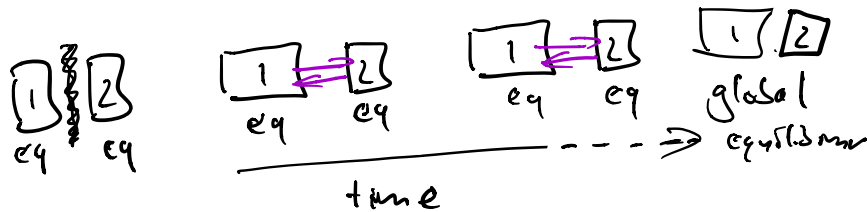


## 1.3 Local equilibrium of continuous systems

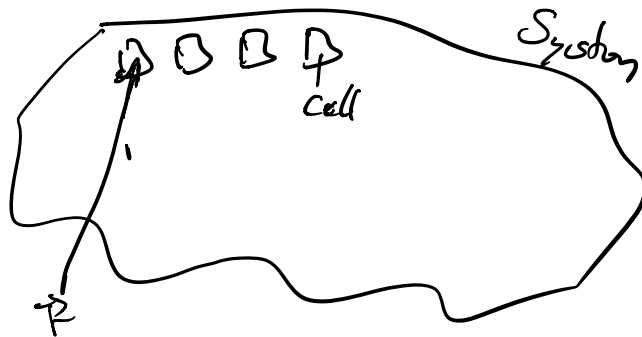
By exploiting a separation of time scales  $\tau_{\text{micro}} \ll \tau_{\text{macro}}$  we argued that non-equilibrium evolution on large time scales can be described by sub-systems evolving through a sequence of equilibrium states



So far we formulated this idea for discrete systems. Now extend to continuous systems in the thermodynamic limit of large system size

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If the system as a whole is sufficiently large, we may divide it into arbitrarily many sub-systems (cells)



such that

- a) extensive quantities  $X_i^{(A)}$  vary little on the scale of individual cells
- b) each cell is large enough to be meaningfully described by thermodynamics

By taking the limit of cell size to zero we obtain a continuous description where each cell is labeled by its space time position  $(t, \vec{r})$

||

Now in taking the limit of small cells, extensive variables



$$X_i^{(A)} \rightarrow 0 \quad \text{meaningless}$$

So instead we need to consider their densities

Non-relativistic systems allow to define two types of densities

- a) wrt to volume (const  $V$  per cell)
- b) wrt to mass (const  $M$  per cell)

So we can define

$$\begin{aligned}
 \text{a) } V^{(a)} = \Delta V \text{ \# cells} & \quad X_i(t, \vec{r}) = \lim_{\Delta V \rightarrow 0} \frac{X_i^{(a)}(t)}{\Delta V} \\
 \text{b) } M^{(a)} = \Delta M \text{ \# cells} & \quad X_i^{(m)}(t, \vec{r}) = \lim_{\Delta M \rightarrow 0} \frac{X_i^{(a)}(t)}{\Delta M}
 \end{aligned}$$

irrespective of what convention is chosen

$$\begin{array}{ccc}
 \text{variables} & X_i^{(A)}(t) & \rightarrow & X_i(t, \vec{r}) & \text{fields} \\
 \text{discrete system} & & & & \text{continuous system}
 \end{array}$$

Evidently the densities in the two cases are related

$$X_i(t, \vec{r}) = \rho(t, \vec{r}) X_i^{(m)}(t, \vec{r})$$

where  $\rho(t, \vec{r}) = \lim_{\Delta V \rightarrow 0} \frac{M^{(m)}}{\Delta V}$  is the mass density

=

So far we can describe densities  $X_i(t, \vec{r})$  in a continuous system. However to describe the actual state of the system in terms of densities  $X_i(t, \vec{r})$  we need to make one additional assumption

local equilibrium assumption:

Each cell is in thermodynamic equilibrium at any  $(t, \vec{r})$ .

