Statistical Mechanics

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Problem sets are due on Tuesdays 12 pm (noon) in the same ITP mailbox

Lecture Content:

§1 Objective and History of Stat Mech

§2 Boltzmann's approach to Statistical Physics

§3 Gibbs's Ensemble Theory

§4 Equilibrium Ensembles

§5 Ideal Gases

§6 Interacting Systems

§ 7 Thermodynamics

§ 8 Theory of Phase Transitions

Recommended Books:

C. Kittel and H. Kroemer, Thermal Physics, Freeman & Co

F. Reif, Fundamentals of Statistical and Thermal Physics, McGraw-Hill

L. D. Landau and E. M. Lifshitz, Statistical Physics

M. Kardar, Statistical Physics of Particles

Shang-Keng Ma, Statistical Mechanics

Kerson Huang, Statistical Mechanics (good for looking up advanced topics)

F. Schwabl, Statistical Mechanics

R. Penrose, The Emperor's New Mind, Oxford University Press (chapter 7 "Cosmology and the Arrow of Time")

§1 Objective and History of Statistical Mechanics

So far we discussed the following "microscopic" theories:

i) classical theories (deterministic)

Mechanics: Lagrange and Hamilton formalism, exact solutions only for few degrees of freedom (three body problem no longer exactly solvable). Description of gases or solids with with $10^{20} - 10^{23}$ degrees of freedom by solving equations of motion is hopeless (molecular dynamics $\leqslant 10^9$ degrees of freedom)

Electrodynamics: electromagnetic fields have infinitely many degrees of freedom (or better $(L/\lambda_c)^3$ with the Compton wave length $\lambda_c = \frac{h}{mc} \approx 2.4 \cdot 10^{-10}$ cm $\rightarrow 10^{31}$ degrees of freedom / cm^3)

Linear theory, hence solution by superposition is possible. However, interaction with matter $\rightarrow$ effectively non-linear.

Even if we could solve the equations of motion, the initial conditions are not known (deterministic chaos: strong dependence on initial conditions)

ii) quantum theories (quantum mechanics, quantum electrodynamics) are statistical theories for the for the results of measurements. Solving the Schroedinger equation for 10^{20} interacting particles is hopeless.

Objective of statistical physics is the explanation of macroscopic properties (pressure, specific heat, conductivities etc.) of many-particle systems, starting from a microscopic description and using concepts like heat, temperature, thermal equilibrium. These concepts can be experienced and observed by humans, but are not part of microscopic theories. At first, this program sounds hopeless, but it turns out that the apparent disadvantage of describing many ($\sim 10^{20}$) degrees of freedom is in fact an advantage: the macroscopic behavior does not depend on details of the many "fast" variables, but only "slow" variables, especially conserved quantities, are important.

Parts of statistical physics are

i) statistical (quantum) mechanics, quantum electrodynamics

ii) theory of disordered solids (impurities in solids with a statistical distribution), theory of neural networks, pre-biological evolution of molecules etc.

iii) quantum mechanics in path integral representation
$(t \leftrightarrow i\hbar\beta)$

Brief History of Statistical Mechanics:

17th century (Ferdinand II): quantitative measurement of temperature (alcohol thermometer)

18th century: Celsius temperature scale

1802 Gay-Lussac : heat expansion of gases

Benjamin Thompson (Count Rumford): equivalence of mechanical and heat energy

1824 N.L.S. Carnot reversible thermodynamic cycles

1847 H. von Helmholz : modern version of energy conservation (1st law of thermodynamics)

1848 W. Thomson (Lord Kelvin): definition of thermodynamic temperature scale via Carnot process

1850 Thomson + Helmholtz: 2nd law of thermodynamics

1857 R. Clausius : equation of state for ideal gases

1860 J.C. Maxwell. Maxwell velocity distribution

1865 R. Clausius: entropy, new formulation of 2nd law

1877 L. Boltzmann: $S = k \ln W$ statistical interpretation of entropy

1876/96/1909 Loschmidt, Zermelo, Mach, Ostwald: critique of the molecular basis of Boltzmann's kinetic theory of gases: reversible equations, Poincaré recurrence theorem not compatible with irreversibility of macroscopic behavior

