The second law of thermodynamics

We have deduced the form taken by four fundamental conservation laws of physics in an idealized macroscopic continuous body.

We think of these laws as being the *macroscopic consequences* of extremely fundamental microscopic conservation laws of mechanics. In our gross macroscopic view we introduce concepts like internal energy and heat flow to aid us in predicting macroscopic observations we might make.
If we adopted a purely [illegible] microscopic point of view, all energy would just be mechanical energy.

We wish to deduce the form taken by one further law of physics, this time one which is a *strictly* *macro*scopic law. The second law of thermodynamics centers on the concept of *entropy*, and this is a strictly macroscopic concept. It makes no sense to speak of the entropy of a few point masses.

Entropy, is a measure in some sense of the state of disorder of a large macroscopic system

We will make quite a lot of use of the concept of entropy in the weeks to come. Those of you who do not remember much in the way of classical thermodynamics would do well to review.

For the classical approach try:

Fermi, Thermodynamics (Dover paperback)
Ch. I - V, good for the first time

More attention to the subtle and tricky details is to be found in Pippard, Classical Thermodynamics (C.U.P. paperback), an excellent book for the second time around Ch. 1-7.

For a more modern axiomatic approach, try Callen, Thermodynamics (Wiley) Ch. 1-11.

25. the second law of thermodynamics

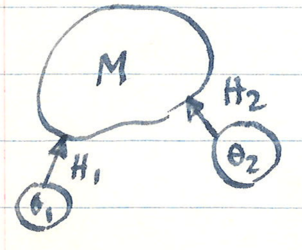
The second law of thermodynamics for homogeneous substances postulates the existence of a function of state called the entropy, such that in any reversible process

$$ds = \left(\frac{\Delta Q}{\theta}\right)_{\text{reversible}}$$

is an exact or perfect differential. In classical thermodynamics, the entropy S is postulated to be a function of the state of the thermodynamic substance, that is a prescribed fcn of the thermodynamic state variables.

This is the first part of the second law. The second part of the second law of thermodynamics says that if a certain mass M of thermodynamic substance acquires amounts of heat $H_1, H_2, \cdots H_n$ from sources at temperatures $\theta_1, \ldots, \theta_n$, then the total entropy change in M is always

$$\boxed{\Delta S \geqslant \sum_{j=1}^{N} \frac{H_j}{\theta_j}}$$



We also introduce the <u>temperature field</u> $\theta_E(\underline{r},t)$ throughout the continuum.

A note on the thermodynamical variables:
We have introduced three thermodynamical variables

temperature $\theta(\underline{r},t)$

these 2 are extensive by assumption $\Big\|$ internal energy density $u(\underline{r},t)$
entropy density $s(\underline{r},t)$.

Classical thermodynamics assumes all three of these to be functions of state. In classical thermodynamics, these are all really only <u>equilibrium concepts</u>. We can strictly only speak of the temperature or the entropy or the internal energy of a substance which is in <u>thermodynamic equilibrium</u>.

It is my opinion that temperature and internal energy are intuitive enough concepts that it does not seem daring to assume that we may discuss them in the absence of equilibrium. The same might not be said to be true of the entropy, but we shall do so anyway.

Actually for most geophysically interesting materials, for any fluid and for a perfectly elastic solid, we will assume, as a part of our constitutive assumptions that a state of local thermodynamic equilibrium does always exist. Thus for these types of materials entropy is on a very firm footing. In any case we will assume that we may speak of $\theta(\underline{r}, t)$, $U(\underline{r}, t)$, and $S(\underline{r}, t)$ for any continuum, even if it is not in l.t.e.

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It is only this second half of the law which we shall postulate to be in general valid for arbitrary continuous media

We do not assume in general that entropy is a state function determined by the instaneous values of the other state variables. The problem comes really in determining what the thermodynamic state variables are.

For many processes we would like to investigate, e.g. work-hardening of steel, the entropy will be determined not just by the instantaneous state of the material but in general by the history of deformation of the material. The same is true of the internal energy. Both S and U must in general be considered to be functionals of the variables. People try to get around this by introducing the concept of hidden variables.

