Eq-of-State

Wednesday, June 10, 2020 11:41 PM

$r(t)$

$v(t) = \dot{r}(t)$

$a(t) = \ddot{r}(t)$

$$\frac{d(r(t)_i \cdot \dot{r}(t)_i)}{dt} = \dot{r}(t)_i \cdot \dot{r}(t)_i + \ddot{r}(t)_i \cdot r(t)_i$$

$$\sum_{i=1}^{N} m \cdot \frac{d}{dt}\left[r(t)_i \cdot \dot{r}(t)_i\right] = \sum_{i=1}^{N} m_i \left[\dot{r}(t)\right]^2 + \sum_{i=1}^{N} \underbrace{m_i \ddot{r}(t)_i}_{F_i} \cdot r(t)_i$$

$$\left\langle \sum_{i=1}^{N} \underbrace{m \cdot \frac{d}{dt}\left[r(t)_i \cdot \dot{r}(t)\right]}_{\text{isolated system.}} \right\rangle = \left\langle 2 \sum_{i=1}^{N} \frac{1}{2} m_i \underbrace{[\dot{r}(t)]^2}_{\vec{v}(t)_i} \right\rangle + \left\langle \sum_{i=1}^{N} \vec{F}_i \cdot \vec{r}(t)_i \right\rangle$$

$$0 = 2\langle K \rangle + \langle W \rangle$$

$\langle K \rangle$ (Kinetic) $\quad \langle W \rangle$ (virial)

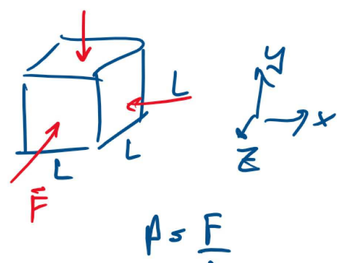
$$\langle K \rangle = \left\langle \sum_{i=1}^{N} \frac{1}{2} m_i V_i^2 \right\rangle = \frac{3}{2} N k_B T \rightsquigarrow \text{Temp.}$$

N atom → each has 3 d.o.f. $\quad \frac{1}{2} k_B T$

$$\langle W \rangle = \left\langle \sum_{i=1}^{N} r(t) \vec{F}_i \right\rangle \rightsquigarrow \text{pressure}$$

$\vec{F}_i = \vec{F}_{i,int} + \vec{F}_{ext}$ ← due to pressure

↳ $\vec{F}_{j \to i}$ all other atoms



$P = \frac{F}{A}$

$F = PL^2$

$$\langle W \rangle = \sum_{i=1}^{N} r(t) \vec{F}_i^{int} + \sum_{i=1}^{N} r(t) \vec{F}_i^{ext}$$

$$\left\langle \sum_{i=1}^{N} r(t)_i \cdot \vec{F}_i^{ext} \right\rangle = 0 - PL^3 + 0 - PL^3 + 0 - PL^3$$

$x=0 \quad x=L \quad y=0 \quad y=L \quad z=0 \quad z=L$

$$= -3PL^3 = -3PV$$

$$2\langle K \rangle + \langle W \rangle = 0$$

$$\frac{2 \cdot 3}{2} N k_B T + \left\langle \sum_{i=1}^{N} \vec{r} \vec{F}_i^{int} \right\rangle - 3PV = 0$$

For gas:

$$3NK_BT + 0 - 3PV = 0$$

$$\boxed{NK_BT = PV}$$ ✱