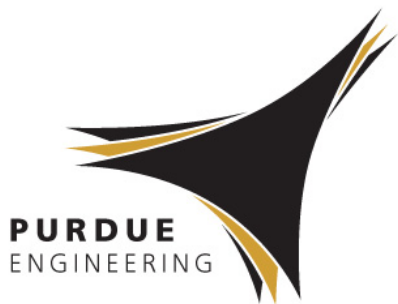


Spring, 2015

# ME 612 – Continuum Mechanics

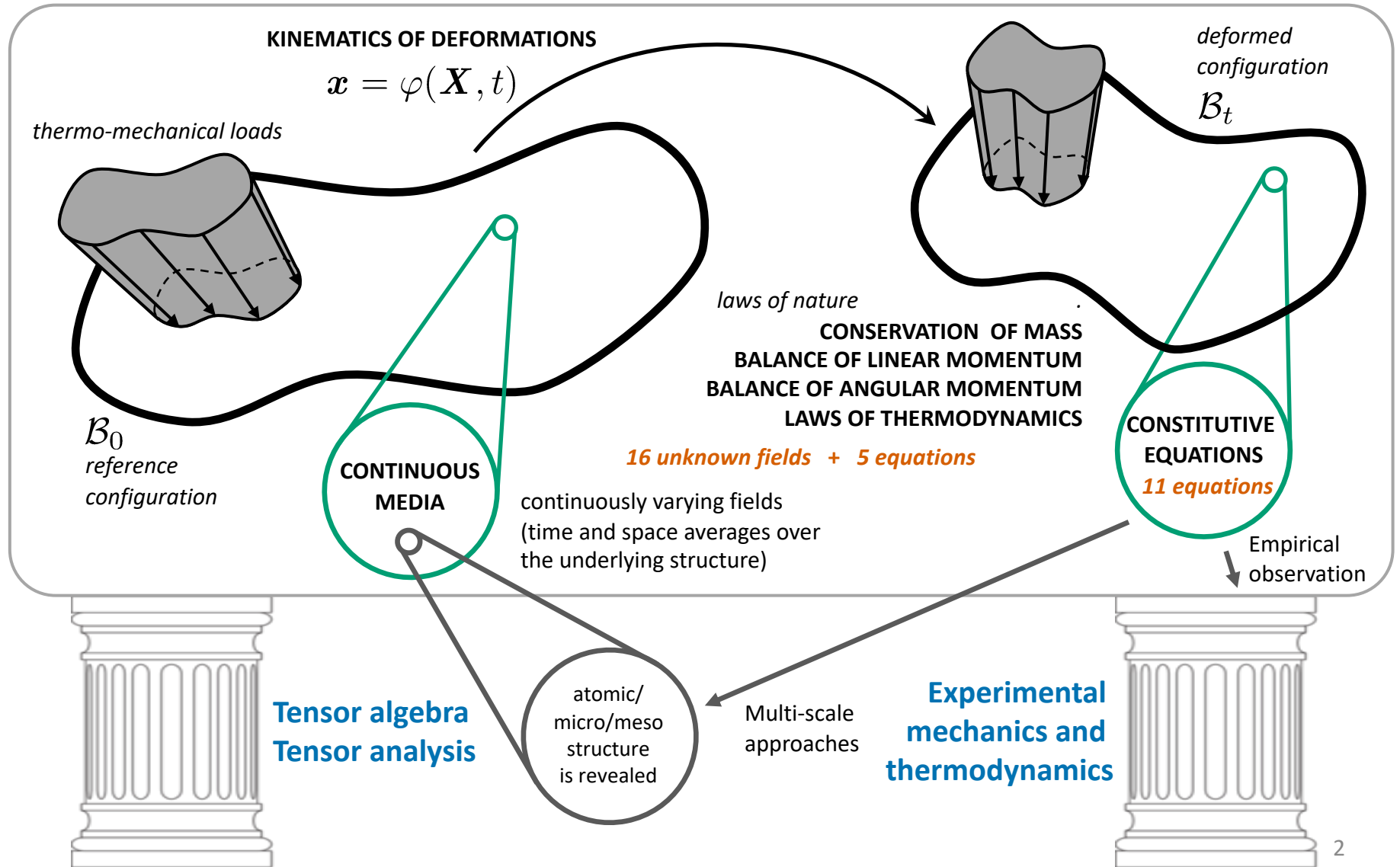
## Lecture 10 Thermodynamics



Instructor: Prof. Marcial Gonzalez

September 21, 2021

# Lecture 10 – Thermodynamics

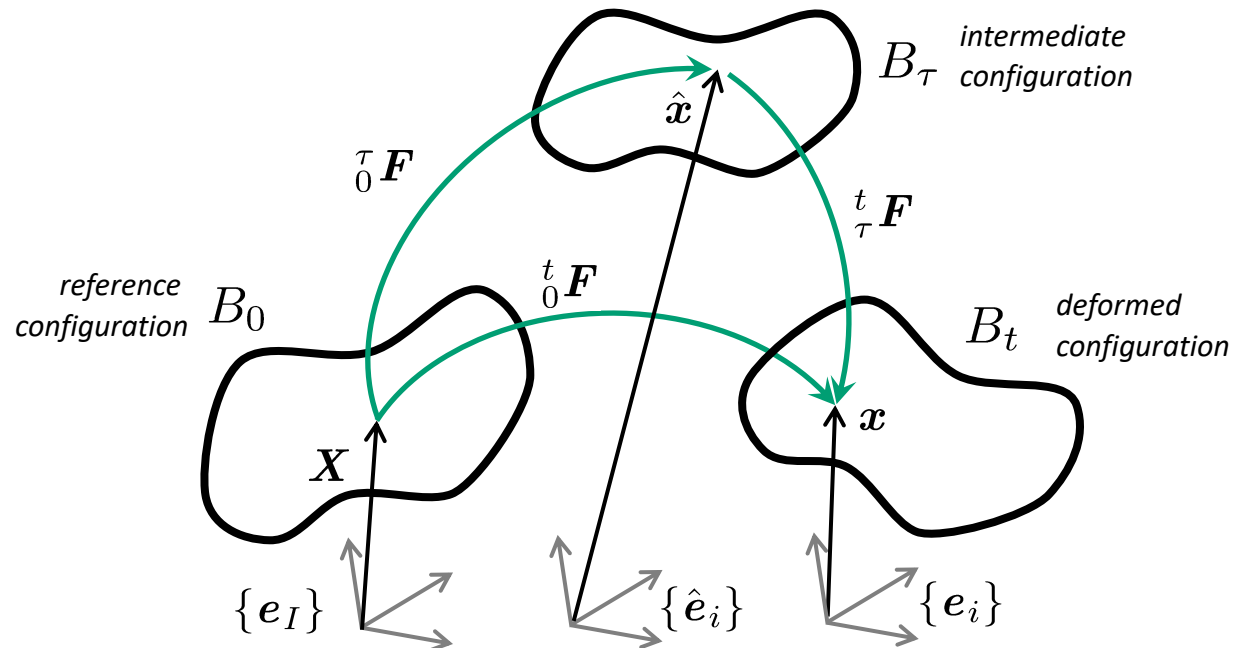


# Lecture 10 – Thermodynamics

## Review + Homework problem

DIY

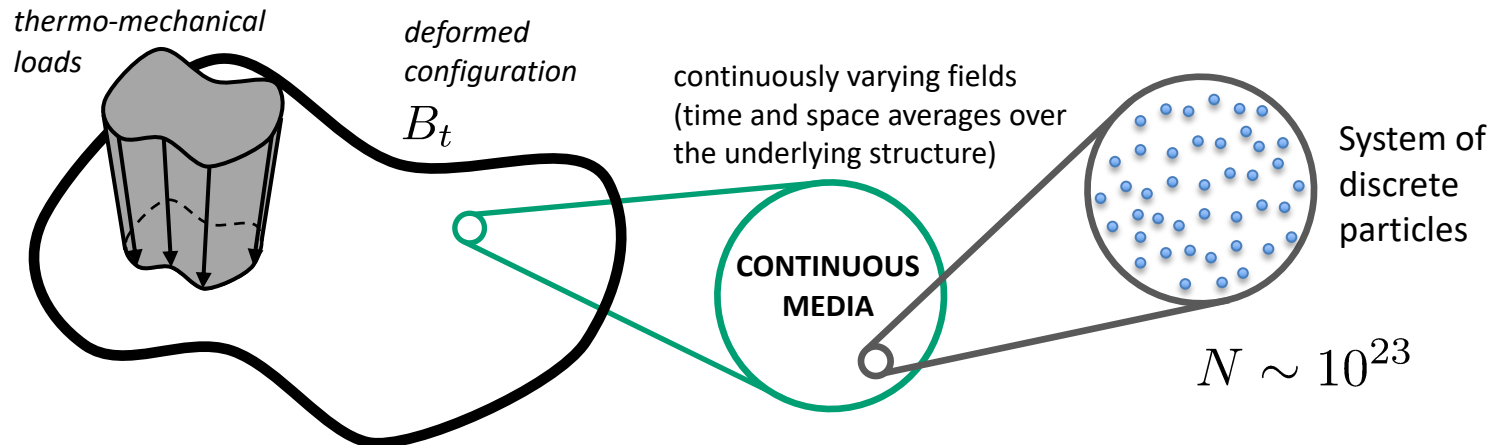
$${}^t_0 E_{IJ} = [{}^\tau \phi^*({}^t_\tau \hat{E}_{ij})]_{IJ} + {}^\tau_0 E_{IJ} \quad \text{Lagrangian strain tensor}$$



# Lecture 10 – Thermodynamics

## Macroscopic observable quantities

- Microscopic kinematics are described by a  $6N$ -dimensional vector space (phase space) with all particle positions and momenta
$$\mathbf{y} = \{\mathbf{r}^1, \dots, \mathbf{r}^N, m^1 \dot{\mathbf{r}}^1, \dots, m^N \dot{\mathbf{r}}^N\}$$
- Macroscopic kinematic quantities  
(e.g., total volume, center of mass position and orientation)
- Macroscopic non-kinematic quantities  
(e.g., total linear and angular momentum, total number of particles, total mass)
- Macroscopic fields  
(e.g., mass density, Lagrangian strain tensor)



# Lecture 10 – Thermodynamics

## Thermodynamic equilibrium

After an external perturbation (of finite duration in time), all systems tend to evolve to a quiescent and spatially homogeneous (at the macroscopic length scale) terminal state where the system's macroscopic observables have constant limiting values.

## Metastable thermodynamic equilibrium

All systems exhibit a two-stage dynamic process:

- Macroscopic observables exhibit a high rate of change during and immediately after the perturbation.
- Macroscopic observables exhibit a rate of change which is orders of magnitude smaller (i.e., the system is in a state of metastable thermodynamic equilibrium).

Note: different materials exhibit different time-scales.

