

DERIVATION OF ENSEMBLE Lec 24 SP15
 AUBD
Microscale momentum eqns.

I)

Ensemble average Version

a) Ref; See Evans & Morriss,
Statistical Mechanics of
Non-equilibrium Liquids,
 pp 64-67. (En-

b)

define local, instantaneous momentum
 density, $\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)$ as

$$\begin{aligned}\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) &= \left\langle \sum_i m_i \mathbf{v}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) \right\rangle \\ &= \int d\Gamma f(\Gamma, t) \sum_i m_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &\quad \uparrow \\ &\quad f(\Gamma, t)\end{aligned}$$

NOTE:

① $\mathbf{v}_i$ and $\mathbf{r}_i$ (in the so-called
 Schrodinger Representation
 shown here, are indep
phase space variables
 and are not fn's of
 time, t .

c) Use same approach as was used for obtaining the ensemble averaged mass cons. eqn

d) Aside For instantaneous version (background):
 (See Lecture entitled: "Stat Mechanics of Interacting Particle Systems - Molecular-scale Conservation Laws - Part 1")

For ensemble-avgd version, see Notes entitled "Derivation of Liouville Theorem"

$$e) i) \left[\frac{\partial}{\partial t} [\rho(\underline{r}, t) \underline{u}(\underline{r}, t)] + \frac{\partial}{\partial t} \int d\Gamma f(\underline{r}, t) \sum_i m_i \underline{v}_i \delta(\underline{r} - \underline{r}_i) \right]$$

$$= \int d\Gamma f_{,t}(\underline{r}, t) \sum_i m_i \underline{v}_i \delta(\underline{r} - \underline{r}_i)$$

$$= \int d\Gamma (iL)f \sum_i m_i \underline{v}_i \delta(\underline{r} - \underline{r}_i) \quad (**)$$

where $iL \equiv \underline{v} \cdot \nabla + \nabla \cdot \underline{v}$

$$= (\dot{q}_1, \dot{q}_2, \dots, \dot{q}_{3N}; \dot{p}_1, \dot{p}_2, \dots, \dot{p}_{3N}) \cdot \nabla + \nabla \cdot \underline{v}$$

$$= \sum_i^{3N} \left(\dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} \right) + \sum_i^{3N} \left[\frac{\partial}{\partial \underline{r}_i} (\dot{\underline{r}}_i) + \frac{\partial}{\partial \underline{p}_i} (\dot{\underline{p}}_i) \right]$$

ii) or

$$\begin{aligned}
 \text{RHS} &= \int d\mathbf{r} \left(\frac{1}{iL} \right) \left(f \sum_i m_i \underline{v}_i \delta(\underline{r} - \underline{r}_i) \right) \\
 &\quad + \int d\mathbf{r} f(\underline{r}, t) \left(\frac{1}{iL} \right) \left[\sum_i^N m_i \underline{v}_i \delta(\underline{r} - \underline{r}_i) \right]
 \end{aligned}$$

iii) Limit attention to molecular-scale systems obeying Hamiltonian dynamics. Thus,

$$\boxed{\nabla \cdot \underline{v} = 0}$$

(See above ref. for proof)

$$\begin{aligned}
 \text{iv) term } \textcircled{I} &= - \int d\mathbf{r} \underline{v} \cdot \nabla (f \Sigma(\underline{r})) \\
 &= \int d\mathbf{r} \left[\nabla \cdot (\underline{v} f \Sigma(\underline{r})) - \nabla \cdot \underline{v} (f \Sigma(\underline{r})) \right] \\
 &= \int_A dA \underline{v} f \frac{1}{\delta(\underline{r} - \underline{r}_i)} \cdot \underline{n}
 \end{aligned}$$

Choose A to be
 surface in phase
 space) to be larger than
 $\text{ball } \underline{r} - \underline{r}_i \Rightarrow \delta(\underline{r} - \underline{r}_i) = 0$
 for all molecules lying
 on A

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$$\begin{aligned}
 \text{v) term II} &= \int d\Gamma f(\Gamma, t) \left[\nabla \cdot \left(\sum_i^N \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) \right) \right] \\
 &= \int d\Gamma f(\Gamma, t) \left[\sum_i^N m_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) + \sum_i^N \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i} \delta(\mathbf{r} - \mathbf{r}_i) \right]
 \end{aligned}$$

indep vbls

$$\begin{aligned}
 &+ \sum_i^N \dot{\mathbf{p}}_i m_i \frac{\partial}{\partial \mathbf{p}_i} \delta(\mathbf{r} - \mathbf{r}_i) \\
 &+ \sum_i^N \dot{\mathbf{p}}_i \delta(\mathbf{r} - \mathbf{r}_i)
 \end{aligned}$$

