I. Overview

- Coverage
- Why do we need Statistical Mechanics?
- Where is Statistical Mechanics in physics?
- Background assumed
- Our strategy in approaching Statistical Mechanics
- Course Learning Outcomes

Our Focus

- Focus on Equilibrium Statistical Mechanics

Microscopic Description [Hamiltonian, energy levels, states]	Macroscopic Description [Thermodynamics]

- How to connect them?
- Key ideas
- Calculation Schemes
- Work out standard problems

  as applied to other subjects in physics
  - gases
  - Solid state physics
  - astrophysics

- Thermodynamics: Formulated without invoking ideas about atoms/molecules and their interactions
- Statistical Mechanics is the microscopic theory of thermodynamics [also called statistical thermodynamics]

Why Stat. Mech.?

- Like thermodynamics, we aim at understanding systems with a large number of particles, i.e. "ordinary" systems

Typically, $\sim 10^{18} - 10^{24}$ in a volume of $\sim 1\,cm^3$

- A Gas of hydrogen vs $\underbrace{H_2 \text{ single molecule}}_{QM}$
- A piece of metal vs $\underbrace{\text{Single sodium atom}}_{QM}$
- Vibrations of atoms in a solid vs $\underbrace{\text{Single harmonic oscillator}}_{\text{Classical Mechanics \& QM}}$
- Neutron Star vs $\underbrace{\text{a neutron}}_{\text{nuclear physics, QCD}}$

$\therefore$ Statistical Mechanics is needed to understand solids, liquids, gases, stars, probably life, thus all interesting physics.

- Number to keep in mind:

Think about the stuff in 1 mole

$N_A = 6.02 \times \underbrace{10^{23}}_{\text{order of magnitude}} \text{mol}^{-1}$ = Avogadro's constant

- Thermodynamics
  - Macroscopic, Empirical ← summarized exp'tal results

System with $\sim 10^{23}$ entities (after atoms/molecules became known)

Yet, describe system by a few variables (e.g. T, V, p, S, U, N)

  - Give relations between variables

$pV = NkT$ (or $pV = nRT$) for ideal gas

Supplemented by measurements of one quantity, then one can obtain other quantities.

[But microscopically, there should be 6×10^{23} variables for specifying the positions and momenta of the entities! Thermodynamics grasps the physics using only a few variables — Great!]

- **Statistical Mechanics:**
  - use knowledge at microscopic level

    [Hamiltonian, $\underbrace{\text{allowed energy states}}_{\text{solutions to Schrödinger Eq.}^{\dagger}}$]

    to deduce the behaviour of a macroscopic system ($N \sim 10^{23}$ particles)

    e.g. calculate entropy S, pressure p, internal energy E, …*

We will make use of background knowledge in thermal physics AND Quantum Physics

should review the contents in these courses by yourself

* Note that U, E, $\langle E \rangle$ are used interchangeably.

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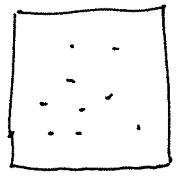
† If one considers classical mechanics, then one could invoke the Hamilton's equations to trace the time evolution of a system.

Examples | **Known from thermodynamics** | **Question**



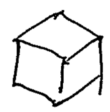
Gas

[Many atoms/molecules]

$pV = NkT$

- Can we derive the expression from $H = \sum_i \frac{p_i^2}{2m}$ + Intra-molecule terms and calculate the thermodynamic quantities e.g. S?

How about rotational, vibrational motions inside molecules?



A piece of insulating solid

[Many atoms]

Exp'tally observed

$C_V \propto T^3$ at low temp.

$C_V \propto$ constant at high temp.

- Can we derive $C_V(T)$ starting from the Hamiltonian?

A piece of non-magnetic solid

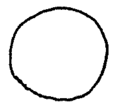
[Many atoms, each has magnetic moment]

Exp'tally observed

$\chi \sim \frac{1}{T}$

χ: magnetic susceptibility $[\vec{M} = \chi \vec{H}]$

- Can we derive $\chi(T)$ from a Hamiltonian describing the interaction of magnetic moments with applied field?



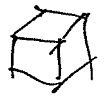
- dying star
- neutron star

[Dense electrons, Dense neutrons]

Read about

Some "degenerate pressure" opposes the gravitational pull

- Can we understand the physics through the stat. mech. of an Ideal Fermi Gas?

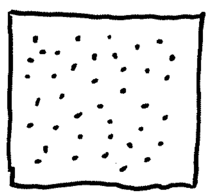


A piece of metal [many free electrons]

Exp'tally observed

$C \propto T$ at very low temp.

- Can we derive C from the physics of an Ideal Fermi Gas?



Denser Gas

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

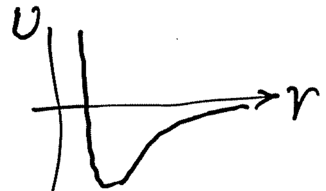
[v = molar volume]

Van der Waal's gas law

[can condense to a liquid]

(phase transition)

- Can we derive it from the physics of interaction between atoms?



