

**Physics 7230: Statistical Mechanics**  
**Lecture set 1: Introduction and Overview**

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## I. INTRODUCTION

### A. Background

Statistical mechanics is an extremely powerful set of ideas with a broad range of applications throughout physics[1–7]. The subject was founded in mid 1800s by scientific giants like Gibbs, Boltzmann, Maxwell, ... Formulated in terms of system's microscopic degrees of freedom, that are governed by basic principles of Newtonian and quantum mechanics, electricity and magnetism, relativity, etc., it allows one to derive macroscopic behavior of extensive systems. These include gases, liquids, crystals, magnets, superfluids and superconductors, and many other states of matter. It thus provides a microscopic theory of thermodynamics for natural phenomena.

Recall that much older phenomenological theory of thermodynamics postulates four laws[1, 2]:

- 0th law: temperature exists,  $T_A = T_B, T_B = T_C \rightarrow T_A = T_C$
- 1st law: energy conservation,  $\Delta U = W + Q$
- 2nd law: entropy of a closed system increases,  $TdS \geq 0$
- 3rd law: vanishing entropy at zero temperature,  $S(T = 0) = 0$ ,

that led to much of early understanding of gases, liquids, and solids. In contrast, a much more powerful microscopic probabilistic theory of statistical mechanics posits a single postulate of *ergodicity*, i.e., that in equilibrium for a closed system at fixed  $E$  (and at all other fixed conserved quantities), all microstates are accessible with equal probability, from which all of thermodynamics emerges via detailed calculations.

### B. Fundamentals and key ideas

- Microstates  $q$ :
  - classical configurations of the system e.g.,  $\{x_i, p_i\}$  phase space for  $N$  particles
  - quantum states in the Hilbert space, e.g., eigenstates of the Hamiltonian  $H$

- Ergodicity: time average  $\rightarrow$  ensemble average

Even under closed system (unitary in quantum case) evolution (see Eigenstate Thermalization Hypothesis [ETH], due to Mark Srednicki[8] and independently by Josh Deutsch[9] in early '90s) a long time limit “relaxes” to equilibrium at energy  $E = \langle H \rangle = \langle \Psi | \hat{H} | \Psi \rangle$ ,

$$\frac{1}{t} \int_0^t dt' O(q(t))_{t \rightarrow \infty} (\text{classical}) = \quad (1)$$

$$\frac{1}{t} \int_0^t dt' \langle \Psi(t') | \hat{O} | \Psi(t') \rangle_{t \rightarrow \infty} (\text{quantum}) = \langle \hat{O} \rangle_{P_E}. \quad (2)$$

- Macroscopic observables of interest (energy, density, magnetization) are averages over microscopic states  $q$  (e.g.,  $x_i, p_i$ , quantum states  $|n\rangle, \dots$ ), with probability distribution  $P(q)$ . In quantum case,  $P(q)$  is given by the density matrix operator  $\hat{\rho}$

$$O = \langle O(q) \rangle = \sum_q O(q) P(q), \quad (3)$$

$$= \text{Trace}[\hat{O} \hat{\rho}], \quad (4)$$

where for a pure closed quantum system  $\hat{\rho}(t) = |\Psi(t)\rangle \langle \Psi(t)|$  is the normalized density matrix. To get a physical intuition for ETH we can express  $|\Psi(t)\rangle$  in terms of many-body eigenstates  $|n\rangle$  and note that for a generic state, contributions off-diagonal in  $n, n'$  will dephase after some time (set by minimum gaps) for a generic spectrum with no large gaps or degeneracies. This is the “relaxation” to a stationary time-independent state. The diagonal terms appear to depend on the initial state  $|\Psi(0)\rangle$  through the expansion coefficients,  $c_n$ , according to  $\sum_n |c_n|^2 O_{nn}$ . ETH proposes that for generic state with a finite excitation energy density (not a ground state)  $\mathcal{E} = E/V$ , the diagonal matrix element of a local operator is independent of  $n$ , depending only on  $\mathcal{E}$ . Thus  $O_{nn}$  can be taken out of the sum, which then reduces to 1, with the result reducing to the microcanonical ensemble. Namely, in a long time limit the expectation value relaxes to an ensemble average of  $O_{nn}$  over eigenstates around energy  $E$  in a range of fixed energy density  $\mathcal{E}$ .

