

OVERVIEW OF MOLECULAR-SCALE FLUID DYNAMICS-STATE OF THE FIELD

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④ Derivation of molecular scale cons. of mass

I) A LONG-TIME GOAL OF STATISTICAL MECHANICS ~~IS TO~~ ~~STAT~~ RIGOROUSLY CONVINCING THE EQNS GOVING ATOMIC/MOLECULAR SCALE DYNAMICS, E.G., THE HAMILTONIAN FOR A (TINY-ON-THE-CONTINUUM-SCALE) N-ptcl system to the known observed continuum-scale behavior of fluids. (as described, for example, by the Navier-Stokes eqns).

ii) According to Feynman (Statistical Mechanics) AND Boon and U.P. (Molecular Hydrodynamics)

THIS GOAL REMAINS UNREALIZED
AT LEAST FOR LIQUIDS.

b) THOSE NOTES WILL
CATALOGUE (BOUNCE)
WHERE THE FIELD
IS A SITUATION.

c) According to Deen and
Yip, The theory of
molecular hydrodynamics $\Rightarrow$
which applies to
Long wavelength ($k \rightarrow 0$)
and Low frequency ($\omega \rightarrow 0$)
molecular dynamics -
[where ~~that~~ the $[k \rightarrow 0]$
limit corresponds to
collective ~~molecular~~
dynamics that occur
on length scales, that
are long relative to

Lec 23

SPG 15

the characteristic

intermolecular spacing

(on the order of a few Å
in Liquids) and the

$[w \rightarrow 0]$ limit corresponds

to dynamics occurring

on time scales, τ , that

are long relative to the

characteristic collision time,

$$\tau_c \sim \frac{\text{atomic spacing}}{\text{thermal speed}} \sim \frac{3 \times 10^{-10} \text{ m}}{2 \times 10^3 \text{ m/s}} \sim \underline{\underline{3(10^{-13}) \text{ s}}}$$

is well-developed and provides
a self-consistent description
of long-wavelength, slow
molecular processes ($k \rightarrow 0, \omega \rightarrow 0$
limit).

d) AGAIN, ACCORDING TO BOON & YIP, what is needed theoretically is a ~~the~~ framework that allows prediction description of ~~both~~ moderate and higher frequency ~~and dynamics~~ and moderate and short wavelength dynamics.

e) One, if not the main reason why we can self-consistently tie hydrodynamic ($\equiv k \rightarrow 0, \omega \rightarrow 0$) molecular dynamics to continuum fluid dynamics is due to the fact that we can make use of the powerful machinery of equilibrium statistical and macroscopic

lec. 23

SP4.15 (3)

Thermodynamics - ABMA

[which are connected through the Bridge relations we've derived

$$S = k \ln \Omega$$

$$A = -kT \ln Q$$

$$\ln q = \frac{PV}{kT}$$

(microcanonical ensemble)

(canonical ens)

(g.c. ens.)

Equilibrium thermo applies since we don't attention / study to time-scales like us that are long relative to the collision time scale. (i.e., $\omega's \rightarrow 0$).

Le. 23

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II) Roadmap for

Deriving the (linear)
Navier-Stokes eqns from
~~the~~ molecular-scale
dynamics

Derive ^{general} molecular-scale
conservation
eqns (mass, momentum, energy)



write down known /
experimentally determined
constitutive relationships
between thermodynamic / ensemble
avg'd fluxes of

mass, momentum, and
energy and continuum-
scale velocity, density,
pressure, and temperature
Fields. Since we
use thermodynamic
averaging, the formulation
is now limited to

The (molecular) hydrodynamic limit, $k \rightarrow 0$, $\omega \rightarrow 0$ (since thermodynamic averaging applies to equilibrium molecular systems)

Thermodynamically average the molecular-scale conservation eqns $\oplus$ insert constitutive relations

The continuum mass, momentum, and energy transport eqns contain (critically important) transport coefficients, each of which, reflects and is determined by ~~the~~ molecular transport processes:

μ = shear viscosity

k = thermal conductivity

μ_B = bulk viscosity

Lec 23

SPG. 15

8

IT TURNS OUT THAT SPACE-TIME
CORRELATIONS OF MOLECULAR-SCALE FLUXES / CURRENTS
OF MOMENTUM AND ENERGY
CAN BE MEASURED, THEN USED
TO DETERMINE THESE TRANSPORT
COEFFICIENTS. WE'LL OUTLINE
AT LEAST ONE AND POSSIBLY
TWO METHODS / FORMULATIONS
THAT ALLOW (INDIRECT)
MEASUREMENT OF $[D]$,
BASED ON MEASURED SPACE-TIME
CORRELATION FUNCTIONS

II) EXACT molecular-scale
CONSERVATION LAWS

(ref: Forster, Hydrodynamic
Fluctuations, Brown Symmetry,
and Correlation Functions,
Ch. 4)

$$(9.1) \quad \frac{\partial n(\underline{r}, t)}{\partial t} + \nabla \cdot \underline{g}(\underline{r}, t) = 0$$

(cons.
MASS)

$$(9.2) \quad \frac{\partial g_i(\underline{r}, t)}{\partial t} + \nabla_j \pi_{ij}(\underline{r}, t) = 0$$

(cons.
Linear
momentum)

$$(9.3) \quad \frac{\partial e(\underline{r}, t)}{\partial t} + \nabla \cdot \underline{j}(\underline{r}, t) = 0$$

(cons.
of energy)

B) Defns: •

$$(9.4) \quad n(\underline{r}, t) = \sum_{j=1}^N \delta(\underline{r} - \underline{r}_j(t)) =$$

instantaneous
number
density
@ $(\underline{r}, t)$

lec 23
 Spg 15

(9.5)

$$g(\underline{r}, t) = \sum_{j=1}^N \frac{p_j(t)}{m} \delta(\underline{r} - \underline{r}_j(t))$$

= instantaneous
momentum
density
 $\rho(\underline{r}, t)$

(9.6)

$$e(\underline{r}, t) = \sum_{j=1}^N \left[\frac{p_j(t)^2}{2m} + \frac{1}{2} \sum_{i \neq j} u(r_{ij}) \right] \delta(\underline{r} - \underline{r}_j(t))$$

= instantaneous
energy density
 $e(\underline{r}, t)$

(9.7)

$$\tau_{ij} = \sum_{a=1}^N \frac{p_i^a p_j^a}{2m} \delta(\underline{r} - \underline{r}_a)$$

$$- \frac{1}{2} \sum_{a \neq b} r_i^{aB} \frac{\partial u(r_{ab})}{\partial x_j} \bigg|_0 \delta(\underline{r} - \frac{\underline{r}_a + \underline{r}_b}{2} - \frac{1}{2} \underline{r}_{ab})$$

= instantaneous ~~of~~ molecular
stress tensor

(9.8)

$$\delta(\underline{r} - \underline{r}_j(t)) \text{ (or } \delta(\underline{r} - \underline{r}_j(t))) = \begin{cases} 1 & \text{for } |\underline{r} - \underline{r}_j(t)| < \epsilon \\ 0 & \text{for } |\underline{r} - \underline{r}_j(t)| > \epsilon \end{cases}$$

a broad/smoothed
delta function

lec. 23
jrg. 15
(16)

See Forster for defn of $j(\epsilon)$.

c) Quick physical interpn.
of above defns.

a) $n(\underline{r}, t)$ is gotten by counting
(at time t) all molecules that are
within a distance $[\epsilon]$
of ~~the~~ position $\underline{r}$, at
time t . The distance
 ϵ is chosen to be
 $\gg$ than molecular
spacing ($\sim 10^{-8}$), but
much smaller than say
 10^{-6} or 10^{-7} m.

b) $\underline{g}(\underline{r}, t)$ is correspondingly
~~likewise~~ the total
(vector) momentum of all
the molecules w/in ϵ of
 $\underline{r}$ (@ time t).

