MSDL presentation

A Brief Introduction to Statistical Mechanics

Indrani A. Vasudeva Murthy

McGill

Modelling, Simulation and Design Lab (MSDL)

School of Computer Science, McGill University, Montréal, Canada

Overview

- The Hamiltonian, the Hamiltonian equations of motion; simple harmonic oscillator.

- Thermodynamics; internal energy and free energy.

- Kinetic theory; phase space and distribution functions.

- Statistical mechanics: ensembles, canonical partition function; the ideal gas.

- Concluding remarks.

Equations of Motion

- Newton's second law: $\mathbf{F} = m\mathbf{a}$.

- Equations of motion: explicit expressions for **F, a**.

- Different formulations give a recipe to arrive at this:
  Lagrangian and **Hamiltonian** approaches.

- In Classical Mechanics, the Lagrangian formulation is most common –
  leading to Lagrange's equations of motion.

- The Hamiltonian formulation leads to Hamilton's equations of motion.

- In Statistical Mechanics and Quantum Mechanics it is more
  convenient to use the Hamiltonian formalism.

The Hamiltonian

- The Hamiltonian $\mathcal{H}$ is defined as follows:

$$\mathcal{H} = T + V.$$

T : kinetic energy of the system,

V : potential energy of the system.

- For most systems, $\mathcal{H}$ is just the total energy E of the system.

- Knowing $\mathcal{H}$, we can write down the equations of motion.

- In Classical Physics, $\mathcal{H} \equiv E$, a scalar quantity.

- In Quantum Mechanics, $\mathcal{H}$ is an operator.

A Brief Introduction to Statistical Mechanics

Generalized Coordinates

- The concept of a 'coordinate' is extended, appropriate variables can be used. For each generalized coordinate, there is a corresponding generalized momentum (canonically conjugate). Notation:

$$q_i \quad : \quad \text{generalized coordinates;}$$

$$p_i \quad : \quad \text{generalized momenta.}$$

- For example,
  $\{q_i\} \equiv$ Cartesian coordinates $\{x, y, z\}$ for a free particle.
  $\{q_i\} \equiv$ the angle θ for a simple pendulum.

- Can transform between the regular coordinates and the generalized coordinates.

- Useful in dealing with constraints.

Generalized Coordinates

- Hamiltonian $\mathcal{H} = \mathcal{H}\left(\{q_i\}, \{p_i\}, t\right) = \mathcal{H}\left(q, p, t\right)$.

- The generalized coordinates and momenta need not correspond to the usual spatial coordinates and momenta.

- In general for N particles, we have $3N$ coordinates and $3N$ momenta.

- Coordinates and momenta are considered 'conjugate' quantities - they are on an equal footing in the Hamiltonian formalism.

- Coordinates and momenta together define a **phase space** for the system.

Equations of Motion

In the Hamiltonian formalism, the equations of motion are given by:

$$\frac{\partial \mathcal{H}}{\partial q_i} = -\dot{p}_i;$$

$$\frac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i;$$

Newton's second law!