1894 W. Wien: black-body radiation
1900 M. Planck: radiation law

1904/11 W. Nernst / M. Planck: 3rd law of thermodynamics

1911 Ehrenfest: foundation of quantum statistics

1924 Bose-Einstein statistics

1925 W. Pauli / E. Fermi: Fermi-Dirac statistics
1931 L. Onsager: theory of irreversible processes

1937 L. Landau: theory of phase transitions, extension to superconductors with Ginzburg

1943 Chandrasekhar, Fowler: application of stochastic methods in astrophysics and astronomy

1944 L. Onsager: exact solution of 2D Ising model (simple model for magnetism and other cooperative phenomena)

1956 Bardeen, Cooper, Schrieffer: explanation of superconductivity as a type of Bose-condensation

1956-58 Landau: theory of Fermi liquids

Since 1960: Matsubara, Abrikosov, Gorkov, Dzyaloshinskii application of quantum field theoretical methods in statistical physics

1966 Kubo: fluctuation-dissipation theorem

Since 1970 Haken, Prigogine: formation of structures away from thermal equilibrium

Wilson, Fisher, Wegner ...: renormalization group for strongly correlated systems

Flory, de Gennes: polymers, liquid crystals

Hawking: evaporation of black holes

Since ca. 1975. Hopfield, Amit theory of neural networks

Since ca. 1985 Bouchaud and others: application of methods of statistical physics in the economy

§2 Boltzmann's approach to statistical physics

2.1 Classical Mechanics

Basis of the Lagrange formalism is the Lagrange function, a function of generalized coordinates $q_1 \dots q_f$ (short hand notation q) and velocities $\dot q_1 \dots \dot q_f$ (short $\dot q$), which depend explicitly on time. Equation of motion is the Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial L}{\partial \dot q_i} - \frac{\partial L}{\partial q_i} = 0$$

and the initial conditions $q_i(0) = q_i^0$ and $\dot q_i(0) = \dot q_i^0$

An alternative is the Hamilton formalism. Here, the Hamilton function $H(q,p,t)$ depends on generalized coordinates q_i and the canonically conjugate momenta $p_i = \frac{\partial L}{\partial \dot q_i}$. Equations of motion are $\dot q_i = \frac{\partial H}{\partial p_i}$ and $\dot p_i = - \frac{\partial H}{\partial q_i}$

Connection between Lagrange- and Hamilton formalism:

$$dL = \sum_{i=1}^{f} \frac{\partial L}{\partial q_i} dq_i + \sum_{i=1}^{f} \frac{\partial L}{\partial \dot q_i} d\dot q_i = \sum_{i=1}^{f} \left[\frac{\partial L}{\partial q_i} dq_i + p_i d\dot q_i \right]$$

$$= \sum_{i=1}^{f} \left[\frac{\partial L}{\partial q_i} dq_i + d(p_i \dot q_i) - \dot q_i dp_i \right]$$

$$d\left(L - \sum_{i=1}^{f} p_i \dot q_i\right) \equiv -dH = \sum_{i=1}^{f} \left[\dot p_i dq_i - \dot q_i dp_i \right]$$

$$= \sum_{i=1}^{f} \left[-\frac{\partial H}{\partial q_i} dq_i - \frac{\partial H}{\partial p_i} dp_i \right]$$

The microscopic state of a system is uniquely described by specifying the canonical variables at a time t, in vector notation

$$\underline{X} = (q_1 \dots q_f, p_1 \dots p_f) = (q, p)$$

The vector X is an element of the $2f$-dimensional phase space Γ, $\underline{X} \in \Gamma$. We denote the volume element in Γ by
$$d\Gamma = dq_1 \dots dq_f \, dp_1 \dots dp_f$$

The time evolution of the phase space point X is described by

$$\frac{d}{dt} \underline{X}(t) = (\dot q, \dot p) = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}\right)$$

As the specification of the microscopic state X together with the equations of motion uniquely determines the future time evolution $X(t)$, trajectories in phase space cannot intersect. A closed (isolated from the environment) mechanical system has $2f-1$ integrals of motion. The equations of motion are supplemented by $2f$ initial conditions for the components of $\underline{X}(t_0)$. However, for an isolated system, the initial time t_0 is arbitrary and one of the constants of motion can be chosen in the form of an additive constant time t $\Rightarrow$ there remain $2f-1$ integrals of motion ($\hat{=}$ conserved quantities).