(e.g., the 'pitch drop experiment', it took from 1927 to 1930 to settle and since then only 9 drops of pitch have fallen)

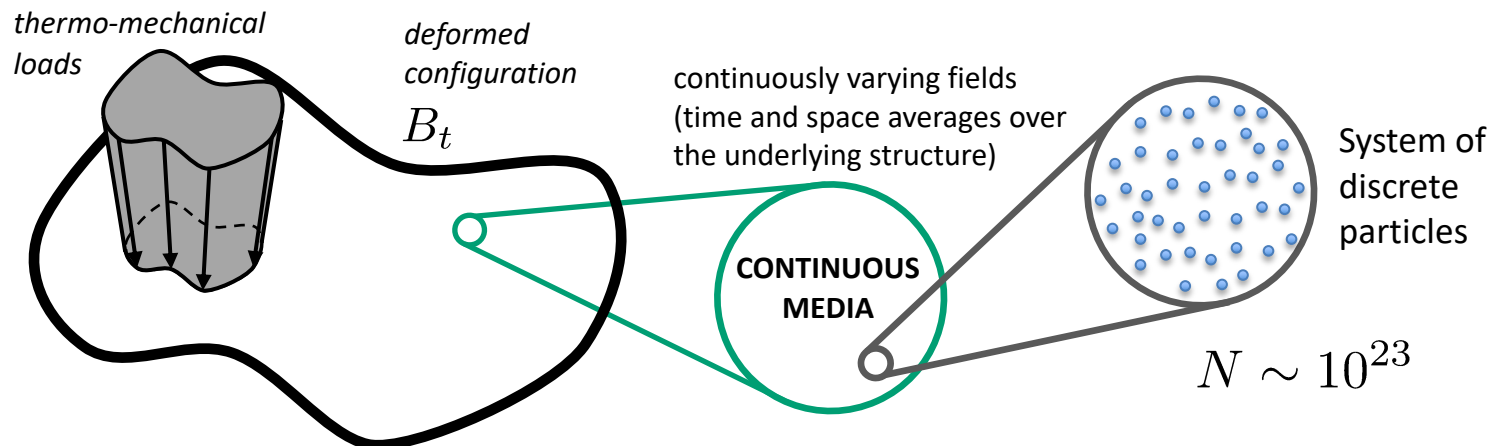
For how long shall we wait?  
(e.g., 'pitch drop experiment')



# Lecture 10 – Thermodynamics

## State variables

- State variables: macroscopic observables that are well defined and single-valued when the system is a state of thermodynamic equilibrium.  
Example: the thermodynamic equilibrium of a gas (or any system in *true* thermodynamic equilibrium) is characterized by the number of particles, the volume, the pressure and the temperature (i.e., 4 state variables).
- Some state variables are kinematic state variables (such as volume and, for solids, strain). A change in a kinematic state variable results in a *thermodynamic tension*)

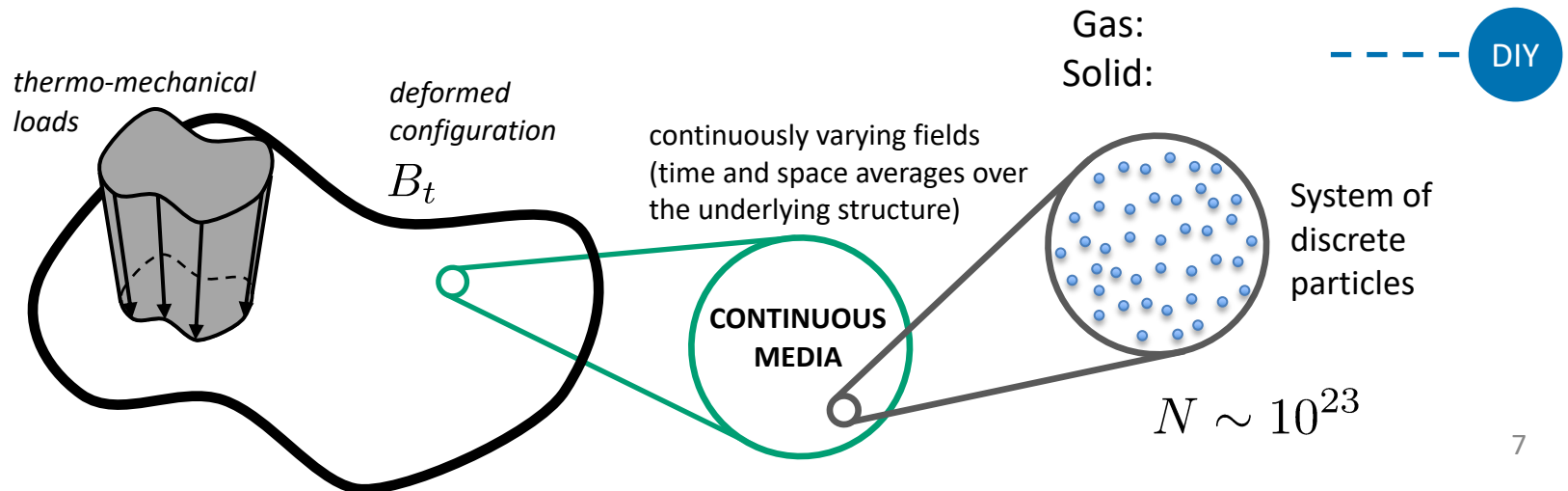


# Lecture 10 – Thermodynamics

## State variables

- Intensive state variables are independent of amount (e.g., temperature, pressure or stress, strain  $\mathbf{E}$  ).
- Extensive state variables depend on amount (e.g., volume, volume strain  $V_0 \mathbf{E}$ , number of particles, mass, internal energy).

