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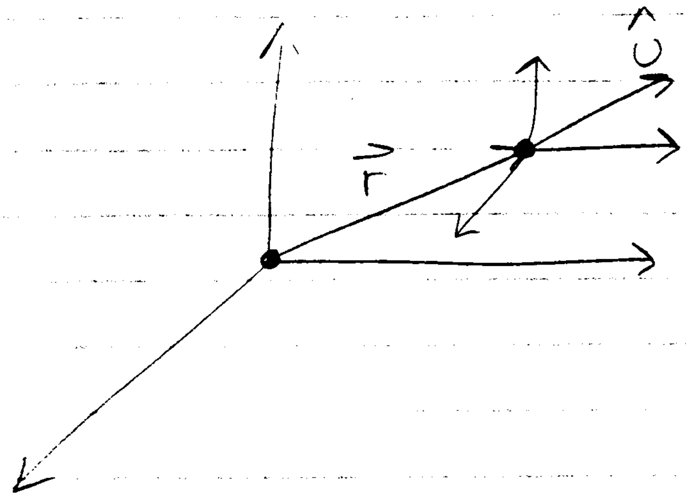


consider Louiville Equation for

$$f_N(\vec{r}^N, \vec{v}^N, \hat{u}^N, \vec{\omega}^N) \longrightarrow f_N(\vec{\Gamma}^N)$$

continuity eqn. $\longrightarrow$

$$\frac{\partial f_N}{\partial t} = -\vec{\nabla}_{\vec{x}} \cdot (f_N \vec{U})$$

$$\hookrightarrow \dot{\vec{x}}$$

f_N is a distribution or probability density and $\vec{U}$ is a generalized velocity corresponding to coordinates that f_N is dependent on.

<u>example</u>

consider $f_N(\vec{r}_1, \dots, \vec{v}_1 \dots)$
w.r.t. $\vec{r}_i$

$$\frac{\partial f_N}{\partial t} = -\vec{\nabla}_{\vec{r}_i} \cdot (f_N \vec{v}_i)$$

$$= -\left(\vec{v}_i \cdot \vec{\nabla}_{\vec{r}_i} f_N + \cancelto{0}{f_N \vec{\nabla}_{\vec{r}_i} \cdot \vec{v}_i}\right)$$

$$= -\vec{v}_i \cdot \vec{\nabla}_{\vec{r}_i} f_N \quad \text{as needed}$$

So it's clear that $\longrightarrow$

$$\hat{L}_N = -\sum_{i=1}^{N}\left(\vec{v}_i \cdot \vec{\nabla}_{\vec{r}_i} + \vec{F}_i \cdot \vec{\nabla}_{\vec{v}_i}\right)$$

consider $\longrightarrow$

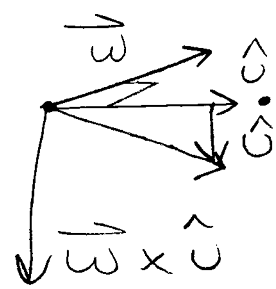
$$f_N(\vec{r}^N, \vec{v}^N, \hat{u}^N, \vec{\omega}^N; t)$$

consider $\hat{u}_i$

$\vec{\omega} \cdot \hat{u} = 0$ for diatomic

$$\frac{\partial f_N}{\partial t} = -\frac{\partial}{\partial \hat{u}_i} \cdot \left(\frac{\partial \hat{u}_i}{\partial t} f_N\right)$$

$$\frac{\partial \hat{u}_i}{\partial t} = \dot{\hat{u}}_i = \vec{\omega}_i \times \hat{u}_i$$



$$\therefore$$

$$\frac{\partial f_N}{\partial t} = -\frac{\partial}{\partial \hat{u}_i} \cdot \left(\vec{\omega}_i \times \hat{u}_i f_N\right)$$

$$= -\vec{\nabla}_{\hat{u}_i} \cdot \left(\vec{\omega}_i \times \hat{u}_i f_N\right)$$

$$\vec{\nabla}_r \times \vec{r} = 0$$

$$\vec{\nabla}_{\hat{u}_i} \cdot \left(\vec{\omega}_i \times \hat{u}_i f_N\right) = \hat{u}_i f_N \cdot \underbrace{\left(\vec{\nabla}_{\hat{u}_i} \times \vec{\omega}_i\right)}_{0} - \vec{\omega}_i \cdot \left(\vec{\nabla}_{\hat{u}_i} \times \hat{u}_i f_N\right)$$

$$\vec{\nabla}_{\hat{u}_i} \times \hat{u}_i f_N = f_N \underbrace{\left(\vec{\nabla}_{\hat{u}_i} \times \hat{u}_i\right)}_{0} - \hat{u}_i \times \vec{\nabla}_{\hat{u}_i} f_N$$