Les 23

Sep 15

c) $e(r, t)$ is thus the
total instantaneous molecular
kinetic and potential
energy of all ~~the~~ molecules
w/in distance ϵ or r . (2)

IV)

IV) Derivation
instantaneous config. of molecular scale
of mass

Lec. 23 SP915

(13)

0) Ref: Evans and Morriss

$$1) \rho(\underline{r}, t) \equiv \sum_{j=1} m \delta(\underline{r} - \underline{r}_j)$$

$$2) FT.(\rho) \equiv \int \rho(\underline{r}, t) e^{i\mathbf{k} \cdot \underline{r}} d\underline{r} \equiv \rho(\underline{k}, t)$$

(instant posn molecule j)

$$= \sum_j \int m \delta(\underline{r} - \underline{r}_j) e^{i\mathbf{k} \cdot \underline{r}} d\underline{r}$$

$$\therefore \rho(\underline{k}, t) = \sum_j m e^{i\mathbf{k} \cdot \underline{r}_j(t)} \quad (2.1)$$

3) Let

$$\underline{J}(\underline{r}, t) \equiv \rho(\underline{r}, t) \underline{u}(\underline{r}, t)$$

$$= \sum_j m \underline{v}_j(t) \delta(\underline{r} - \underline{r}_j(t))$$

$$\underline{v}_j(t) = \frac{d\underline{r}_j}{dt}$$

$$4) \therefore FT\{\underline{J}(\underline{r}, t)\} \equiv \underline{J}(\underline{k}, t) = \int \rho(\underline{r}, t) \underline{u}(\underline{r}, t) e^{i\mathbf{k} \cdot \underline{r}} d\underline{r}$$

$$= \sum_j \int m \underline{v}_j(t) \delta(\underline{r} - \underline{r}_j(t)) e^{i\mathbf{k} \cdot \underline{r}} d\underline{r}$$

$$\therefore \underline{J}(\underline{k}, t) = \sum_j m \underline{v}_j(t) e^{i\mathbf{k} \cdot \underline{r}_j(t)} \quad (2.2)$$

5)

using 2):

$$\frac{\partial}{\partial t} \rho(\underline{k}, t) = i\mathbf{k} \cdot \sum_j m \underline{v}_j(t) e^{i\mathbf{k} \cdot \underline{r}_j(t)}$$

$$\underline{v}_j(t) = \frac{d\underline{r}_j}{dt}$$

$$\frac{\partial}{\partial t} \rho(\underline{k}, t) = i\mathbf{k} \cdot \underline{J}(\underline{k}, t) \quad (2.3)$$

6) Now,

$$\begin{aligned}
 FT \{ \nabla \cdot \underline{J} \} &= \int e^{i\mathbf{k} \cdot \mathbf{r}} \nabla \cdot \underline{J} \, d\mathbf{r} \\
 &= \int (\nabla \cdot (e^{i\mathbf{k} \cdot \mathbf{r}} \underline{J})) \\
 &\quad - (\underline{J} \cdot \nabla) e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} \\
 &= e^{i\mathbf{k} \cdot \mathbf{r}} \left. \underline{J} \right|_A^{\infty} \overset{\text{Assume}}{\text{Surface}} \\
 &\quad - i\mathbf{k} \cdot \int \underline{J} e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r}
 \end{aligned}$$

$$\therefore \boxed{FT \{ \nabla \cdot \underline{J} \} = -i\mathbf{k} \cdot \underline{J}(\mathbf{k}, \omega)} \quad (2.4)$$

$$7) \therefore \boxed{\text{RHS. of (2.3)} \Leftrightarrow -FT \{ \nabla \cdot \underline{J} \}} \quad (2.5)$$

8) Finally,

$$\begin{aligned}
 \frac{\partial}{\partial t} FT \{ \rho \} &= \frac{\partial}{\partial t} \rho(\mathbf{k}, t) \\
 &= \frac{\partial}{\partial t} \int \rho(\mathbf{r}, t) e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} \\
 &= \int \rho_{,t}(\mathbf{r}, t) e^{i\mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r} \\
 &\boxed{=} FT \{ \rho_{,t} \} \quad (2.6)
 \end{aligned}$$