It appears somewhat paradoxical that a closed quantum system evolving under pure unitary, norm-preserving evolution, nevertheless exhibits “relaxation”, with accompanying growth of sub-system’s entanglement entropy (see below). The resolution is

that local observables gets “dressed” and thereby spread into operators that are non-local in coordinate and in operator space. Thus, while there is no loss of information or many-body norm, under growth of entanglement the information delocalizes and thereby becomes unobservable through local low-order operators measured in typical experiments. Thus from the perspective of accessible local observables, the system relaxes to equilibrium value of these observables.

There are notable exceptional closed quantum systems (typically in the presence of local random heterogeneities, i.e., “quenched disorder”), that are not ergodic. They do not equilibrate and thus violate ETH, exhibiting the so-called “many-body localization” (MBL)[10], that is currently vigorously studied[11]. More generally, “integrable” systems have infinite number of conserved quantities (that thereby cannot relax) violate ETH, with MBL being only one example where such integrability is emergent.

We will assume ETH throughout and will typically use the canonical ensemble (in which calculations are usually simpler).

- Thermal equilibrium

Want  $P(q)$  to be time independent, stationary. Thus take it to be a function of  $H(q)$ , i.e.,  $P(q) = f[H(q)]$ , as dictated by Liouville’s theorem. Then

$$\partial_t P(q) = -i[P(H(q)), H] = \{P(H(q)), H\} = 0$$

- Quantum vs Classical

- Classical:  $P(q)$  is clear as  $q$  are just c-numbers, so directly sum/integrate over them
- Quantum: first diagonalize the Hamiltonian  $H|n\rangle = E_n|n\rangle$ , then averages are sum over quantum states  $|n\rangle$  with distribution  $P(E_n)$

### C. Thermodynamic potentials

- $E, F, H, G, \Pi$  are related by Legendre transforms
- functions of state with exact differentials  $\rightarrow$  give Maxwell’s relations
- Entropy  $S(E, V, N)$

- equivalently Internal energy

$$E(S, V, N) \rightarrow dE = TdS - PdV + \mu dN$$

- fully closed to  $E, V, N$  exchange

- Helmholtz free energy

$$F(T, V, N) = E - TS \rightarrow dF = -SdT - PdV + \mu dN$$

- open to  $E$  controlled by  $T$  (or  $\beta \equiv 1/k_B T$  Lagrange multiplier)

- closed to  $V, N$  exchange

- Enthalpy

$$H(S, P, N) = E + PV \rightarrow dH = TdS + VdP + \mu dN$$

- open to  $V$  change controlled by  $P$  (Lagrange multiplier)

- closed to  $E, N$  exchange

- Gibbs free energy

$$G(T, P, N) = E - TS + PV = F + PV = H - TS \rightarrow dG = -SdT + VdP + \mu dN$$

- open to  $E$  controlled by  $T$  (or  $\beta \equiv 1/k_B T$  Lagrange multiplier) and to  $V$  change controlled by  $P$  (Lagrange multiplier)

- closed to  $N$  exchange

- Grand potential

$$\Pi(T, P, \mu) = E - TS + PV - \mu N = F + PV - \mu N = H - TS - \mu N$$

$$\rightarrow d\Pi = -SdT + VdP - Nd\mu$$

- open to  $E, V, N$  controlled by  $T, P, \mu$  Lagrange multipliers

## D. Ensembles

There are a number of statistical ensembles that can be used to calculate system's properties, and these are in one to one correspondence to thermodynamic potentials above

- Micro-canonical Ensemble

For closed system with fixed energy  $E$ , number of constituents  $N$ , volume of the system  $V, \dots$ , and all other extensive variables

- Canonical Ensemble

For system open to energy  $E$  exchange (with mean value tuned by Lagrange multiplier  $\beta = 1/k_B T$ ), but closed to number of particles exchange, fixed at  $N$

- Grand-canonical Ensemble

For system open to energy  $E$  and number of particles  $N$  exchange, (with mean values tuned by Lagrange multipliers  $\beta = 1/k_B T$  and chemical potential  $\mu$ , respectively)

- Generalized Gibbs Ensemble

Average conserved quantities fixed by a set of Lagrange multipliers,  $\beta_i$

In the thermodynamic limit of  $N \gg 1$ , satisfied by (most) macroscopic systems, central limit theorem dictates that fluctuations around the average are small (scaling as  $\sqrt{N} \ll N$ ), thus the choice of an ensemble is a matter of convenience, leading to equivalent average predictions for a bulk system.