$\therefore$

$$\vec{\nabla}_{\hat{u}_i} \cdot \left(\vec{\omega}_i \times \hat{u}_i f_N\right) = \vec{\omega}_i \cdot \left(\hat{u}_i \times \vec{\nabla}_{\hat{u}_i} f_N\right)$$

$$\frac{\partial f_N}{\partial t} = - \vec{\omega}_i \cdot \left(\hat{u}_i \times \vec{\nabla}_{\hat{u}_i} f_N\right)$$

See Doi + Ed.
p 294

$\dot{\vec{\omega}} = \hat{u} \times (\vec{\omega} \times \hat{u}) =$ $\qquad \hat{u} \perp \vec{\omega}$

$\dot{\hat{u}} = (\hat{u} \times \dot{\hat{u}}) \times \hat{u}$ ← needs $\hat{u} \cdot \dot{\hat{u}} = 0$

see → set C $\quad \dot{\hat{U}}_i = \vec{\omega}_i \times \hat{U}_i \longrightarrow \vec{\omega}_i = \hat{U}_i \times \dot{\hat{U}}_i$ for (rigid) diatomic

See set A aside 1

Aside 3 f

$$\frac{d\vec{\omega}_i}{dt} = \cancel{\dot{\hat{U}}_i \times \dot{\hat{U}}_i}^{\,0} + \hat{U}_i \times \ddot{\hat{U}}_i$$

$\therefore$

$$\frac{\partial f_N}{\partial t} = -\vec{\nabla}_{\vec{\omega}_i} \cdot \left(\hat{U}_i \times \ddot{\hat{U}}_i f_N\right)$$

$$\vec{\nabla}_{\vec{\omega}_i} \cdot \left(\hat{U}_i \times \ddot{\hat{U}}_i f_N\right) = \ddot{\hat{U}}_i f_N \cdot \cancel{\left(\vec{\nabla}_{\vec{\omega}_i} \times \hat{U}_i\right)}^{\,0} - \hat{U}_i \cdot \left(\vec{\nabla}_{\vec{\omega}_i} \times \ddot{\hat{U}}_i f_N\right)$$

$$\Rightarrow \vec{\nabla}_{\vec{\omega}_i} \times \ddot{\hat{U}}_i f_N = f_N \cancel{\left(\vec{\nabla}_{\vec{\omega}_i} \times \ddot{\hat{U}}_i\right)}^{\,0} - \ddot{\hat{U}}_i \times \vec{\nabla}_{\vec{\omega}_i} f_N$$

$$\vec{\nabla}_{\vec{\omega}_i}\left(\hat{U}_i \times \ddot{\hat{U}}_i f_N\right) = \hat{U}_i \cdot \left(\ddot{\hat{U}}_i \times \vec{\nabla}_{\vec{\omega}_i} f_N\right)$$

$\therefore$

$$\frac{\partial f_N}{\partial t} = -\hat{U}_i \cdot \left(\ddot{\hat{U}}_i \times \vec{\nabla}_{\vec{\omega}_i} f_N\right)$$

$$= -\ddot{\hat{U}}_i \cdot \left(\vec{\nabla}_{\vec{\omega}_i} f_N \times \hat{U}_i\right)$$

$$= \ddot{\hat{U}}_i \cdot \left(\hat{U}_i \times \vec{\nabla}_{\vec{\omega}_i} f_N\right)$$

$$\frac{\partial f_N}{\partial t} = -\vec{\nabla}_{\vec{\Gamma}_i}\cdot\left(f_N\,\dot{\vec{\Gamma}}_i\right)$$

Liouville eqn. $\longrightarrow$

$$\frac{\partial f_N}{\partial t} = -\sum_{i=1}^{N}\vec{v}_i\cdot\vec{\nabla}_{\vec{r}_i} f_N - \sum_{i=1}^{N}\vec{F}_i\cdot\vec{\nabla}_{\vec{v}_i} f_N$$

$$-\sum_{i=1}^{N}\vec{\omega}_i\cdot\left(\hat{u}_i\times\vec{\nabla}_{\hat{u}_i}\right)f_N + \ddot{u}_i\cdot\left(\hat{u}_i\times\vec{\nabla}_{\vec{\omega}_i}\right)f_N$$

$$\frac{\partial f_N}{\partial t} = -\sum_{i=1}^{N}\vec{v}_i\cdot\frac{\partial f_N}{\partial\vec{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{N*}\vec{F}_{ij}\cdot\frac{\partial f_N}{\partial\vec{v}_i}$$

$$-\sum_{i=1}^{N}\vec{\omega}_i\cdot\left(\hat{u}_i\times\frac{\partial f_N}{\partial\hat{u}_i}\right) + \sum_{i=1}^{N}\sum_{j=1}^{N*}\ddot{\hat{u}}_{ij}\cdot\left(\hat{u}_i\times\frac{\partial f_N}{\partial\vec{\omega}_i}\right)$$

$*\quad i \neq j \longrightarrow i = j \equiv 0$