→ thermodynamic relations such as  $S = S(X_i(t, \vec{r}))$  and  $dS = \sum_i Y_i X_i$  are valid at the level of each arbitrarily small cell at any time



→ can associate entropy  $S(t, \vec{r})$   
with each cell

Since entropy is extensive, it is again  
better to consider entropy density

$$S(t, \vec{r}) = \lim_{\Delta V \rightarrow 0} \frac{S^{(A)}(t)}{\Delta V}$$

or specific entropy density  $S_{\text{ent}}(t, \vec{r})$

the total entropy of the system  
is recovered as

$$S^{\text{tot}}(t) = \sum_A S^{(A)}(t) = \sum_A \Delta V_A \frac{S^{(A)}(t)}{\Delta V_A} \xrightarrow{\Delta V_A \rightarrow 0} \int_{\vec{r}} S(t, \vec{r})$$



Since thermodynamic relations are assumed to be valid at the level of each cell, changes of the entropy are given by Gibbs fundamental relations

$$dS(t, \vec{r}) = \sum_i Y_i(t, \vec{r}) dX_i(t, \vec{r})$$

with the only difference that  $dX_V = 0$  in the volume scheme

Define local intensive variables

$$Y_i(t, \vec{r}) = \frac{\partial S(t, \vec{r})}{\partial X_i(t, \vec{r})} = \frac{\delta S^{\text{tot}}(t)}{\delta X_i(t, \vec{r})}$$

partial derivative
functional derivative

Since by virtue of the local equilibrium assumption, the dependence of  $S(t, \vec{r})$  on  $X_i(t, \vec{r})$  is assumed to be same as that of  $S$  on  $X_i$  it follows that  $Y_i(t, \vec{r})$  satisfy

Local EOS:  $Y_i(t, \vec{r}) = Y_i(X_i(t, \vec{r}))$

which are of the same form as the global thermodynamic EOSs

Easy to transition between  $X_i$  to  $x_i$   
e.g. ideal gas

$$U = \frac{3}{2} N k_B T \Rightarrow k_B T = \frac{2}{3} \frac{U}{N} \Rightarrow k_B T(t, \vec{r}) = \frac{2 e(t, \vec{r})}{3 n(t, \vec{r})}$$

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Now let us investigate the  
criteria for local equilibrium assumption

Conditions: 1) Thermodynamic fluctuations  
need to be small compared  
to average for thermodynamics  
to be meaningful

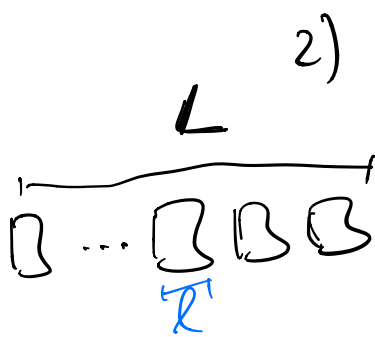


$$\frac{\delta X_i^{(l)}}{X_i^{(l)}} \ll 1$$

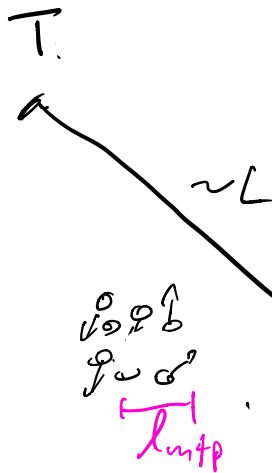
So if  $d$  is the  
interparticle distance then

$$l \gg d$$

Now how large/small a cell can be  $\rightarrow$   
 determined by the variation of the  
 thermodynamic quantities



2) Variations of thermodynamic  
 quantities have to be small  
 on the size of a cell  
 so if  $\nabla X_i \sim \frac{1}{L} X_i$



$$L \gg l \gg d$$

Variations of thermodynamic  
 quantities have to be slow  
 to not drive the system  
 out of equilibrium

Since equilibrium is restored by interparticle  
 interactions, the relevant microscopic time  
 scale is given by

$lump$  mean-free path between interactions

So we also need

$L \gg l_{\text{int}}$

$T_{xi} \gg l_{\text{int}}/v$

in order to approximate local equilibrium  
in the presence of space/time gradients