## II. COURSE OVERVIEW

### A. Technicalities

With the background in place, we now overview the systems and subjects that we will cover in this course. Statistical mechanics (especially when extended to fields, i.e., field theory) is extremely powerful and can be used to treat any macroscopic system from polymers, liquid crystals, biological membranes and other complex systems to quantum magnets, superconductors, superfluids, phonons, metals, etc, in and near equilibrium. However, here

will focus on equilibrium statistical mechanics as a tiny subset of basic pedagogical systems. These will be

- Classical Boltzmann gas
  - microstates: continuous phase space coordinates  $\{p_i, x_i\}$
- Langevin paramagnetism (classical and quantum)
  - microstates:  
continuous spin orientation  $\mathbf{S}_i$  (classical)  
discrete  $2s + 1$ -dimensional Hilbert space of  $-s, -s + 1, \dots, s - 1, s$  for each spin  $i$  (quantum)
- Harmonic oscillator (classical and quantum)
  - microstates:  
continuous phase space coordinates  $\{p_i, x_i\}$  (classical)  
discrete oscillator states  $n \in \mathbb{Z}$  quantum numbers (quantum)

## B. Outline

### 1. Lecture set 1: Introduction and Overview

- Foundations and background
- Ergodicity and Eigenstate Thermalization Hypothesis (ETH)
- Breakdown in integrable and many-body localized (MBL) systems
- Ensembles
- Course overview

### 2. Lecture set 2: Microcanonical ensemble

- Fundamentals
- Reduced density matrix
- Entanglement entropy

- Information theory
- Langevin paramagnetism (classical and quantum)
- Boltzmann gas
- Harmonic oscillator (classical and quantum)

### 3. Lecture set 3: Canonical ensemble

- From microcanonical to canonical ensemble
- Langevin paramagnetism (classical and quantum)
- Boltzmann gas
- Lattice gas
- Harmonic oscillator (classical and quantum)
- Equipartition and its quantum breakdown

### 4. Lecture set 4: Grand canonical ensemble

- From microcanonical to grandcanonical ensemble
- Boltzmann gas
- Lattice gas

### 5. Lecture set 5: Density matrix

- Density matrix basics
- Time evolution
- Pure vs Mixed states
- Thermal equilibrium
- Spins, particles, harmonic oscillator examples
- Path integral formulation
- Perturbation and variational theory
- Eigenstate Thermalization Hypothesis (ETH)
- Entanglement entropy



- Relation to information theory

## 6. Lecture set 6: Quantum statistics and applications

- Quantum statistics
- Bosons:
  - photons black-body radiation
  - phonons in a solid
  - BEC and superfluidity
- Fermions: - metals thermodynamics - neutron star and degeneracy pressure - Pauli paramagnetism

## 7. Lecture set 7: Ferromagnetism via mean-field theory

- Curie magnetism
- Exchange interactions
- Heisenberg, XY and Ising models
- Curie-Weiss mean-field theory
- Infinite-range exchange
- Variational mean-field theory
- Landau mean-field theory

## 8. Lecture set 8: Phase transitions: Landau theory

- Ising PM-FM transition
- Liquid-gas transition
- Normal-to-superfluid transition
- Tricritical point
- Liquid crystals: Isotropic-Nematic transition, Nematic-Smectic-A transition

## 9. Lecture set 9: Equilibrium and Non-equilibrium Hydrodynamics (unlikely to get to)

- Brownian motion (Einstein, Smoluchowski, Langevin theories) Fokker-Planck equation
  - Fluctuation-dissipation theorem
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