A systems in thermodynamic (or metastable) equilibrium is characterized by a set of  $n^\Gamma$  independent extensive kinematic state variables  $\mathbf{\Gamma} = (\Gamma_1, \dots, \Gamma_{n^\Gamma})$



# Lecture 10 – Thermodynamics

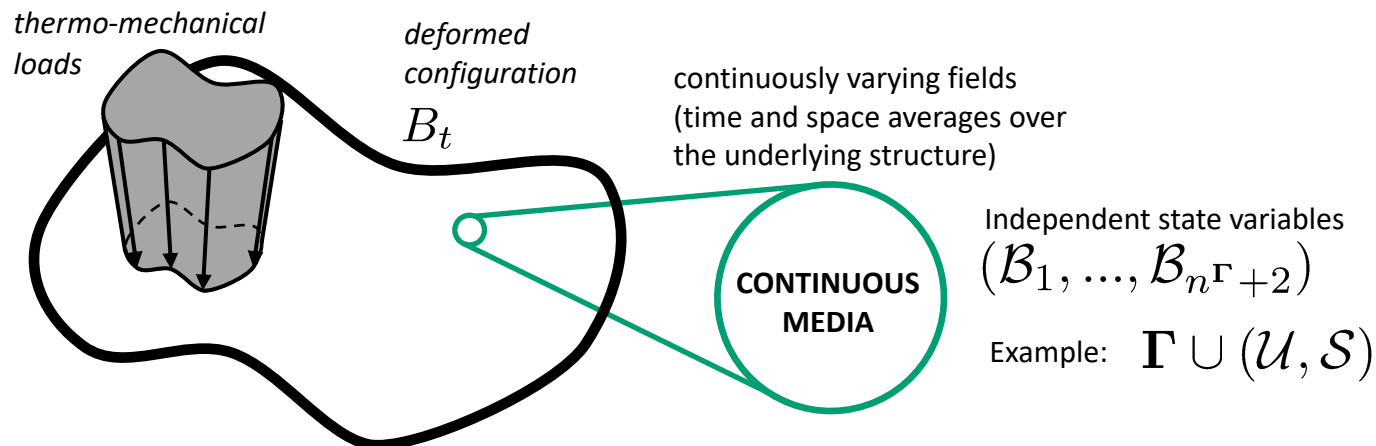
## Independent state variables

Any systems in *true* thermodynamic equilibrium is fully characterized by a set of three independent state variables.

Any system in metastable thermodynamic equilibrium is fully characterized by  $n^\Gamma + 2$  independent state variables, where  $n^\Gamma$  is the number of independent kinematic state variables that characterize the system.

$$\mathcal{B} = (\mathcal{B}_1, \dots, \mathcal{B}_{n^\Gamma+2}, \dots) \quad \mathcal{B}_{n^\Gamma+2+j} = f_j(\mathcal{B}_1, \dots, \mathcal{B}_{n^\Gamma+2}) \quad j = 1, 2, \dots$$

All state variables                      Equations of state





# Lecture 10 – Thermodynamics

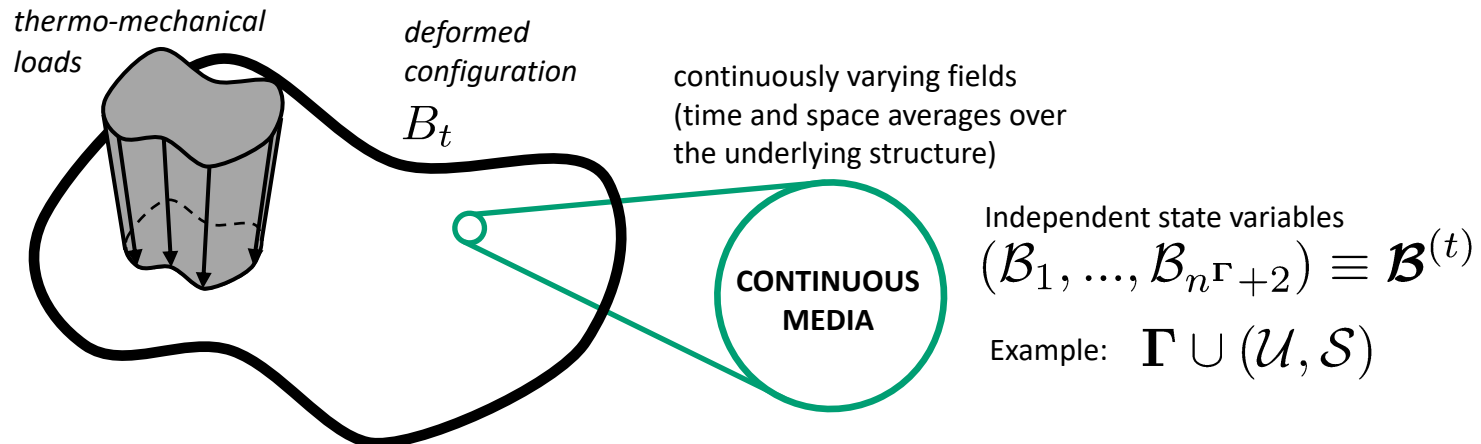
## Thermodynamic processes

A thermodynamic process is a sequence of equilibrium states.

A quasistatic process is a sequence of equilibrium states that involve small increments to the state variables.

Example: the limit of a real world system where small perturbations occur on a time scale that is significantly slower than that required for the system to reach equilibrium.

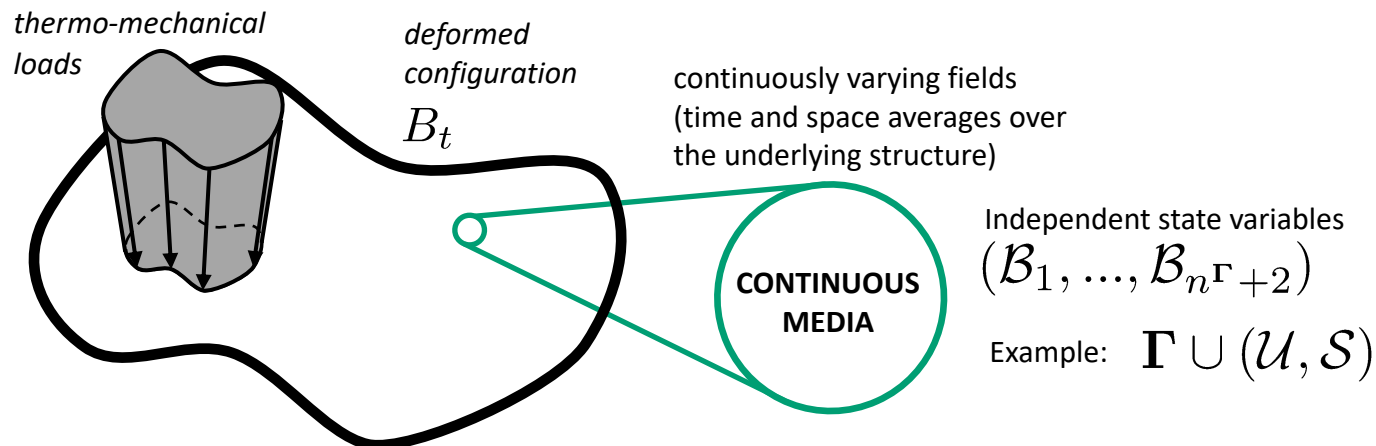
Example: the proper limit of infinitesimal changes of states is used to derived the thermodynamic theory we will introduce later.