(8)

9) Combining (2.3), (2.5) & (2.6) we see that

$$\{FT\}[p_{it}] = FT\{-\nabla \cdot \underline{J}\}$$

or

$$\boxed{p_{it} = -\nabla \cdot \underline{J}} \quad * (6.1)$$

⊕ This is ^{fully} equivalent to

$$\frac{\partial n(\underline{r}, t)}{\partial t} + \nabla \cdot \underline{g} = 0$$

Above

⊕ (6.1) applies to any
fast / slow (molecular / continuous)
scale / scale)
short / long (" / ")
wave length molecular-scale
process scale

Rough Notes

$$1) \rho(\underline{r}, t) = \sum_j m \delta(\underline{r} - \underline{r}_j)$$

$$2) \rho(\underline{k}, t) = \int d\underline{r} e^{i\underline{k} \cdot \underline{r}} \rho(\underline{r}, t)$$

$$= \sum_j m \int d\underline{r} e^{i\underline{k} \cdot \underline{r}} \delta(\underline{r} - \underline{r}_j)$$

$$3) \quad n = \frac{m \sum_j e^{i\underline{k} \cdot \underline{r}_j(t)}}{1}$$

let

$$3) \quad J(\underline{r}, t) = \rho(\underline{r}, t) \underline{v}(\underline{r}, t) = \sum_j m \underline{v}_j \delta(\underline{r} - \underline{r}_j)$$

$$4) \quad \therefore J(\underline{k}, t) = \sum_j m \int d\underline{r} \underline{v}_j e^{i\underline{k} \cdot \underline{r}} \delta(\underline{r} - \underline{r}_j) \\ = \sum_j m \underline{v}_j(t) e^{i\underline{k} \cdot \underline{r}_j(t)}$$

$$5) \quad \begin{aligned} & \text{2) } \Rightarrow \rho_{it}(\underline{k}, t) = m i \underline{k} \cdot \sum_j \underline{v}_j e^{i\underline{k} \cdot \underline{r}_j(t)} \\ & \text{from (4)} \quad \boxed{\rho_{it}(\underline{k}, t) = i \underline{k} \cdot J(\underline{k}, t)} \end{aligned}$$

$$6) \quad \text{now } \nabla \cdot J e^{i\underline{k} \cdot \underline{r}}$$

$$\begin{aligned} \boxed{FT(\nabla \cdot J)} &= \int e^{i\underline{k} \cdot \underline{r}} \nabla \cdot J d\underline{r} \\ &= \int (\nabla \cdot (e^{i\underline{k} \cdot \underline{r}} J) - J \cdot \nabla e^{i\underline{k} \cdot \underline{r}}) d\underline{r} \\ &= e^{i\underline{k} \cdot \underline{r}} J \Big|_0^\infty - i \underline{k} \cdot \int J e^{i\underline{k} \cdot \underline{r}} d\underline{r} \\ &= -i \underline{k} \cdot J(\underline{k}, t) \end{aligned}$$

$$\Rightarrow \boxed{\text{RHS of (5)} = -FT(\underline{D} \cdot \underline{J})}$$

7) ~~stage~~

$$\frac{\partial}{\partial t} 2) \Rightarrow \frac{\partial}{\partial t} \rho(\underline{r}, t) = -FT(\underline{D} \cdot \underline{J})$$

$$\text{7a) } \overset{\text{but}}{\Rightarrow} \frac{\partial}{\partial t} (FT \{ \rho \}) = -FT \{ \underline{D} \cdot \underline{J} \}$$

$$\begin{aligned} \text{from (1) } \rho(\underline{r}, t) &= \frac{1}{(2\pi)^3} \int \rho(\underline{r}, t) e^{i\underline{k} \cdot \underline{r}} d\underline{r} \\ &= \int \rho(\underline{r}, t) e^{i\underline{k} \cdot \underline{r}} d\underline{r} \\ &= FT \{ \rho \} \end{aligned}$$

$$\therefore \boxed{\rho(\underline{r}, t) = -\underline{D} \cdot \underline{J}}$$