This difficulty does not arise:

1. for any fluid
2. for a perfectly elastic solid

But still to be completely general, we will postulate only that

There exists a function $S(\underline{r},t)$ defined throughout the continuum such that

$$\mathcal{S} = \int_V \rho S \, dV$$

is the total entropy of the material in the volume V

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Given a volume $V(t)$ moving with the material (always consists of the same matter). The total entropy change in $V(t)$ during an inf. short time δt is always $\geq \sum_{j=1}^{n} H_j/\theta_j$ recieved by the material during the time δt

$$\Delta \int_{V(t)} \rho S \, dV \geq \left[- \int_{\partial V(t)} \frac{\underline{H} \cdot \hat{n}}{\theta} dA + \int_{V(t)} \frac{h}{\theta_s} dV \right] \delta t$$

or dividing by δt and letting $\delta t \to 0$

$$\boxed{\frac{d}{dt} \int_{V(t)} \rho S \, dV \geq - \int_{\partial V(t)} \frac{\hat{n} \cdot \underline{H}}{\theta} dA + \int_{V(t)} \frac{h}{\theta_s} dV}$$

the rate of entropy increase of any volume $V(t)$ is $\geqslant$ the rate of entropy input by heat transfer

In the above eqn θ_s is the temp. of the source of heat per unit volume h

e.g.

if h is absorption of sunlight, $\theta_s =$ surface temp of sun

if h is nuclear energy, $\theta_s =$ kinetic temp of nuclear decay products ~ several mev ~ 10^9 °C.

We assume that the only important property of h is its amount and that θ_s has no effect on the motion except directly through its effect on h then we can replace the actual source of h by any other source capable of supplying the same amount of heat. But a source h at θ_s' can supply heat h to the material at temp θ iff $\theta_s' \geqslant \theta$

Thus in our eqn we may replace θ_s by any temp. $\theta_s' \geqslant \theta$; the inequality will remain true. This is the assumption

The smaller we make θ_s the larger the r.h.s. above.

Thus the stronger is the inequality regarded as a bound on $d/dt \int_{V(t)} \rho S \, dV$.

We get the strongest $\ne$ by using θ instead of θ_s.

~~If we seek the greatest lower bound, we replace θ_s by θ in the eqn.~~

$$\boxed{\frac{d}{dt}\int_{V(t)} \rho S \, dV \geqslant -\int_{\partial V(t)} \frac{\hat{n}\cdot \underline{H}}{\theta}\, dA + \int_{V(t)} \frac{h}{\theta}\, dV}$$

Note: say $h=0$ and $\underline{H}=0$ on $\partial V(t)$. Then $\frac{dS}{dt} \geq 0$, the total entropy cannot decrease. Note and that this does not $\Rightarrow$ that $S(\underline{r},t)$ is necessarily non-decreasing at all $\underline{r},t$.

now $$\frac{d}{dt}\int_{V(t)} \rho S \, dV = \int_{V(t)} \rho D_t S \, dV$$

$$\int_{\partial V(t)} \frac{\hat{n}\cdot \underline{H}}{\theta}\, dA = \int_{V(t)} \nabla\cdot\left(\underline{H}/\theta\right) dV \text{, so}$$

$$\int_{V(t)} \left[\rho D_t S + \nabla\cdot\left(\underline{H}/\theta\right) - h/\theta\right] dV \geq 0$$

Since this inequality is true for every volume $V(t)$, by an obvious extension of the vanishing integral theorem, the integrand must be positive throughout the material

$$\boxed{\rho D_t S + \nabla \cdot (\underline{H}/\theta) - \frac{h}{\theta} \geqslant 0}$$

This is the form taken by the second law of thermodynamics in an arbitrary continuum.

It is usually referred to as the

Clausius - Duhem inequality

note the special case of an adiabatic deformation ($\underline{H}=\underline{0}$, $h=0$)

The CDI asserts that $D_t S \geqslant 0$ at all points.

It does not appear as immediately useful as the other laws we have derived. Note that it does not help out in our no. of equns. vs. unknowns problems.

It introduces two more unknown $S(\underline{r},t)$ and $\theta(\underline{r},t)$ and it is not even an equation, but an inequality

It is however a quite general physical law and it in fact plays a very important role in the modern theory of constitutive relations.