# Lecture 10 – Thermodynamics

## Laws of thermodynamics

- Zeroth law of thermodynamics (...concept of temperature)  
Thermodynamic temperature (or absolute temperature):  $T \geq 0$
- First law of thermodynamics (...statement of conservation of energy)  
(...it leads to the idea of internal energy)
- Second law of thermodynamics (...directionality of thermodynamic processes)  
(...it leads to the idea of entropy)



# Lecture 10 – Thermodynamics

## Laws of thermodynamics

- First law of thermodynamics

$$\Delta \mathcal{U} = \Delta \mathcal{W}^{\text{def}} + \Delta \mathcal{Q} \qquad \Delta \mathcal{E} = \Delta \mathcal{W}^{\text{ext}} + \Delta \mathcal{Q}$$

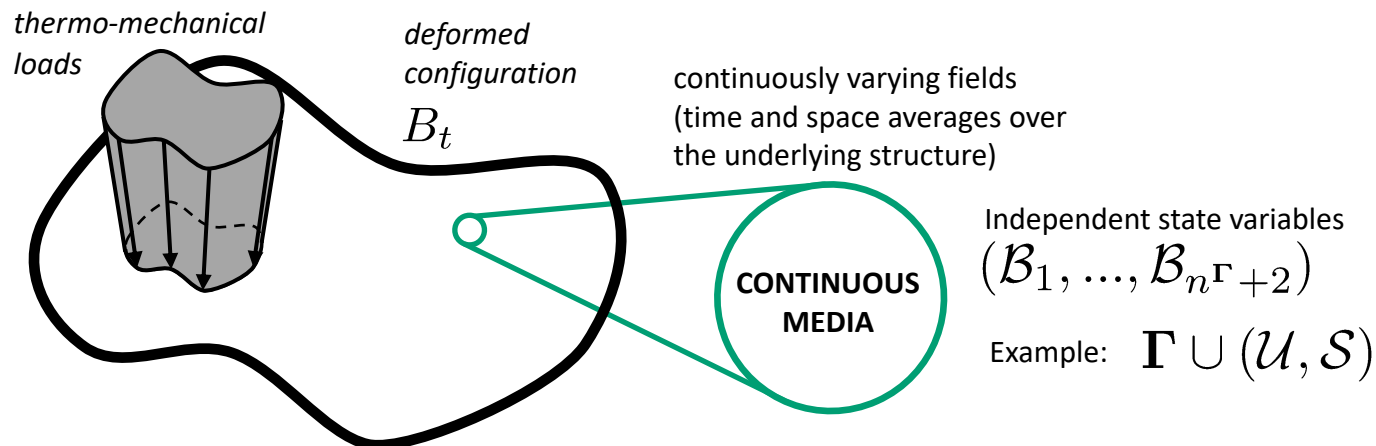
$\Delta \mathcal{U}$  internal energy

$\Delta \mathcal{Q}$  heat supplied to the system

$\Delta \mathcal{W}^{\text{def}}$  work of deformation performed on the system

$\mathcal{E} \equiv \mathcal{K} + \mathcal{U}$  total energy (kinetic and internal energies)

$\Delta \mathcal{W}^{\text{ext}} = \Delta \mathcal{K} + \Delta \mathcal{W}^{\text{def}}$  total external work performed on the system



# Lecture 10 – Thermodynamics

## Laws of thermodynamics

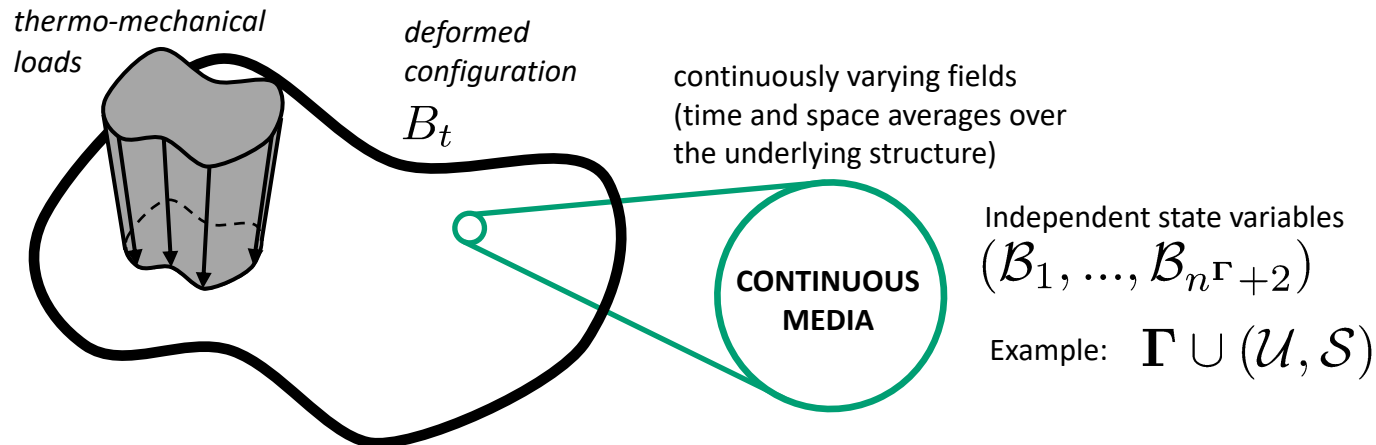
- First law of thermodynamics

$$\Delta \mathcal{U} = \Delta \mathcal{W}^{\text{def}} + \Delta \mathcal{Q}$$

$$\Delta \mathcal{E} = \Delta \mathcal{W}^{\text{ext}} + \Delta \mathcal{Q}$$

Observations:

1. The internal energy is an extensive state variable (it depends only on the state of thermodynamic equilibrium)  $\mathcal{U} = \hat{\mathcal{U}}(N, \mathbf{\Gamma}, T)$
2. Work of deformation and heat transfer are not state variables (i.e., associated functions  $\mathcal{Q}$  and  $\mathcal{W}^{\text{ext}}$  do not exist!)



# Lecture 10 – Thermodynamics

## Laws of thermodynamics

- First law of thermodynamics

$$\Delta \mathcal{U} = \Delta \mathcal{W}^{\text{def}} + \Delta \mathcal{Q}$$

$$\Delta \mathcal{E} = \Delta \mathcal{W}^{\text{ext}} + \Delta \mathcal{Q}$$

Ideal gas:  $n^{\Gamma} = 1$      $\Gamma_1 = V$      $\mathcal{B}_1 = n$  (moles)     $\mathcal{B}_2 = T$

Equation of state  $\mathcal{U} = \hat{\mathcal{U}}(n, V, T) = n\mathcal{U}_0 + nC_v T$

where the molar heat capacity at constant volume is  $C_v = \frac{1}{n} \left. \frac{\partial \hat{\mathcal{U}}}{\partial T} \right|_{N,V}$

DIY

thermo-mechanical  
loads

deformed  
configuration  
 $B_t$

continuously varying fields  
(time and space averages over  
the underlying structure)

CONTINUOUS  
MEDIA

Independent state variables  
 $(\mathcal{B}_1, \dots, \mathcal{B}_{n^{\Gamma}+2})$

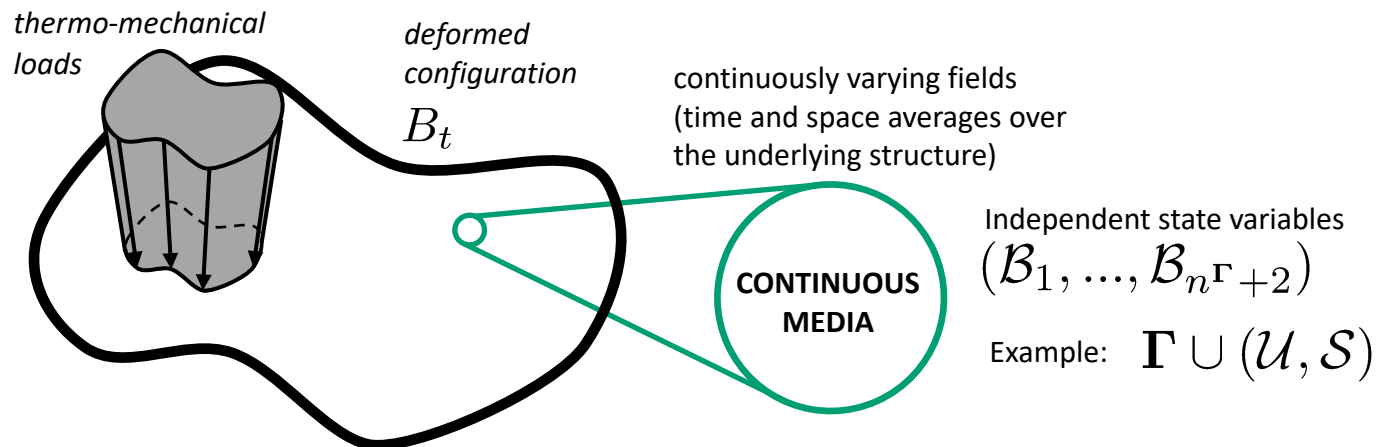
Example:  $\Gamma \cup (\mathcal{U}, \mathcal{S})$

# Lecture 10 – Thermodynamics

## Laws of thermodynamics

- Entropy

1. Extensive state variable, that is  $\mathcal{S}^{A+B+C} = \mathcal{S}^A + \mathcal{S}^B + \mathcal{S}^C$
2. A monotonically increasing function of the internal energy when it is written as  $\mathcal{S} = \bar{\mathcal{S}}(N, \mathbf{\Gamma}, \mathcal{U})$
3. A continuous and differentiable function of its arguments. Thus, it is invertible and  $\mathcal{U} = \bar{\mathcal{U}}(N, \mathbf{\Gamma}, \mathcal{S})$