Not all conserved quantities are equally important, often they are difficult to find. Important conserved quantities are energy, momentum, and angular momentum. They are a consequence of the homogeneity of time (H does not depend on time explicitly), homogeneity and isotropy of space.

In many applications of statistical mechanics, momentum and angular momentum are not conserved. For example, gas atoms may be confined to a container which violates homogeneity and isotropy of space

As a consequence, energy is the most important conserved quantity, and the trajectory $\underline{X}(t)$ lies on an energy surface $H(\underline{X}) = E_0$, a $2f-1$-dimensional subspace of Γ.

The microscopic equations of motion are reversible, i.e. a given time evolution can happen both in "forward" and "backward" direction:

$$\frac{d}{dt}\underline{X}(t) = (\dot{q}, \dot{p}) = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}\right)$$

Now we apply a time reversal transformation $t \to -t$, and as a consequence $\dot{q} \to -\dot{q}$ and $p \to -p$, $\dot{p} \to \dot{p}$

$$\Rightarrow \quad -\frac{d}{dt}\underline{X}(t) = (-\dot{q}, \dot{p}) = \left(-\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}\right)$$

The new trajectory $\tilde{q}_i(t) = q_i(-t)$, $\tilde{p}_i = -p_i(-t)$ only differs by the direction of evolution from $q_i(t)$, $p_i(t)$. In the presence of an ~~external~~ magnetic field, we find from Maxwell's equations that $B(t) \to -B(-t)$ in addition.

The important question we want to address in this chapter is:

How can the irreversible behavior of macroscopic systems be explained starting with the reversible microscopic equations of motion?

Before we answer this question, we discuss the Liouville theorem and the Poincaré recurrence theorem.

We now consider not only a single system, but a large number N of copies of the system. Each of these copies is described by a point $\underline{X}_\nu$, $\nu = 1 \ldots N$ in phase space. Each trajectory $\underline{X}_\nu(t)$ corresponds to different initial conditions. These points move in analogy to non-interacting particles in a fluid => concept of an ensemble fluid or ensemble. We define the phase space density

$$\rho(\underline{X},t) = \frac{1}{N}\sum_{\nu=1}^{N} \delta\left(\underline{X}-\underline{X}_\nu(t)\right)$$

at a point $\underline{X}$, which is normalized to unity

$$\int \rho(q_1 \ldots q_f, p_1 \ldots p_f, t)\, d\Gamma = 1.$$

As the total number N of points in phase space is conserved, the current $\dot{\underline{X}}\rho$ satisfies the continuity equation

$$0 = \frac{\partial\rho}{\partial t} + \mathrm{div}\,(\dot{\underline{X}}\rho) = \frac{\partial \rho}{\partial t} + \dot{\underline{X}}\,\mathrm{grad}\,\rho + \rho\,\mathrm{div}\,\dot{\underline{X}}$$

From the equations of motion we find

$$\mathrm{div}\,\dot{\underline{X}} = \underbrace{\sum_{i=1}^{f}\left(\frac{\partial}{\partial q_i}\dot{q}_i + \frac{\partial}{\partial p_i}\dot{p}_i\right)}_{\text{definition of divergence}} = \sum_{i=1}^{f}\left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i}\right) = 0$$

Using this result, we find for the total time total time derivative (which describes the change in time of ρ in a frame moving with the flow of phase space points $\underline{x}_\nu$)

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \dot{\underline{x}}\,\mathrm{grad}\,\rho = \frac{\partial \rho}{\partial t} + \dot{\underline{x}}\,\mathrm{grad}\,\rho + \underbrace{\rho\,\mathrm{div}\,\dot{\underline{x}}}_{0}$$

$$= \frac{\partial \rho}{\partial t} + \mathrm{div}(\dot{\underline{x}}\rho) \underset{\substack{\uparrow \\ \text{continuity equation}}}{=} 0$$

On the other hand, we can write

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \dot{\underline{x}}\,\mathrm{grad}\,\rho = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{f} \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i}$$

$$\Rightarrow \boxed{\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{H, \rho\} = 0}$$

Liouville theorem

from previous argument using the continuity equation

The physical interpretation is that the density of the ensemble fluid surrounding a given phase space point stays constant during the motion => the ensemble fluid is incompressible. The simplicity of this result follows from $\mathrm{div}\,\dot{\underline{x}} = 0$. In general, this condition is no longer satisfied if we use the $\dot{q}_i$ instead of the p_i