

I)

Derivation of continuum-scale governing conservation eqns via the Kirkwood procedure.

DERIVATION OF Liouville Theorem

A) Ref. Statistical Mechanics of Non-equilibrium Liquids, by D. J. Evans and G. P. Morriss

B) The procedure relies heavily on the Liouville Egn. which describes the ~~then~~ evolution of state points / representative points within phase space

a) Liouville Egn assumes classical dynamics at the microscopic level

C) Derivation of Liouville Egn.

a) LBT Γ represent the (say) $\tilde{N}(6N)$ -dim.

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phase space associated with $\tilde{N}$ copy
systems within a given ensemble where each
system N has N particles (say N atoms), and
the dynamics of position, and
where each pte is
described by 3 momenta,

$p_1^{(x)}, p_1^{(y)}, p_1^{(z)}$, and 3 position
coordinates, $q_1^{(x)}, q_1^{(y)}, q_1^{(z)}$

b) LDF

$$\tilde{N} \delta N = f(\underline{q}, \underline{p}, t) d\underline{q} d\underline{p}$$

represent the total number
of systems - from the $\tilde{N}$ -
member / ensemble - located
w/in the 6N-diml volume,
 $d\underline{q} d\underline{p}$, about the phase
point, $\underline{q}, \underline{p}$, at time t .

i) $f(\cdot) =$ the density of
systems, at the point
 $(\underline{q}, \underline{p}, t)$

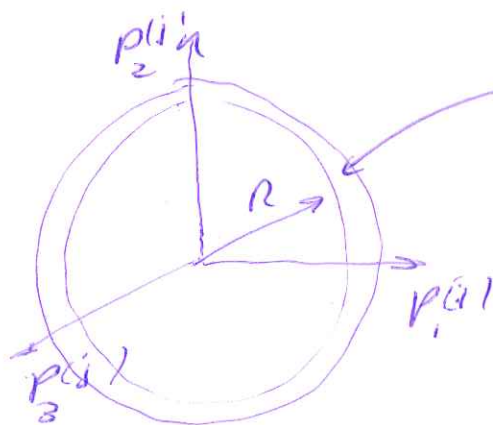
ii) Liouville's eqn governs

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The evolution of Γ w/in
the $6N$ -diml space spanned
by (q, p)

iv) some examples of phase
spaces:

BK. I: $[N]$ gas ptcls. in a box;
microcanonical ens.
ptcl i q.p space

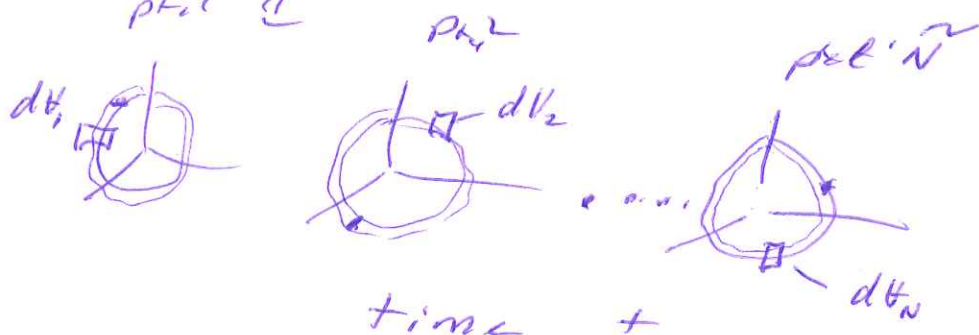


④ we showed
that the
prob. density
for a single
ptcl is
uniform
when δ
a shell
(at least for
a quantum
ptcl.); Let's
assume same
here.

EX. I CONT'D

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The phase space for $\tilde{N}$ Ideal gas ptcls each considered a system would thus be viewed as an $\tilde{N}$ -page book



System = 1 ptcl

$$\Rightarrow f(\underline{q}, \underline{p}, t) = f(\underline{p}, t) \text{ here}$$

EX. II = the probability of observing
The phase space for a box of

N Ideal gas ptcls, w/ each box capable of exchanging energy w/ ~~the~~ ^{its} surroundings

(and thus ~~can~~ most naturally modelled via the canonical ensemble), would then be