In the case where the entropy $S(\underline{r},t)$ really is a state fcn determined at every point by the instantaneous condition of the material (any fluid, viscous or non-viscous and any perfectly elastic solid, then the *first part* of the second law allows one to deduce a *conservation law for the entropy*. The Clausius - Duhem *inequality* is of course *not* a conservation law, it is an *inequality* but it is a physical law.

~~Let's now begin our study of particular kinds of continua. The first idealized continuum we will treat will be *fluids*.~~

Lecture #10

22. Boundary conditions (kinematic b.c.)

We have derived four conservation equations p.d.e. which govern the dynamics of any given continuum.
Throughout the discussion we have assumed that whenever we needed a partial derivative it existed.

At a bdry separating two different continua (e.g. the air-sea surface), the density, velocity, etc. may not even be continuous, much less differentiable.

Our equations are valid inside any single continuum, but we must give separate attention to the behavior of a boundary between two continua. What do the laws of physics tell us about such bdries?
We will assume that if we approach the boundary from either side then all physical quantities have well-defined limits, but the limits may not be the same on the two sides.
(e.g. density at the air-sea interface

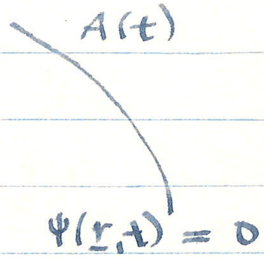
We have seen already that any boundary two different continua must always consist of the same material particles. This property will be called preservation of boundaries

It is a rigorous physical consequence of the various assumptions we have made about the lack of kinking and tearing of our continua, and the consequent cont. differ. of $\underline{r}(\underline{x},t)$

There are three types of b.c.

1. those governing the <u>kinematics</u> of the bdry
2. those governing the dynamics of the bdry.
3. thermal b.c. (better to call <u>energetic</u>)

<u>Kinematic b.c.</u>



Suppose that a surface A(t) moves in a known manner, its eqn at time t being

$$\psi(\underline{r},t) = 0$$

On one side of this surface is a material continuum, (e.g. H_2O) which always remains in contact with A(t) but which may slip <u>along</u> A(t)

If we choose we may regard the value of ψ at a material particle as a property of that particle. The value of ψ at a particle may change with time but particles on A(t)

remain there and hence always have $\psi = 0$
At such a bdry particle

$$\boxed{\begin{array}{l} D_t \psi = 0 \quad \text{on} \quad A(t) \quad \text{or} \\ \partial_t \psi + \underline{u} \cdot \nabla \psi = 0 \end{array}}$$

This is the cond. which must be satisfied by the velocity of the material to insure that the material does not separate from or cross the surface $A(t)$ whose eqn at time t is $\psi(\underline{r}, t) = 0$

If $\exists$ two continua, one on each side of $A(t)$ with velocities $\underline{u}_{(1)}$ and $\underline{u}_{(2)}$, we have

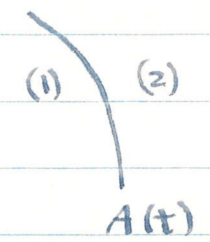
$$\partial_t \psi + \underline{u}_{(1)} \cdot \nabla \psi = \partial_t \psi + \underline{u}_{(2)} \cdot \nabla \psi \quad \text{or}$$

$$\underline{u}_{(1)} \cdot \nabla \psi = \underline{u}_{(2)} \cdot \nabla \psi$$

now $\hat{n}(\underline{r}, t)$ the unit normal to $A(t)$ at $\underline{r}, t$ is

$$\hat{n}(\underline{r}, t) = \nabla \psi(\underline{r}, t) / |\nabla \psi(\underline{r}, t)|$$

hence the cond. that the two continua remain in contact at $A(t)$ without interpenetrating or separating is



$$\hat{n} \cdot \underline{u}_{(1)} = \hat{n} \cdot \underline{u}_{(2)}$$

This eqn makes sense. Note that it permits the two continua to slip past one another

If they are not to slip (a welded boundary) we must have

$$\boxed{\underline{u}_{(1)} = \underline{u}_{(2)}}$$

Which of these two conditions is appropriate depends on the problem under study. For example:
2. two welded solid or elastic media
1. bdry between a non-viscous fluid and a solid — or a fault

