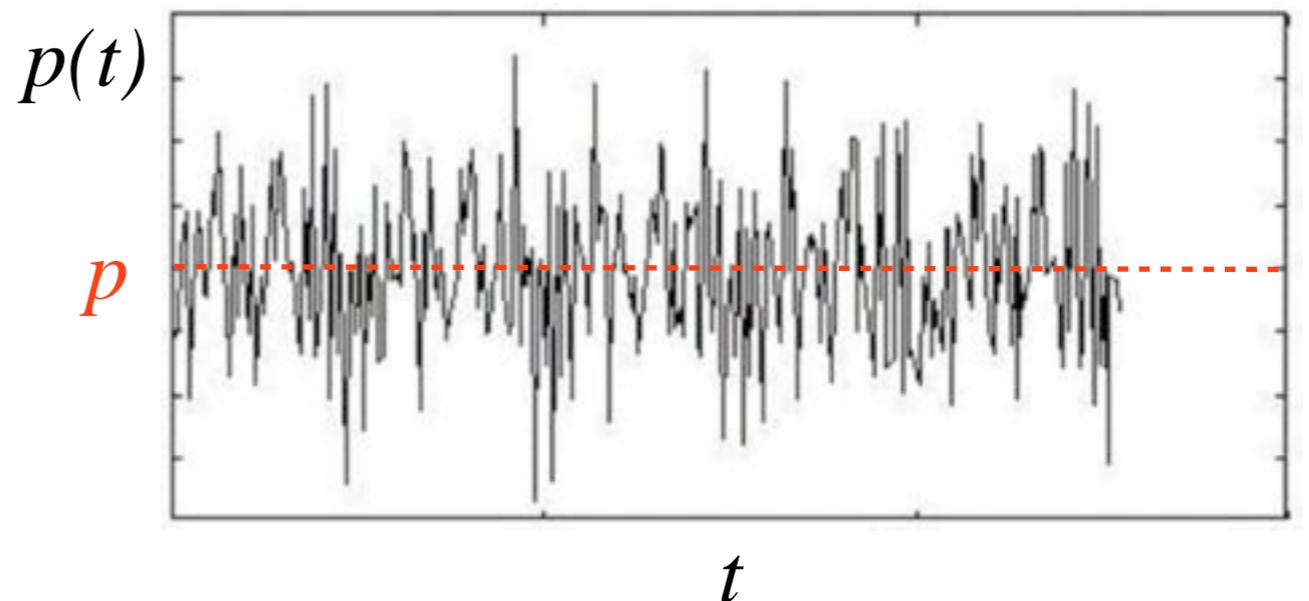
$$p = \frac{1}{3} n m \overline{v^2} = \frac{2}{3} n \overline{\varepsilon}$$

