Theory 4. Statistical Physics.
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Course summary
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In this final lecture, we will summarize (and synthesize) the main concepts and themes of the course.

The first concept is energy, which is familiar from classical mechanics via the consideration of kinetic and potential energy. The novelty here is the consideration of thermal energy, encapsulated as the 1st law of thermodynamics. So, we are exploring the consequences of having heat energy as a new way to affect dynamics of particles.

As a consequence, we want to study not just the impact of having thermal energy but also the notion of dynamic equilibrium or steady state behavior. Phenomenologically, we observe that any system of particles with an arbitrary initial configuration and some set of interactions will reach an "equilibrium" configuration whereby a second system with a different initial configuration but same interactions (and thus same Hamiltonian) can be connected to the first, and after some indeterminate time, no net particle exchange, heat exchange, or work exchange will be observed.

If we isolate to only heat exchange, this exchange of energy implies the existence of an equation of state that characterizes the dynamic equilibrium condition. In such an equation of state, we typically introduce the notion of temperature, which is conceptually a simple placeholder for a second (arbitrary) system prepared as before but has already equilibrated. This is the central principle of the 0th law of thermodynamics. The variables that construct the equation of state are thus "thermodynamic coordinates" or "state variables."

The second law of thermodynamics says that heat energy is fundamentally different from work energy in that the non-negativity of temperature (in the vast majority of isolated systems) requires that systems undergoing cyclic processes (engine processes) must have an efficiency of converting heat to work or vice versa that is $\leq 100\%$. (It is only 100% if the cold sink is at $T_{cold} = 0K$.) Otherwise, there is always heat loss to the environment that cannot be recovered as useful work energy.

In order to quantify or understand the microscopic origin of this heat loss, we needed to realize that temperature is the conjugate

variable to an extensive property of the system which we called entropy. Other examples of intensive (characterize the system regardless of system size) and extensive (scales with system size) variables include [pressure, volume] or [chemical potential, number of particles], respectively.

By analyzing classical dynamics, where systems are deterministic and entirely predicted by the Hamiltonian, we could analyze the approximate effect of interactions following the truncation in the Boltzmann equation ($L[\phi] = C[\phi]$, LHS is Liouville operator, RHS is collision operator) afforded by the BBGKY hierarchy. We constructed the H-theorem, which showed the subtlety of ~~Kosing~~ having dynamics that were not aggregate/system-wide time-reversal invariant even though the original/microscopic Hamiltonian is time-reversal invariant. A related & important concept here was the characterization of microstates of a thermal system as trajectories in phase space (equivalent to an initial condition for all $\{\vec{p}_i, \vec{q}_i\}$ of particles in the system) and the knowledge that "holes" in phase space prevented us from defining sensible differentials in phase space density unless we adopt the limiting differential relation:

$$\rho(\vec{p}, \vec{q}, t) = d\Gamma = \lim_{N \to \infty} \frac{dN(\vec{p}, \vec{q}, t)}{N}$$

The behavior of $\rho(t)$ is governed by Liouville's theorem, which states that $\rho(t)$ time-evolves as an incompressible fluid. In other words, a probability density based on $\rho(t)$ will preserve probability density, since the Hamiltonian is then a unitary time-evolution.

This connected the construction of microstates (individual trajectories) to macrostates (collections of trajectories that share macroscopic properties like same total E). This also necessitated the introduction of the ergodic hypothesis, where time-averages of a given system (to characterize steady-state behavior) were traded for ensemble averages of systems with shared features but only for finite time. Intuitively, the two types of averaging are only formally equivalent in the infinite time limit.

Using the phase space density let us construct the Maxwell Boltzmann velocity distribution for a noninteracting gas. The key aspect of the derivation was that the different velocities of a gas molecule in the system were probabilistically distributed by the Boltzmann factor from one velocity magnitude to the next,

$$g(v_x) \propto e^{-\frac{1}{2}mv_x^2/k_BT}.$$

This study of the kinetic theory of gases let us reproduce many of the known results of the Ideal gas law, such as heat capacities at const. volume or pressure, but also showed the equipartition theorem, which connected the probabilistic Boltzmann factor with the number of degrees of freedom present in the system.

In fact, the intuition of using the Boltzmann factor to suppress/enhance probabilities of microstates relative to a reference microstate is the central idea in statistical mechanics and the construction of the microcanonical, canonical, Gibbs, and grand canonical ensembles. In all cases, the possible exchange of the system with its environment is a transfer of some energy flow (heat energy, work energy, chemical energy in various combinations): the probabilistic weight for such an energy exchange to occur is always suppressed by $\exp\left(\frac{-\Delta E}{k_B T}\right) = \exp(-E\beta)$. Then, a complete specification of all microstates accessible to the system is enumerated by the relevant partition function, which sums all microstates with the required probabilistic weight.

Depending on the type of ensemble, the energy exchange changes the appropriate energy functional / thermodynamic potential to the Helmholtz free energy, Gibbs free energy, or enthalpy, grand potential. These formally correspond to Legendre transforms about the functional dependence of the equation of state, which also led to useful equations relating diff. extensive & intensive variables as partial derivative relations called Maxwell relations. The thermodynamic limit of all ensembles meant that all ensembles are essentially equivalent since ext. reservoirs can be thought as fixed constraints of particular state variables. The fluctuations about these constraints typically vanish in the thermodynamic limit as a consequence of the central limit theorem. (We can generally analyze thermodynamic properties via moments & cumulants of the partition fcn.)

This gives a microscopic definition of entropy, $S = k_B \ln \Omega$ or Gibbs entropy, $S = -k_B \sum P_i \ln P_i$ (sum over macrostates). These used prob. fcns. that needed to impose indistinguishability to resolve the Gibbs paradox / entropy of mixing and restore extensivity. This also recovers the third law of entropy, where entropy at $T \to 0$ K is a universal constant for all systems & can be taken as 0.

Finally, the power of stat. mech. in enumerating all microstates of a given system lets us to understand thermodynamic coordinates away from the thermodynamic limit. Unfortunately, it is generally difficult to solve exactly Hamiltonians (ie. energy eigenvalues) + partition fcns. when we include interactions. We illustrated this by the van der Waals gas, which showed the emergence of phase transitions from possible non-linearities in the free energy functional. This also let us construct a classification of phase transitions (a la Ehrenfest) as ~~discontinuities~~ zeroes in the derivs. of the free energy.

Returning to non-interacting models, we saw photons (massless relativistic gas) + the ultraviolet catastrophe from the Rayleigh-Jeans approx. + the importance of the energy level quantization. We also saw phonons + the Einstein + Debye models.

In pure quantum statistics, the impact of exchange symmetry produced two distinct distrib. functions: Fermi-Dirac + Bose-Einstein, reflecting spins of half-integer (+ Pauli exclusion) or integer, respectively. These gave very diff. behavior for $T \to 0K$, as a fermi sea + fermi surfaces, and Bose-Einstein condensates.

Further topics that you are welcome to study:

Critical phenomena, phase transitions.
Monte Carlo methods + stochastic evaluation of prob. distributions
Lasers - Einstein A+B coeff., population inversion
Cosmology - Boltzmann eqn. & collisions/interactions
DM relic density
Density matrix + quantum many-body theory & renormalization, functional ren. group.
+ much more.

Statistical physics has very wide applicability & techniques are extremely useful in many open problems in physics. Have fun exploring!

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