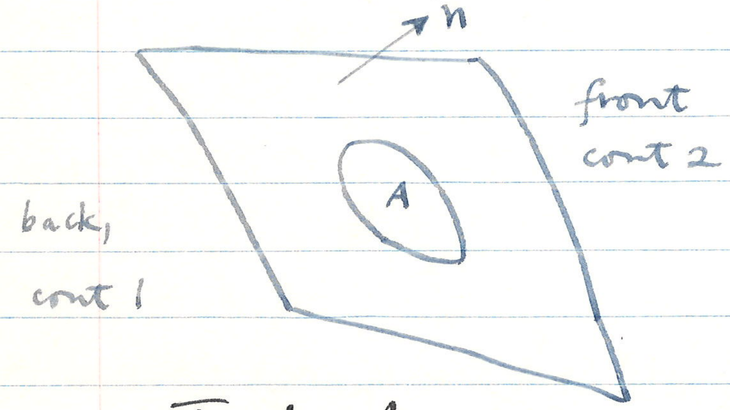
For the most part we discuss this later

23. Dynamic b.c. at a simple boundary

The form of the dynamical b.c. depends critically on the nature of the boundary under consideration. For now we consider only the simplest kind of boundary between two continua, a so-called simple boundary

This is simply the surface of contact between two different continua. Lets be more exact.

Given two continua in contact along and separated by a surface $\tilde{A}$ with unit normal $\hat{n}$ pointing into continuum 2.



Let A be a not necessarily small patch on A

The force exerted *on* A by cont. 2 is

$$\int_A \hat{n} \cdot \underline{\underline{T}}_{(2)} \, dA$$

where $\underline{\underline{T}}_{(2)}$ is the limiting value of the stress tensor on $\tilde{A}$ in cont. 2.

Treat A as a *separate* *2-d* *continuum* *hypersurface* (one *must* do this for the massive tense boundary)

The force exerted *on* A by cont. 1 is

$$\int_A (-\hat{n}) \cdot \underline{\underline{T}}_{(1)} \, dA$$

The total force exerted on A by the two continua is

$$\int_A \hat{n} \cdot [\underline{\underline{T}}_{(2)} - \underline{\underline{T}}_{(1)}] \, dA = \underline{F}_A$$

If there are no other forces on A and if there is no mass per unit area on A, A is called a *simple interface*

Homework problem: include effect of "body" forces and surface tension, a so-called massive tense bdry.

If $\tilde{A}$ is a simple bdry then the total momentum of the patch A is zero since it has no mass. The eqn.

$$\text{force on } A = \frac{d}{dt}(\text{momentum of } A)$$

reduces to $\underline{F}_A = 0$ ↑ here, especially, A is a 2-d continuum hypersurface.

Thus if $\tilde{A}$ is simple and A is any patch on $\tilde{A}$

$$\int_A \hat{n} \cdot [\underline{\underline{T}}_{(2)} - \underline{\underline{T}}_{(1)}]\, dA = 0$$

By the vanishing integral thm (in two dim)

$$\boxed{\hat{n} \cdot \underline{\underline{T}}_{(2)} = \hat{n} \cdot \underline{\underline{T}}_{(1)}}$$

The normal stress or the net traction must be continuous across simple interfaces. The total stress need not be cont. across simple interfaces

This is the dynamical b.c.

Special case: if $\underline{\underline{T}}_{(1)}$ and $\underline{\underline{T}}_{(2)}$ are both isotropic (e.g. bdry between two non-viscous fluids)

$$\underline{\underline{T}}_{(1)} = -p_{(1)} \underline{\underline{I}}$$
$$\underline{\underline{T}}_{(2)} = -p_{(2)} \underline{\underline{I}}$$

$$\hat{n} \cdot \underline{\underline{T}}_{(1)} = -p_{(1)} \, \hat{n} \cdot \underline{\underline{I}} = -p_{(1)} \hat{n}$$

$$\hat{n} \cdot \underline{\underline{T}}_{(2)} = -p_{(2)} \, \hat{n} \cdot \underline{\underline{I}} = -p_{(2)} \hat{n} \quad \text{or}$$

$$\boxed{p_{(1)} = p_{(2)}}$$

pressure is cont. across a simple interface if both media have isotropic stress tensors.

Hand out homework problem: the massive, tense boundary. For $\mu = \gamma = 0$ reduces to the above eqn.