$\delta(\mathbf{r}, \mathbf{j})$

$$= \int d\Gamma f(\Gamma, t) \left[\sum_i^N \dot{\mathbf{p}}_i \delta(\mathbf{r} - \mathbf{r}_i) + \sum_i^N m_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) \right]$$

$F_i \rightarrow (\text{Newton on state } i)$

$$\begin{aligned}
 &= - \frac{\partial}{\partial \mathbf{r}} \int d\Gamma f(\Gamma, t) \sum_i^N m_i \dot{\mathbf{r}}_i \delta(\mathbf{r} - \mathbf{r}_i) \\
 &+ \int d\Gamma f(\Gamma, t) \sum_i^N \dot{\mathbf{p}}_i \delta(\mathbf{r} - \mathbf{r}_i)
 \end{aligned}$$

(Ia)
(IIa)

va) Focus first on term (Ia)
(and follow Evans and Morris):

vi) contin

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first compute:

$$(Ib) = \langle \sum_i m_i (v_i(t) - u(r_i, t)) (v_i(t) - u(r_i, t)) \rangle + \langle \sum_i m_i \frac{d}{dt} (v_i(t) u(r_i, t)) \rangle$$

$$= -2u(r, t) \langle \sum_i m_i v_i \delta(r - r_i) \rangle + u(r, t) u(r, t) \langle \sum_i m_i \delta(r - r_i) \rangle$$

$$+ \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle$$

$$(Ib) = -\rho(r, t) u(r, t) u(r, t) + \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle$$

also

$$(Ib) = \rho(r, t) u(r, t) u(r, t) + \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle$$

$$\Rightarrow \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle = \langle \sum_i m_i (v_i - u(r, t)) (v_i - u(r, t)) \rangle$$

thus, we confirm EVANS AND MORRIS;

$$(Ia) = -\frac{d}{dt} \int d\Omega \rho(r, t) \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle$$

$$= -\frac{d}{dt} \langle \sum_i m_i v_i v_i \delta(r - r_i) \rangle$$

$$(Ia) = -\frac{d}{dt} \left[\langle \sum_i m_i (v_i(t) - u(r, t)) (v_i(t) - u(r, t)) \rangle + \rho(r, t) u(r, t) u(r, t) \right] \quad (5.1)$$

vii) i.e. using (5.1) For term (Ia) on pg 4;
then ~~using~~ (Ia) and (IIa) (pg. 4)
For term II top of pg. 3, then finally
plugging term II into (xx) pg 2
we get:

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$$\begin{aligned} & \frac{\partial}{\partial t} \rho(\underline{r}, t) u(\underline{r}, t) + \frac{\partial}{\partial \underline{r}} \cdot [\rho(\underline{r}, t) \underline{u}(\underline{r}, t) \underline{u}(\underline{r}, t)] \\ &= \int d\Gamma f(\underline{r}, t) \sum_i \underline{F}_i \delta(\underline{r} - \underline{r}_i) \\ &= \frac{\partial}{\partial \underline{r}} \cdot \left\langle \sum_i m_i (\underline{v}_i(t) - \underline{u}(\underline{r}, t)) (\underline{v}_i(t) - \underline{u}(\underline{r}, t)) \right\rangle_{\underline{r}(t) = \underline{r}} \end{aligned} \quad (6.1)$$

viii) Evans and Morriss show that

$$\begin{aligned} & \int d\Gamma f(\underline{r}, t) \sum_i \underline{F}_i \delta(\underline{r} - \underline{r}_i) = \\ &= -\frac{1}{2} \frac{\partial}{\partial \underline{r}} \cdot \left[\int d\Gamma f(\underline{r}, t) \sum_{i,j} \underline{r}_{ij} \Lambda_{ij} \left(\delta(\underline{r} - \underline{r}_i) \frac{\partial \phi_{ij}}{\partial \underline{r}_i} \right) \right] \end{aligned} \quad (6.2)$$

where

$$\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$$

$$\Lambda_{ij} = 1 - \frac{1}{2} \underline{r}_{ij} \cdot \frac{\partial}{\partial \underline{r}} + \dots + \frac{1}{n!} \left(-\underline{r}_{ij} \cdot \frac{\partial}{\partial \underline{r}} \right)^n$$

$$\underline{F}_i = \sum_{j \neq i} \frac{\partial \phi_{ij}}{\partial \underline{r}_i} = \text{sum of interparticle potentials}$$