Statistical Mechanics

Solid State Physics
- Heat capacity of insulators
- Properties of metals
- Semiconductor physics
- Magnetic properties

Astrophysics
- Star formation (equation of state)
- Neutron Stars (Fermi Gas)

Computational Physics
- Monte Carlo Simulations (e.g. magnetic systems)
- Molecular Dynamics (e.g. Clusters, biophysics)

Ultracold atoms/Molecules
- Bose-Einstein Condensation
- Well-controlled condensed matter systems

Information Theory
- Shannon Entropy
- Maximum Likelihood

Physical Chemistry
- Gases, liquids
- Kinetics
- chemical equilibrium

Many Others:
- Materials Physics, Percolation, Epidemics, Scaling, Self-organized phenomena, diffusion processes...

Study of Stat. Mech. is supported by (in our curriculum)

- Classical and Quantum Mechanics
  - Hamiltonian, Phase space, Dynamics, Normal modes
  - Atomic physics, Molecular Physics
  - Standard problems: particle-in-a-box
    harmonic oscillator
    rotor (or rotator)
- Thermodynamics
  - $dU = TdS - pdV + \mu dN$
  - $F = U - TS$
  - ...
- Electromagnetic Theory
  - $-\vec{p}\cdot\vec{E}$ (interaction energy of electric dipole in an electric field)
- Mathematical Methods
  - Partial Derivatives (the Math of thermodynamics and Stat. Mech.)
  - Integrals

That's why it is a Year 4 course!

Topics include: (Equilibrium Statistical Mechanics)

- Quick review on key thermodynamic relations
- Basic ideas of statistical mechanics
  [context: isolated systems, i.e. fixed E]
  - Macrostate vs microstates
  - Most probable state
  - All accessible microstates are equally probable
  - entropy S and number of accessible states W
  - microcanonical ensemble
- System in equilibrium with a heat bath
  [context: fixed temperature T]
  - Boltzmann distribution
  - Partition function $Z(T,V,N)$
    - using Z to calculate other thermodynamic quantities via the free energy $F(T,V,N)$ [where $F = E - TS$]
  - Applications
  - Canonical ensemble

- Non-interacting particles
  - Fermi-Dirac and Bose-Einstein distributions [Method of Lagrange multipliers]
  - Density of single-particle states
  - Equations for Ideal Fermi/Bose Gases
- System in equilibrium with a heat bath and a particle bath
  [context: fixed temperature T and chemical potential μ] (Grand canonical Ensemble)
  - Gibbs distribution
  - Grand Partition function $\mathcal{Q}(T,V,\mu)$
    - using $\mathcal{Q}$ to calculate other thermodynamic quantities via the grand potential $\Omega(T,V,\mu)$ [where $\Omega = E - TS - \mu N$]
  - Fermi-Dirac and Bose-Einstein distributions
- Physics of Ideal Fermi Gas
- Physics of Ideal Bose Gas
- Classical Statistical Mechanics
- Phase Transitions and Critical Phenomena

<u>Remarks</u>

- While the formulations are <u>general</u>, examples and exercises are mostly about <u>non-interacting systems</u> [∵ "easier" to work out]
- The course is about <u>calculation schemes</u> (ensemble theories) on getting thermodynamic quantities starting from <u>microscopic considerations</u>. Therefore, <u>be prepared to do many calculations</u>.
- <u>Strategy in Learning Statistical Mechanics</u>
  - There are many ways
  - Since <u>you learned some thermodynamics</u>, we will not pretend that you don't know the subject. Our strategy is then to get at one essential quantity (e.g. $S(E,V,N)$) by Stat. Mech., and then apply thermodynamic relations to get at the physics of a system.

The strategy of equilibrium statistical mechanics:

- specifying the microscopic states ("microstates") of the system
- select properly a set of microstates to form an ensemble of systems [the selection follows from results of statistical mechanics]
- establish a connection to some observable quantities (i.e., thermodynamics)
- use the connection to calculate a thermodynamic quantity
- once a quantity is calculated using stat. mech., use thermodynamic relations to get other thermodynamic quantities

- The very least thermodynamics in order to proceed:

1st law + 2nd law gives

$$\boxed{dE = TdS - pdV}$$

or more generally

$$\boxed{dE = TdS - pdV + \mu dN} \qquad E(S,V,N)$$

$$\therefore \quad \boxed{dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN}$$

[knowing $S(E,V,N) \Rightarrow \frac{1}{T}, \frac{p}{T}, \frac{-\mu}{T}$ through derivatives]

- Helmholtz free energy $\boxed{F = E - TS}$

$$\boxed{dF = -SdT - pdV + \mu dN}$$

[knowing $F(T,V,N) \Rightarrow S, p, \mu$ through derivatives]

PHYS4031 Statistical Mechanics

Learning Outcomes

1.	To appreciate the connection between statistical mechanics and thermodynamics and to realize that many results in statistical physics come from the same fundamental postulate.
2.	To understand the ensemble theories in statistical mechanics.
3.	To carry out calculations of thermodynamic properties for typical (mostly non-interacting) physical systems using ensemble theories.
4.	To make connections to concepts acquired in other physics courses, e.g. thermodynamics, quantum mechanics, solid state physics and astrophysics.
5.	To apply statistical mechanics to ideal Fermi gas and ideal Bose gas, and to relate results to physical problems.
6.	To acquire and apply mathematical skills related to counting, Stirling's formula, Gaussian integrals, summations, method of Lagrange multipliers, and integrals involving Fermi-Dirac and Bose-Einstein distributions.
7.	To acquire the basic principles for further studies on the statistical mechanics of interesting systems.