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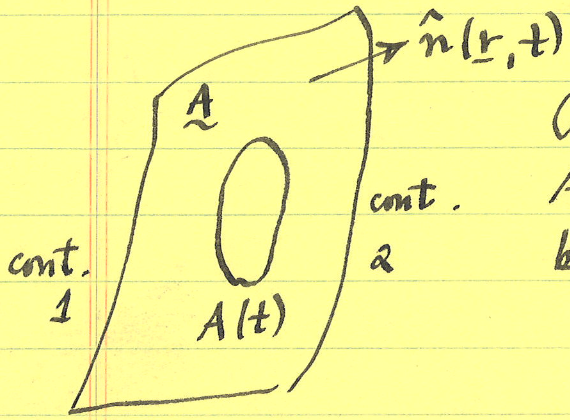
If there is *slip* on the boundary, can also add energy by tractions doing work on the 2-d continuum hypersurface; that rate of mechanical work is $\int_{A(t)} [\hat{n}\cdot\mathbf{T}\cdot\mathbf{u}]^{+}_{-}\, dA$

This leads to $[\hat{n}\cdot(\mathbf{H}+\mathbf{T}\cdot\mathbf{u})]^{+}_{-}=0$

$$[\hat{n}\cdot\mathbf{H}]^{+}_{-} = -[\hat{n}\cdot\mathbf{T}\cdot\mathbf{u}]^{+}_{-}$$

Right hand side is rate of frictional heating e.g. on a *fault*.

There is also a <u>thermal</u> <u>boundary</u> <u>condition</u> at a <u>simple boundary</u>



Consider once again a patch A(t) on the boundary between 2 continua.

The net <u>rate</u> at which the patch A(t) of particles is gaining energy due to heat flow $\underline{H}_1(\underline{r},t)$ in cont. 1 is

$$\int_{A(t)} \hat{n}\cdot\underline{H}_1\,dA$$

The net rate at which the patch A(t) of particles is gaining energy due to heat flow $\underline{H}_2(\underline{r},t)$ in cont. 2 is

$$-\int_{A(t)} \hat{n}\cdot\underline{H}_2\,dA$$

<u>NB</u>: This assumes no slip on boundary.

We define a <u>simple</u> <u>boundary</u> as one in which:

1. $\int_{A(t)} \hat{n}\cdot[\underline{H}_1-\underline{H}_2]\,dA$ is the <u>net</u> rate of accession of energy.

2. The boundary has no way of storing energy ($\exists$ no <u>surface</u> internal energy : this is <u>not</u> a consistent assumption for a massive, tense boundary)

Hence for a <u>simple</u> boundary , we may write

$$\text{net rate of accession of energy of } A(t) \equiv \frac{d}{dt}\left(\text{energy of } A(t)\right)$$
$$\equiv 0$$

Thus if $\underset{\sim}{A}$ is simple and $A(t)$ is any patch of particles on $\underset{\sim}{A}$, we have

$$\int_{A(t)} \hat{n} \cdot \left[\underline{H}_1 - \underline{H}_2 \right] dA = 0$$

By the vanishing integral theorem , we have

$$\boxed{\begin{gathered} \hat{n} \cdot \underline{H}_1 = \hat{n} \cdot \underline{H}_2 \quad \text{or} \\ \left[\hat{n} \cdot \underline{H} \right]_{-}^{+} = 0 \end{gathered}}$$

This called <u>Fourier's condition</u> (1822)

Summarizing the <u>boundary</u> <u>conditions</u> at an interface between two media

<u>Kinematic</u>: (1): $[\hat{n} \cdot \underline{u}]^{+}_{-} = 0$, tangential slip, or

(2): $[\underline{u}]^{+}_{-} = 0$, no slip (welded, e.g.)

Which is appropriate depends on the assumed nature of the media

e.g. (1) is for a solid - perfect fluid bdry

(2) is for a welded solid-solid bdry

(2) is also for a solid - viscous fluid bdry, as we shall see later

<u>Dynamic</u> (for a <u>simple boundary</u>): $[\hat{n} \cdot \underline{\underline{T}}]^{+}_{-} = 0$

<u>traction</u> is continuous

(stress $\underline{\underline{T}}$ need not be)

<u>Thermal</u>: (for a <u>simple</u> <u>bdry</u>): $[\hat{n} \cdot \underline{H}]^{+}_{-} = 0$

<u>normal</u> component of heat flow vector is continuous

($\underline{H}$ itself need not be)

$\rho(\underline{r},t)$, $U(\underline{r},t)$, $S(\underline{r},t)$, and $\theta(\underline{r},t)$ may all be discontinuous across a simple bdry.

