

Thermodynamics: Study of restrictions on possible properties of matter that follow from symmetry properties of fundamental laws of physics.

→ remain unchanged under some transformation

Noether's Theorem: For every continuous symmetry in physical system, there is conserved quantity

CPT [charge, parity (space), time] symmetry

Macroscopic/Thermodynamic Coordinates: Time independent makes macroscopically observable because  
Macroscopic Measurements: slow on atomic time scale, coarse on atomic scale of distance

"normal coordinates" → only coarse spatial averages

→ accessible normal modes are undersampled by averaging because homogeneous structure

• Studies of mechanics, electricity focus on two distinct sets of surviving coordinates

• Thermodynamics studies atomic coordinates which do not explicitly appear in macroscopic description of system because of observational/coarseness

→ things that don't survive time/space averaging

• Hidden modes can store energy → Energy transferred to mechanical mode is mech. work

-  $PdV$

→ "

"electrical mode is clean work"

-  $E_e dP$  ( $E_e$  is electric field,  $P$  is dipole moment)

→ Force on charged particles in space

→ Vector quantity representing separation of +/- charges, measures overall polarity

→ "

"hidden modes is HEAT"

-  $SdT$

Initial focus on "simple systems": macroscopically homogeneous, isotropic, unchanged, regular surface effects because of size, not affected by electric, magnetic, grav. fields

Extensive Parameters: Have value in composite system equal to sum of values in subsystems

Development Timeline:

• 1643, Leibniz → conservation principle for kinetic & potential energy

• 1748, Count Rumford → Cannon Boring (Heat & Work)

• 1905, Einstein → relativistic rest-mass energy

• Darcy, Carnot, Mayer, Joule (1840/50)

• 1930s, Fermi → Neutrino, to maintain conservation principle in nuclear reactions

look to America

Macroscopic systems have definite & precise energies, subject to a definite conservation principle.



- Only <sup>energy</sup> differences matter in physical states
- any energy above "fiducial" (benchmark) state matters
- is called internal energy,  $U$  |  $U, V, N$  are all extensive

> All systems tend to equilibrium states where properties are determined by intrinsic factors and not previously applied external influences  
 TD seeks to describe these

Postulate 1. Equilibrium states of simple systems solely macroscopically defined by  $U, V, N$  exist.

- Willow to determine system in equilibrium (quiescent, static)?

↳ extensive properties defining system, must be  $\epsilon$  independent / independent of path

↳ ex: glass depends on process characteristics, not in equilibrium

Non-equilibrium state of matter: analogous continuous irreversible mass & energy changes

↳ detected by failure of TD formalism based on equilibrium

Atomic point of view: macroscopic equilibrium state indicates incessant & rapid transitions among all atomic states consistent w/ boundary conditions  $\rightarrow$  equilibrium = all states

↳ if system stuck in state or too slow, averaging doesn't work  $\rightarrow$  Non-Equilibrium

↳ more common in solids because <sup>fluids</sup> all random atomic collisions free with few restrictions

Few systems in absolute, true equilibrium

Metastable Equilibrium: Relevant processes or spontaneous evolution, <sup>done</sup> can be described by small number of parameters  $\Rightarrow$  all we need for TD

In summary: System is in equilibrium if properties consistently described by thermodynamic theory [circular]



like mechanics, we don't toss theory if it fails  $\rightarrow$  just add more terms!