# Lecture 10 – Thermodynamics

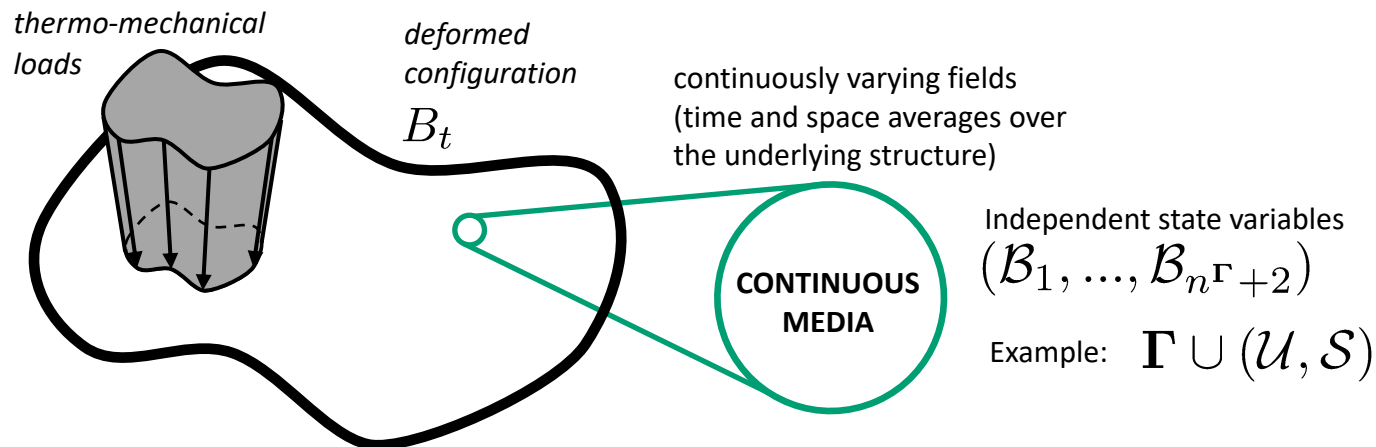
## Laws of thermodynamics

- Second law of thermodynamics

An isolated system in thermodynamic equilibrium adopts the state that has the maximum entropy of all states consistent with the imposed kinematic constraints.

The entropy of an isolated system can never decrease in any process. It can only increase or stay the same.

$$\Delta S = \Delta \bar{S}(N, \Gamma, \mathcal{U}) \geq 0$$



# Lecture 10 – Thermodynamics

## Laws of thermodynamics

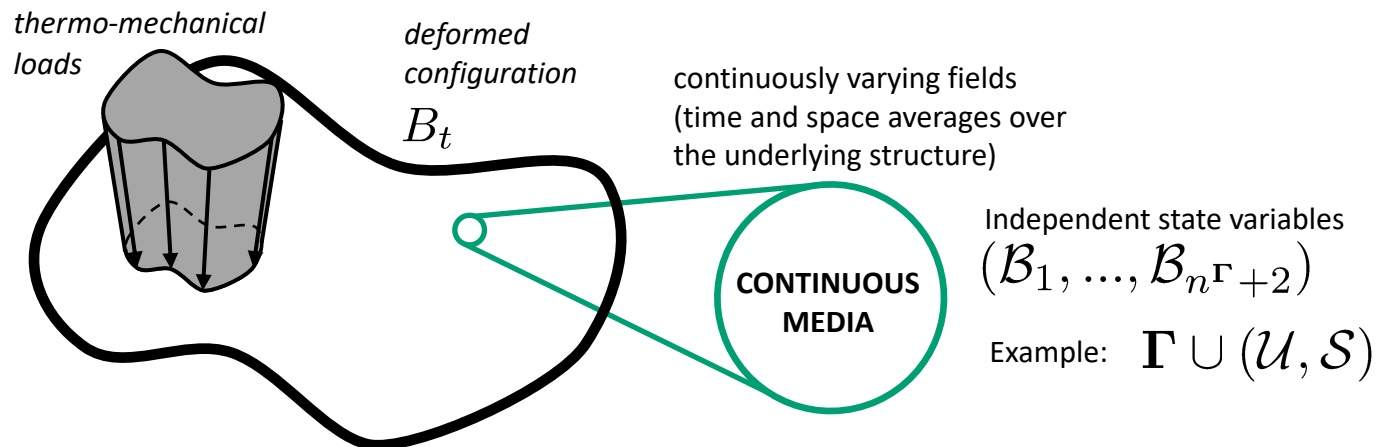
- Material stability

Recall: equilibrium states are homogeneous states.

However, a system can transition to a system with a spatially inhomogeneous mixture of equilibrium states (e.g., phase transition)

$$\left. \frac{\partial^2 \bar{\mathcal{S}}}{\partial \mathcal{U}^2} \right|_{N, \Gamma} \leq 0 \quad \text{Material is stable with respect to changes in internal energy}$$

Stable material 





# Lecture 10 – Thermodynamics

## Laws of thermodynamics

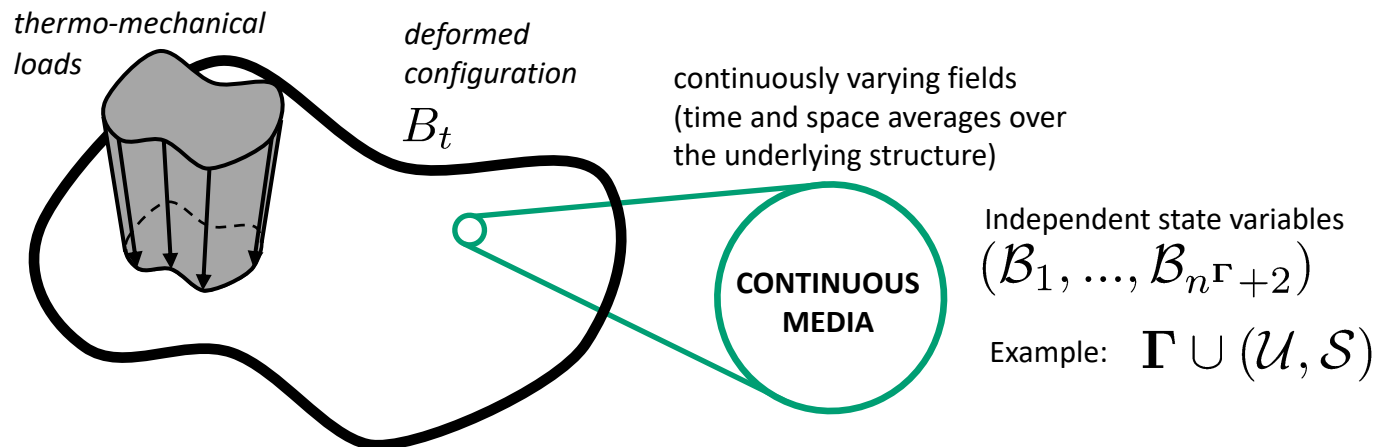
- Thermal equilibrium of stable materials