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ix) Finally, write (6.1) in terms of the molecular-scale, ensemble-average stress tensor $\underline{P}$:

$$(7.1) \quad \left[\frac{\partial}{\partial t} (\rho(\underline{r}, t) \underline{u}(\underline{r}, t)) + \frac{\partial}{\partial \underline{r}} \cdot [\rho(\underline{r}, t) \underline{u}(\underline{r}, t) \underline{u}(\underline{r}, t)] \right] = \frac{\partial}{\partial \underline{r}} \cdot \underline{P}$$

where

$$\frac{\partial}{\partial \underline{r}} \equiv \nabla \cdot$$

$$(7.2) \quad \underline{P} = - \left\langle \sum_i m_i (\underline{v}_i(t) - \underline{u}(\underline{r}, t)) (\underline{v}_i(t) - \underline{u}(\underline{r}, t)) \right\rangle_{\underline{r}(t)=\underline{r}} - \frac{1}{2} \left[\int d\underline{r}' \rho(\underline{r}', t) \sum_{i,j}^{\underline{r}, \underline{r}'} \underline{\Lambda}_{ij} \left\{ \sigma(\underline{r} - \underline{r}') \frac{\partial \phi_{ij}}{\partial \underline{r}_i} \right\} \right]$$

NOTES

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1) (7.1) & (7.2) assume Hamiltonian dynamics

2) (7.1) incorporates/includes the cons. of mass, using the chain rule and

$$\rho_{tt} + \nabla \cdot (\rho \underline{u}) = 0 \quad \text{on the LHS of (7.1) leads to}$$

$$\rho(\underline{r}, t) \frac{\partial \underline{u}(\underline{r}, t)}{\partial t} + \rho(\underline{r}, t) \nabla \cdot \underline{u} = \nabla \cdot \underline{p}$$

3) (7.2) Indicates that the microscopic stress tensor, $\underline{p}$, arises due to:

i) Molecular transport of random molecular momentum, $m_i(\underline{v}_i - \underline{u}(\underline{r}, t))$, by the random velocity components $\underline{v}_i - \underline{u}(\underline{r}, t)$.

ii)

Notes cont'd

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4) THIS approach to obtaining the ensemble-avgd conservation eqn. is referred to as the Irving-Kirkwood procedure

5) THE Form of the $\underline{P}$

Given in (7.2) is presumably useful / used in, e.g., (MD) molecular-dynamics simulations.

i) In MD, an interparticle potential, ϕ , is assumed;

The r^6 , r^{12} potential is often used.

~~Next~~

~~6) For calculations on~~

6) In order to circumvent the expense/difficulty of calculating the dynamics of individual molecules (i.e., e.g., MD simulations)

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or to carry out modeling/calculations
on length scales that are

>> (molecular), ~~but~~ $\ll$ and

large enough to allow for
local thermodynamic equilibrium
(i.e., large enough so that

$$N = \frac{\text{the no. of molecules in the vol. } dV}{dV} \gg 1 \quad \square, \text{ a}$$

Empirically-based
" CONSTITUTIVE relationship

must be introduced for

$$P_{ij} \in \text{ijth comp. of } \underline{P}.$$

The simplest such relationship
for a fluid is the linear
Navier-Stokes ($\equiv$ Newtonian
fluid) relation:

$$\boxed{P_{ij} = -P\delta_{ij} + \mu(u_{i,j} + u_{j,i}) - \frac{2}{3}\mu\nabla_k u_k \delta_{ij} - \mu P_{ij} \delta_{ij}}$$

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Notes carry

- 7) THE phase space density function, $f = f(p, x)$,
can correspond to, e.g.,
a canonical distn.

$$f(p, x) = \frac{e^{-\beta H(p, x)}}{\int e^{-\beta H(p, x)} dp}$$

- i) I'm not sure how things work out if we assume a microcanonical or grand canonical density. I would assume everything works out.

- 8) Since the Irving-Kirkwood approach uses phase space averaging, then it applies to classical molecular systems