宏观可观测量

微观量的统计平均

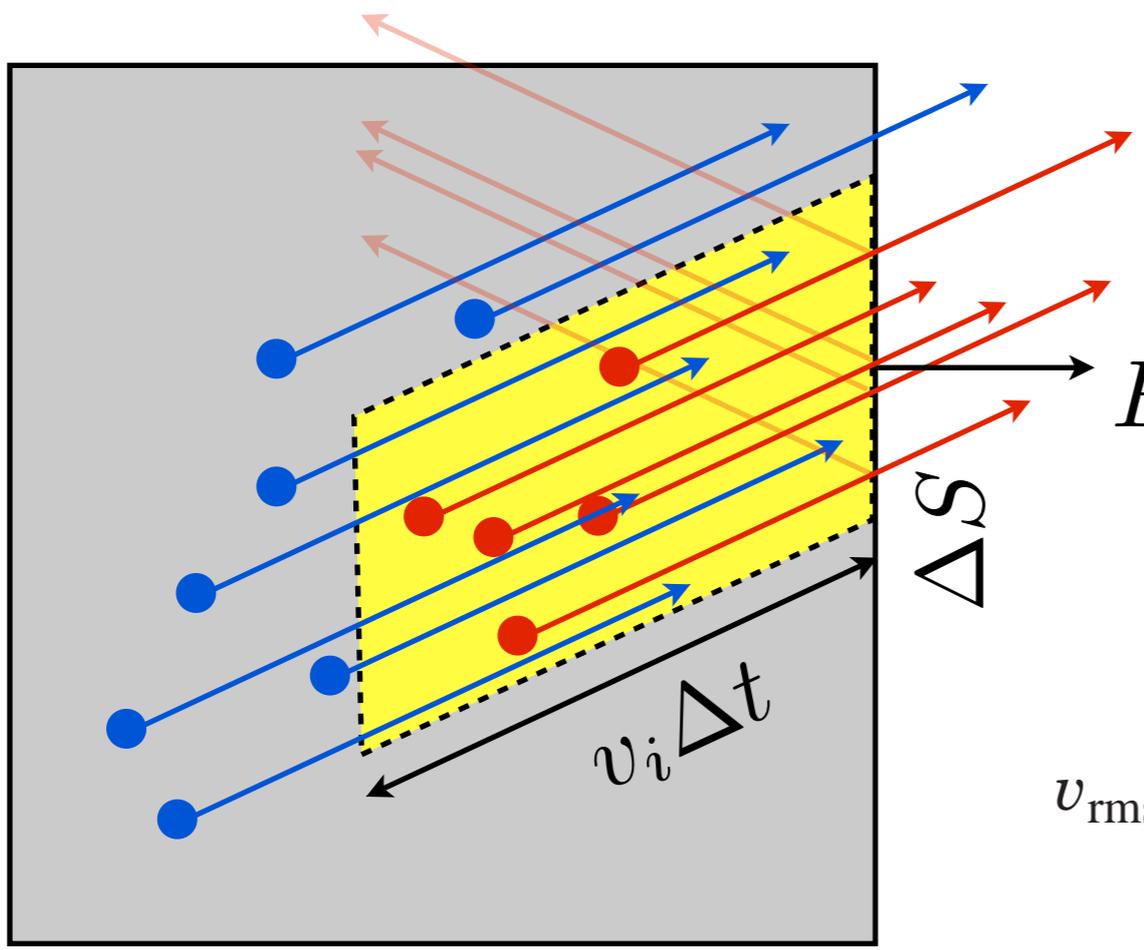
$$p = \overline{p(t)} = \frac{1}{T} \int_0^T p(t) dt$$

涨落： $\Delta p = p(t) - p$



# 温度的统计意义

## 1、非相对论情形



$$p = \frac{1}{3}nm\overline{v^2} = \frac{2}{3}n\overline{\varepsilon}$$

宏观可观测量

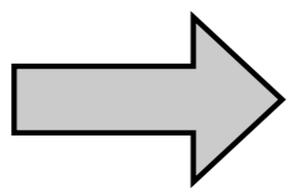
微观量的统计平均

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{5.31 \times 10^{-26} \text{ kg}}}$$