Quantified by the Knudsen number

$$Kn = \frac{l_{\text{int}}}{L} \ll 1$$

Even though these appear to be  
rather stringent criteria, they are  
satisfied to rather good extent in  
many macroscopic systems

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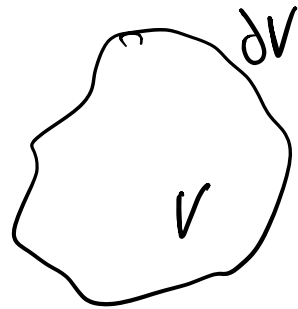
## 1.4 Affinities & fluxes in continuous media

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Now that we understand how to characterize continuous systems based on local equilibrium assumptions, we need to understand conservation laws (allowed variations of  $x_i(t, \vec{r})$ ) and entropy production.

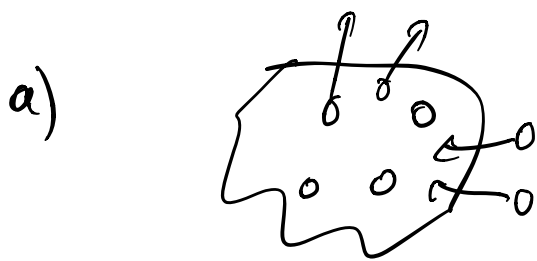
### Balance equations:

We consider fixed subvolume  $V$  bounded by  $\partial V$  and investigate the scalar amount of an extensive quantity contained inside  $V$



$$G_V(t) = \int_V g(t, \vec{r}) d^3\vec{r} = \int_V g_{(m)}(t, \vec{r}) \rho(t, \vec{r}) d^3\vec{r}$$

Now if we are interested in the change of  $G_V(t)$  as a function of time there are essentially two possibilities how  $G_V(t)$  can change

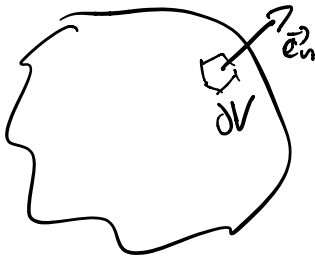


Net flux of  $G$   
from the Volume  $V$



Local production  
of  $G$  inside  $V$

a) So if we consider the net flux of  $G$   
then this is given by flux  $\vec{J}_G(t, \vec{r})$   
through the surface  $\partial V$



$$\frac{\delta G_V^{(a)}(t)}{\delta t} = - \int_{\partial V} \vec{J}_G(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2 \vec{r}$$

b) Local change of  $G$  characterised  
by a source term  $\mathcal{G}$

$$\frac{\delta G_V^{(b)}(t)}{\delta t} = \int_V \mathcal{G}(t, \vec{r}) d^3 \vec{r}$$

So combining a) and b)

$$\frac{dG(t)}{dt} + \int_{\partial V} \vec{J}_G(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2r_s = \int_V d^3r \sigma_G(t, \vec{r})$$

Since the volume  $V$  is fixed we  
can so-express

$$\frac{dG(t)}{dt} = \int_V d^3r \frac{\partial g(t, \vec{r})}{\partial t}$$

and use Gauss theorem  
to rewrite the in/out-flux  
as

$$\int_{\partial V} \vec{J}_G(t, \vec{r}) \cdot \vec{e}_n(\vec{r}) d^2r_s = \int_V \vec{\nabla}_r \cdot \vec{J}_G(t, \vec{r}) d^3r$$

thus all terms are given by  
volume integrals

$$\int_V d^3r \left[ \frac{\partial g(t, \vec{r})}{\partial t} + \vec{\nabla}_r \cdot \vec{J}_G(t, \vec{r}) - \sigma_G(t, \vec{r}) \right] = 0$$



Since this is true for any  
fixed volume  $V$ , the integrand  
must vanish

Local balance equation:

$$\frac{\partial g(t, \vec{r})}{\partial t} + \vec{\nabla}_r \cdot \vec{J}_G(t, \vec{r}) = \sigma_G(t, \vec{r})$$

Conserved quantity:

Now in the special case where  
the extra source quantity  $G$  is conserved  
one has  $\sigma_G(t, \vec{r}) = 0$

$$\text{Continuity equation: } \frac{\partial g(t, \vec{r})}{\partial t} + \vec{\nabla}_r \cdot \vec{J}_G(t, \vec{r}) = 0$$

expressing local conservation law

If  $G=S$  is the entropy then

$$\frac{dS_V}{dt} + \underbrace{\int_{\partial V} \underbrace{\vec{J}_S(t, \vec{r}) \cdot \vec{e}_n(t, \vec{r})}_{\text{entropy current}} d^2r_S}_{\text{exchange of entropy}} = \underbrace{\int_V \underbrace{\sigma_S(t, \vec{r})}_{\text{entropy production rate}} d^3r}_{\text{entropy production}}$$

the source term for entropy production  
 $\sigma_S(t, \vec{r})$  is positive semi-definite

$$\sigma_S(t, \vec{r}) \geq 0$$

with positive contributions describing  
dissipative phenomena

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## Entropy current, affinity & fluxes

Based on Gibbs fundamental relation,  
for local equilibrium states, we also  
know

$$\square \quad \frac{\partial S(t, \vec{r})}{\partial t} = \sum_i Y_i(t, \vec{r}) \frac{\partial X_i(t, \vec{r})}{\partial t} \quad \left| \quad \left( \frac{\partial X_V}{\partial t} = 0 \right) \right. \\ \text{const. } V$$

Characterizing change of entropy density  $S$   
in an equilibrium system at rest

Now if we consider a moving equilibrium  
system, Galilean invariance of  
non-relativistic systems suggests  
that the currents should satisfy  
a similar relation

$$\square \rightarrow \quad \vec{J}_S(t, \vec{r}) = \sum_i Y_i(t, \vec{r}) \vec{J}_i(t, \vec{r}) \\ \text{entropy flux} \qquad \qquad \qquad \text{flux of } X_i(t, \vec{r})$$

with  $J_V = 0$  as there is no volume flux

Now looking again at the balance equation for  $S(t, \vec{r})$

$$\frac{d}{dt} S(t, \vec{r}) + \vec{\nabla} \cdot \vec{J}_S(t, \vec{r}) = \sigma_S(t, \vec{r})$$

and using that  $x_i(t, \vec{r})$  are conserved

$$\frac{d}{dt} x_i(t, \vec{r}) + \vec{\nabla} \cdot \vec{J}_i(t, \vec{r}) = 0$$

we get

$$\sum_i y_i(t, \vec{r}) \frac{d x_i(t, \vec{r})}{dt} + \vec{\nabla} \cdot \sum_i y_i(t, \vec{r}) \vec{J}_i(t, \vec{r}) = \sigma_S(t, \vec{r})$$

$$\sum_i y_i(t, \vec{r}) \left( \underbrace{\frac{d x_i(t, \vec{r})}{dt} + \vec{\nabla} \cdot \vec{J}_i(t, \vec{r})}_{= 0 \text{ (continuity equation)}} \right) + \sum_i (\vec{\nabla} y_i(t, \vec{r})) \cdot \vec{J}_i(t, \vec{r}) = \sigma_S(t, \vec{r})$$

entropy production rate

$$\sigma_S(t, \vec{r}) = (\vec{\nabla} y_i(t, \vec{r})) \cdot \vec{J}_i(t, \vec{r})$$

Note that the structure is essentially  
the same as for the discrete system.

$$\text{with } Y_i^{(A)} - Y_i^{(B)} \rightarrow \vec{\nabla} Y_i(t, \vec{r})$$

in particular if we identify the

$$\text{affinity } \vec{F}_i(t, \vec{r}) \equiv \vec{\nabla} Y_i(t, \vec{r})$$

the entropy production takes the  
same bilinear form

$$\sigma_S(t, \vec{r}) = \sum_i \vec{F}_i(t, \vec{r}) \cdot \vec{J}_i(t, \vec{r})$$

So far we have discussed balance  
equations for scalar conserved  
quantities, but the same logic  
applies to vectorial quantities  
eg momentum as we will see  
in the context of hydrodynamics