$$\mathcal{S} = \bar{\mathcal{S}}(N, \mathbf{\Gamma}, \mathcal{U})$$

$$\left. \frac{\partial \bar{\mathcal{S}}}{\partial \mathcal{U}} \right|_{N, \mathbf{\Gamma}} = \frac{1}{T} \quad (\text{inverse relation}) \quad \left. \frac{\partial \mathcal{U}}{\partial \mathcal{S}} \right|_{N, \mathbf{\Gamma}} = T$$

$$\left. \frac{\partial^2 \bar{\mathcal{S}}}{\partial \mathcal{U}^2} \right|_{N, \mathbf{\Gamma}} = -\frac{1}{T^2 n C_v} \leq 0 \quad (\text{the molar heat capacity at a constant volume of a stable material has to be positive})$$

DIY



# Lecture 10 – Thermodynamics

## Fundamental thermodynamic relations

$$\mathcal{S} = \bar{\mathcal{S}}(N, \mathbf{\Gamma}, \mathcal{U}) \quad \mathcal{U} = \bar{\mathcal{U}}(N, \mathbf{\Gamma}, \mathcal{S})$$

Absolute temperature  $T = \bar{T}(N, \mathbf{\Gamma}, \mathcal{S}) = \left. \frac{\partial \bar{\mathcal{U}}}{\partial \mathcal{S}} \right|_{N, \mathbf{\Gamma}}$

Chemical potential  $\mu = \bar{\mu}(N, \mathbf{\Gamma}, \mathcal{S}) = \left. \frac{\partial \bar{\mathcal{U}}}{\partial N} \right|_{\mathbf{\Gamma}, \mathcal{S}}$

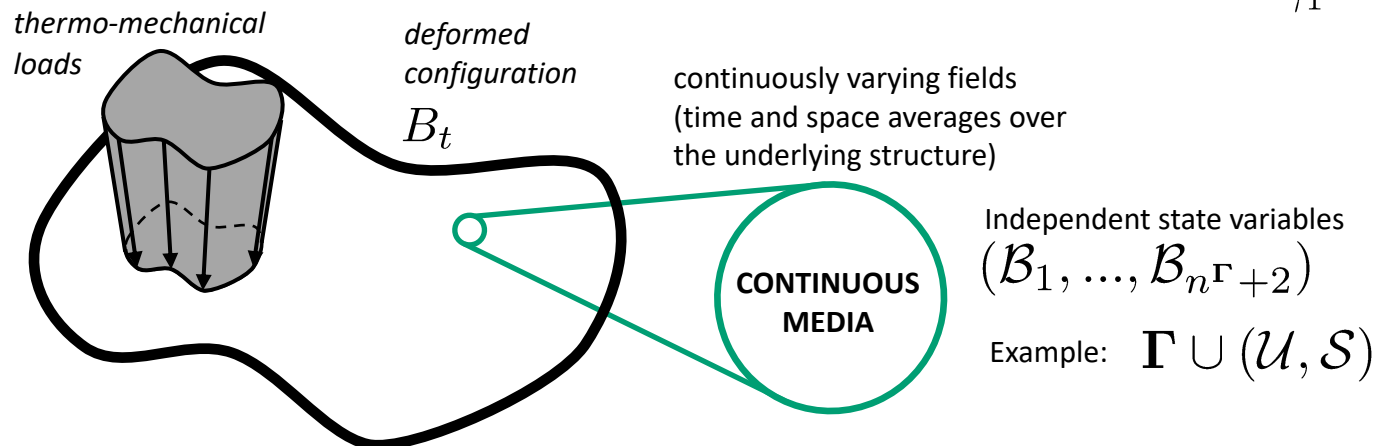
Thermodynamic tension  $\gamma_\alpha = \bar{\gamma}_\alpha(N, \mathbf{\Gamma}, \mathcal{S}) = \left. \frac{\partial \bar{\mathcal{U}}}{\partial \Gamma_\alpha} \right|_{N, \mathcal{S}}$

Example

$$\Gamma_1 \equiv V$$

$$\gamma_1 \equiv -p$$

DIY



# Lecture 10 – Thermodynamics

## Fundamental thermodynamic relations

$$\mathcal{S} = \bar{\mathcal{S}}(N, \mathbf{\Gamma}, \mathcal{U})$$

$$\mathcal{U} = \bar{\mathcal{U}}(N, \mathbf{\Gamma}, \mathcal{S})$$

DIY

Ideal gas: Equation of state  $\mathcal{U} = \hat{\mathcal{U}}(n, V, T) = n\mathcal{U}_0 + nC_v T$

$$\mathcal{U} = \bar{\mathcal{U}}(n, V, \mathcal{S}) = nK e^{\mathcal{S}/nC_v} \left( \frac{V}{n} \right)^{-R_g/C_v}$$

Now we can compute  
 $\mu, p, T$

thermo-mechanical  
loads

deformed  
configuration  
 $B_t$

continuously varying fields  
(time and space averages over  
the underlying structure)

CONTINUOUS  
MEDIA

Independent state variables  
 $(\mathcal{B}_1, \dots, \mathcal{B}_{n\Gamma+2})$

Example:  $\mathbf{\Gamma} \cup (\mathcal{U}, \mathcal{S})$

# Lecture 10 – Thermodynamics

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Any questions?