a shelf of $\boxed{\tilde{N}}$ N -page books, each book representing

The ~~evolution~~ ^{an} dynamic
state of ~~the~~ ^{an} N-ptcl.
5 bts system

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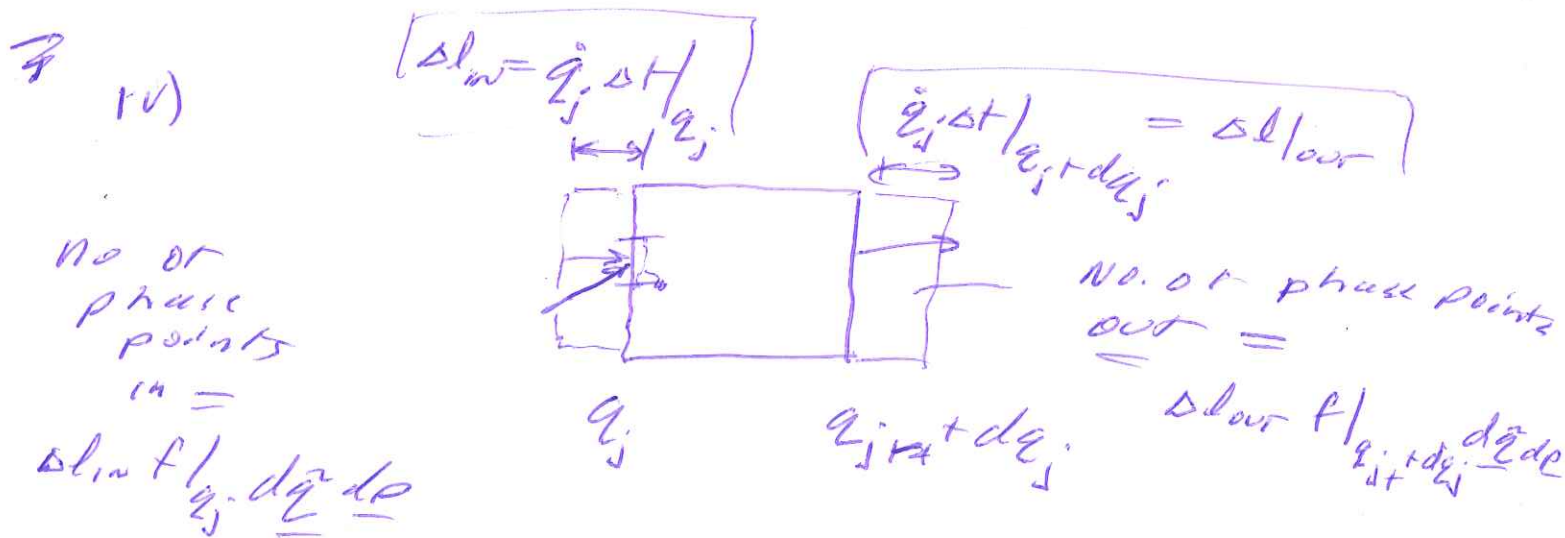
c) Let $\frac{d(N \delta N)}{dt} \bigg|_{q_j}$ represent the
rate of accumulation/loss
of system points w/in a
phase space vol. $dq dp \mp dV$
produced by advection of
phase points into and out of
 dV .

i) a phase point represents
the instantaneous dynamical
state of a given system

ii) within the phase space
 Γ , the ^{dynamical} evolution of
each of N copy
systems w/in our ensemble

is represented / captured by the motion of the phase point associated w/ the system.

iii) It is possible ^{but improbable} for more than one phase point to occupy a given point, $(\underline{q}, p)$ w/in Γ at any given instant. This would correspond to 2 (or more) systems w/in the ensemble ~~being~~ being in exactly the same dynamical state



$d \tilde{q} = d \underline{q}$ w/ $d q_j$ removed
 $d \tilde{q} d p =$ the $6N-1$ -diml area of volume $d \underline{q} d p$

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$$v) \quad \Delta(\tilde{N} \oint \vec{N}) \Big|_{q_j} = \tilde{N} \oint_{\vec{N}} f|_{q_j} d\vec{q} d\vec{p} \\ - \tilde{N} \oint_{\vec{N}} f|_{q_j + dq_j} d\vec{q} d\vec{p}$$

or

$$\frac{\Delta(\oint \vec{N})}{\Delta t} \Big|_{q_j} = (\dot{q}_j \cdot \vec{f})|_{q_j} d\vec{q} d\vec{p}$$

$$- (\dot{q}_j \cdot \vec{f})|_{q_j + dq_j} d\vec{q} d\vec{p}$$

↓ Taylor expand about q_j

$$\therefore \frac{\partial}{\partial t} \left(\oint \vec{N} \cdot \vec{f} d\vec{q} d\vec{p} \right) \Big|_{q_j} = - \frac{\partial (\dot{q}_j \cdot \vec{f})}{\partial q_j} d\vec{q} d\vec{p}$$

$$\therefore \left[\frac{\partial \oint \vec{N} \cdot \vec{f}}{\partial t} \Big|_{q_j} = - \frac{\partial (\dot{q}_j \cdot \vec{f})}{\partial q_j} \right]$$

vi) so summing all of the net fluxes on the $12-N$ ~~faces~~ opposing faces enclosing $d\vec{q} d\vec{p}$

we get

(8.1) (v.i) Liouville eqn

$$\left. \frac{\partial f}{\partial t} \right|_{\text{TOTAL}} = - \sum_{j=1}^{3N} \left[\frac{\partial(q_j, R)}{\partial q_j} + \frac{\partial(p_j, R)}{\partial p_j} \right]$$

vii)

(8.1) can be restated in a (later) useful form as:

$$f_{,t} = - \sum_j \left[f \frac{\partial q_j}{\partial q_j} + \dot{q}_j \frac{\partial f}{\partial q_j} + f \frac{\partial p_j}{\partial p_j} + \dot{p}_j \frac{\partial f}{\partial p_j} \right]$$

(8.2) Liouville eqn

$$f_{,t} = -(\underline{v} \cdot \nabla) f - f(\underline{p} \cdot \nabla)$$

where

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

$$\nabla = \hat{e}_1 \frac{\partial}{\partial q_1} + \hat{e}_2 \frac{\partial}{\partial q_2} + \dots + \hat{e}_{3N} \frac{\partial}{\partial q_{3N}} + \hat{e}_{3N+1} \frac{\partial}{\partial p_1} + \dots + \hat{e}_{6N} \frac{\partial}{\partial p_{3N}}$$