24. Constitutive equations

From the laws of mechanics and thermodynamics, we have deduced the following equations for a continuum

Equation	name	source
$\partial_t \rho + \nabla\cdot(\rho \underline{u}) = 0$	cont. eqn	cons. of mass
$\rho D_t \underline{u} = \nabla\cdot\underline{\underline{T}} + f$	momentum eqn	cons. of momentum
$\underline{\underline{T}} = \underline{\underline{T}}^T$	angular momentum eqn	cons. of angular momentum in materials with negligible $\underline{l}$, $\underline{m}$, and $\underline{\underline{M}}$.
$\rho D_t U + \nabla\cdot\underline{H} = \underline{\underline{T}}\cdot\underline{\underline{\epsilon}} + h$	internal energy eqn	first law of thermodynamics
$\rho D_t S + \nabla\cdot\left(H/\theta\right) - \frac{h}{\theta} \geq 0$	Clausius-Duhem ≠	second law of thermodynamics

the above eqns involve the 23 quantities

$$\rho,\ \underset{\substack{\uparrow\\3}}{\underline{u}},\ \underset{\substack{\uparrow\\9}}{\underline{\underline{T}}},\ \underset{\substack{\uparrow\\3}}{\underline{f}},\ U,\ \underset{\substack{\uparrow\\3}}{\underline{H}},\ h,\ S,\ \theta$$

For a complete description of a continuum we must know all 23 of these quantities at every pt. $\underline{r}$ and for all times t.

<u>Central problem</u> (mechanics of a single-phase chemically homog. material): to predict the values of these 23 quantities for all $\underline{r}, t$ given their 23 values at $t = 0$, and given the external influences, if any, exerted on the continuum.

This is a formidable math. and physical problem. Known to be soluble only in a few special cases.

One difficulty appears immediately.

If we have no infor. besides initial cond., external influences, and the above eqns, the problem is insoluble. We have only 9 relations among 23 unknowns, and one is not even an eqn.

Consider only the eqns (∃ 8 eqns for 21 unknowns)

cont eqn 1

mom. eqn 3

ang mom eqn 9, 3 trivial ($T_{11}=T_{11}$), only 3 <u>independ</u>

energy eqn 1

Lets assume for the moment that $\underline{f}$ and h are <u>entirely</u> due <u>to external causes</u> (we must neglect that part of $\underline{f}$ due to self-gravitation and we must neglect any internally generated h such as radioactivity). The first is easy to get around for <u>self-gravitation</u>; we merely add Poisson's eqn - see normal modes. Then $\underline{f}$ and h will be known

So we have 8 relations among remaining 17 quantities, or eliminating $\underline{\underline{T}} = \underline{\underline{T}}^T$

5 relations among

$\rho, u_1, u_2, u_3, T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, T_{33}, U, H_1, H_2, H_3$.

14 quantities.

We clearly need nine more relations in general to determine these quantities.

Physically its clear what we need

1. how to compute three components of heat flow vector from values of other quantities (<u>heat flow equation</u>)
2. how to compute six stress components in terms of other quantities (the <u>stress-strain relations</u>)

We shall find that many useful (in geophysics) const. relations require the intro. of S and θ as variables.

For real substances, these relations cannot be computed or deduced from the atomic theory of matter.
(accurate approx. are available for some motions of certain solids and gases.)

Nine missing relations must be obtained by laboratory measurements. They are empirical statements, the result of fitting curves to laboratory data.
One makes simple idealized models of various kinds of continua, and these in certain instances adequately approximate various real substances.

These extra relations are called constitutive relations, they define the type of continuum which one wishes to study.
The constitutive relations do not have the generality of the conservation eqns.

The most noteworthy recent developments in cont. mech. have been in the theory of constitutive relations. The modern theories are theories of theories. set limitations on form certain individual theories can take, once the proposed dep. and ind. variables have been chosen.