$$= 484 \text{ m/s} = 1740 \text{ km/h} = 1080 \text{ mi/h}$$

$$p = \frac{2}{3}n\overline{\varepsilon}$$

$$p = nkT$$



微观量的统计平均

$$\overline{\varepsilon} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

宏观可观测量

# 热力学第零定律的微观图像

$$v_x = \frac{(m - m')v_{0x} + 2m'v'_{0x}}{m + m'}$$

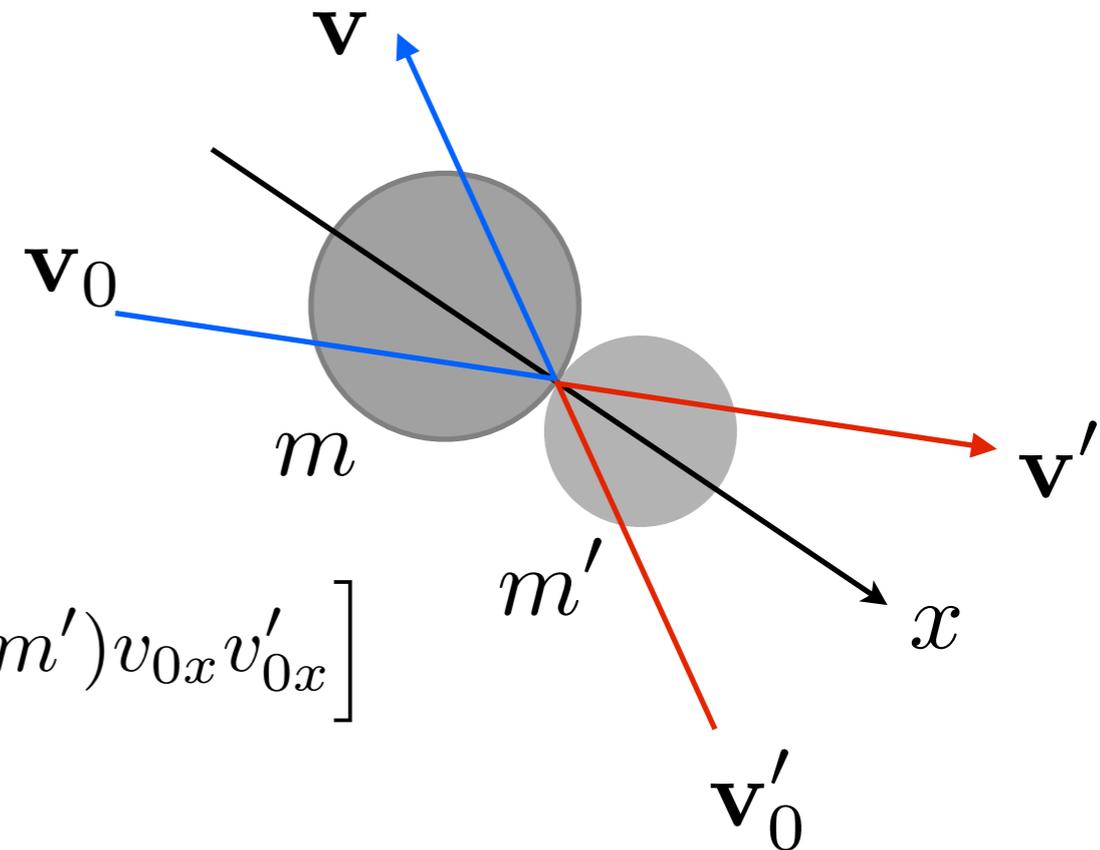
$$\Delta\varepsilon = \frac{1}{2}m(v_0^2 - v^2) = \frac{1}{2}m(v_{0x}^2 - v_x^2)$$

$$= \frac{2mm'}{(m + m')^2} \left[ mv_{0x}^2 - m'v'_{0x}{}^2 + (m - m')v_{0x}v'_{0x} \right]$$

$$\overline{\Delta\varepsilon} = \frac{2mm'}{(m + m')^2} \left[ m\overline{v_{0x}^2} - m'\overline{v'_{0x}{}^2} + (m - m')\overline{v_{0x}v'_{0x}} \right]$$

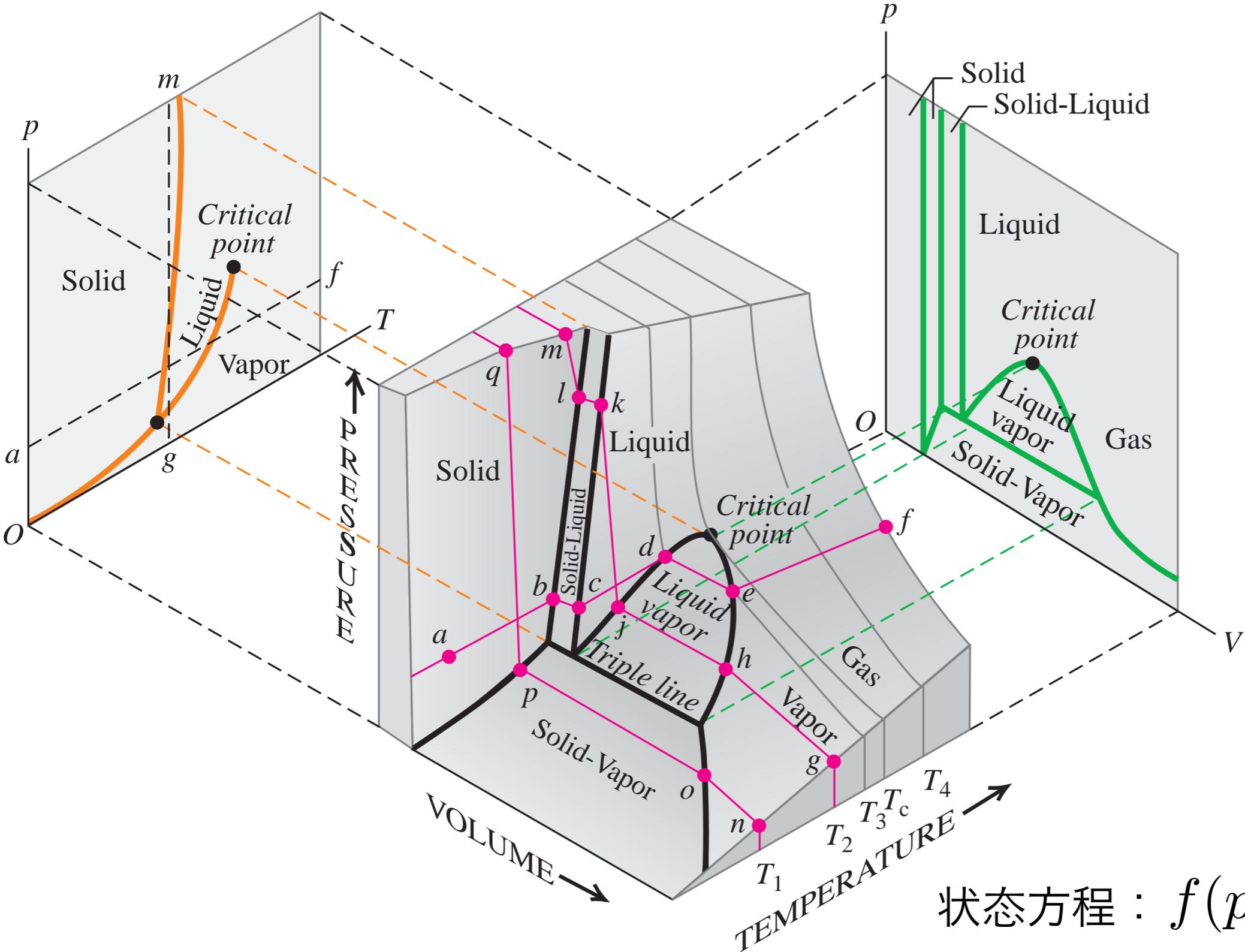
$$= \frac{2mm'}{3(m + m')^2} \left[ m\overline{v_0^2} - m'\overline{v_0'^2} \right]$$

$$\propto \frac{1}{2}m\overline{v_0^2} - \frac{1}{2}m'\overline{v_0'^2} \propto T - T'$$



$$\overline{\varepsilon} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

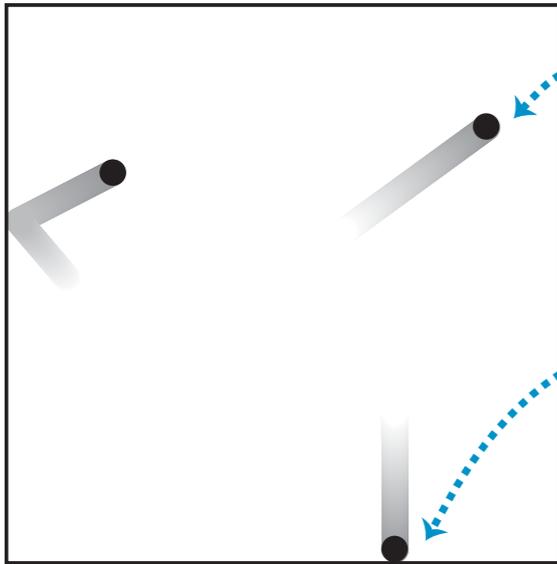
# 实际气体状态图



状态方程： $f(p, V, T) = 0$

# 实际气体状态方程

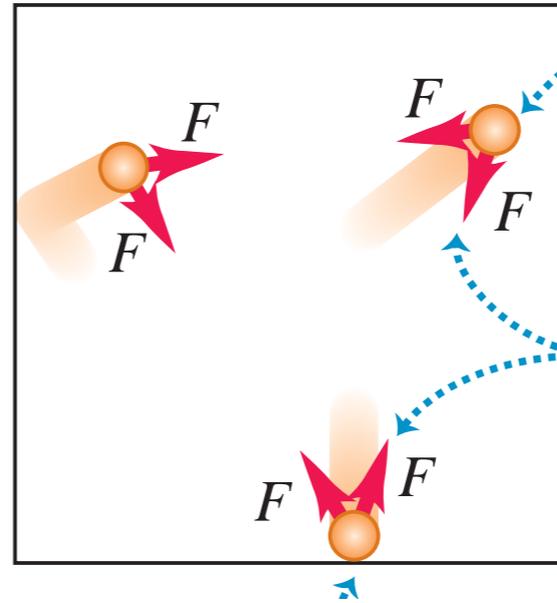
理想气体



Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

实际气体



Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

理想气体状态方程：

$$pV = \nu RT$$

考虑分子大小：

$$p(V - \nu b) = \nu RT$$

范德瓦尔斯方程：

$$\left(p + \frac{\nu^2 a}{V^2}\right) (V - \nu b) = \nu RT$$

$$p = \frac{\nu RT}{V - \nu b} - \frac{\nu^2 a}{V^2}$$