Equations of Motion

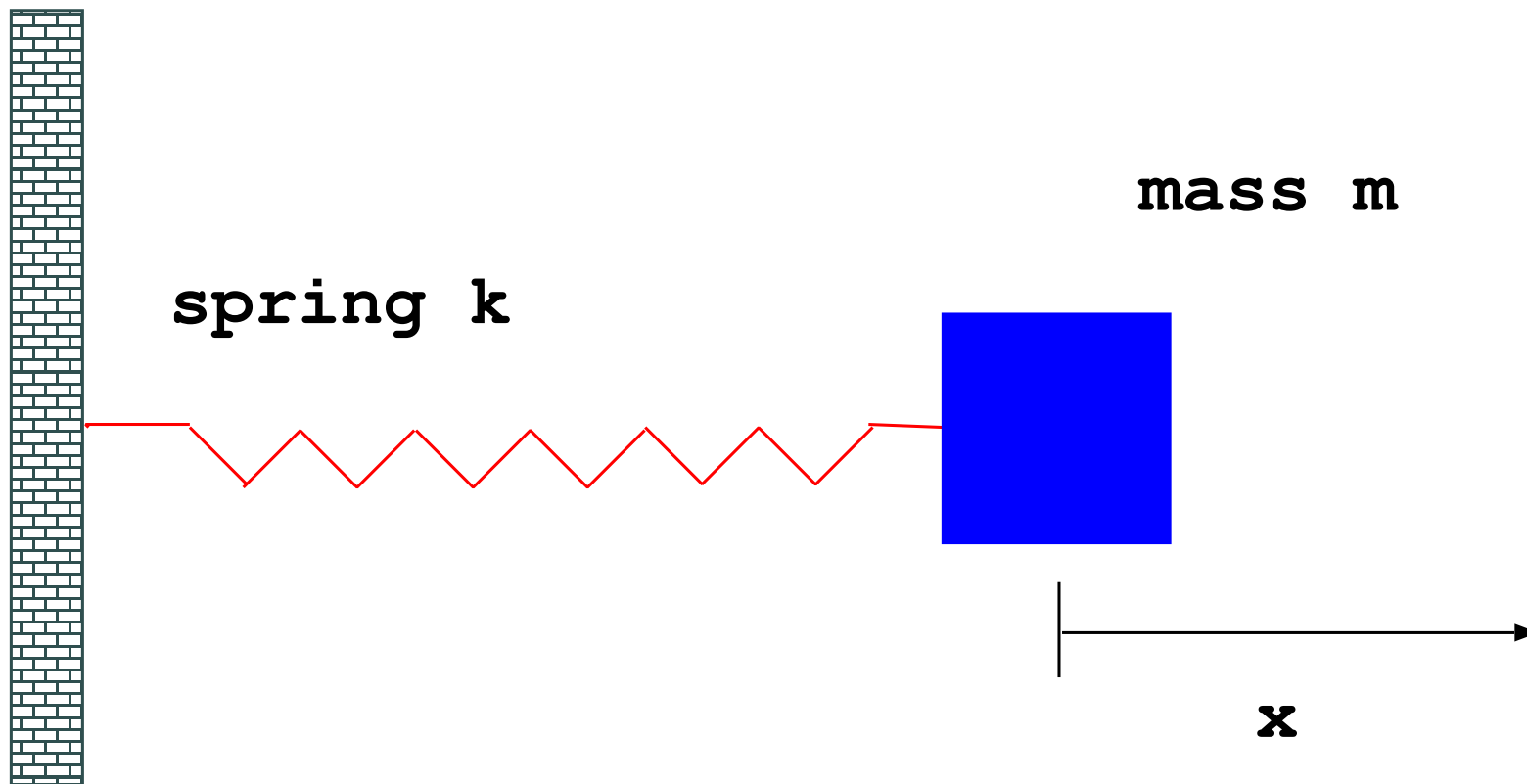- If there is no explicit time dependence in the Hamiltonian, then

$$\mathcal{H}(q,p,t) \quad = \quad \mathcal{H}(q,p);$$

$$\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{H}}{\partial t} \quad = \quad 0.$$

$\implies$ The energy of the system does not change with time, and it is conserved.

- Symmetries of the Hamiltonian $\implies$ conserved quantities.

Simple Harmonic Oscillator (1-D)

mass m

spring k

x

Example: Simple Harmonic Oscillator (1-D)

- Consider a block of mass m connected by a spring with spring constant k.

- Its displacement is given by x, has velocity v, momentum $p = mv$.

- One generalized co-ordinate x, its conjugate momentum p.

- The total energy : kinetic energy + potential energy

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2.$$

Simple Harmonic Oscillator

The Hamiltonian:

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2.$$

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2.$$

Hamilton's equations of motion:

$$\frac{\partial \mathcal{H}}{\partial x} = -\dot{p};$$

$$\frac{\partial \mathcal{H}}{\partial p} = \dot{x}.$$

Simple Harmonic Oscillator

$$
\begin{aligned}
kx &= -\dot{p}; \\
\frac{p}{m} &= \dot{x};
\end{aligned}
$$

Rearrange, two first order ODEs:

$$
\begin{aligned}
\frac{dp}{dt} &= -kx; \quad \text{Newton's Law} \\
\frac{dx}{dt} &= \frac{p}{m}.
\end{aligned}
$$

Can get the usual second order ODE:

$$
\frac{d^2 x}{dt^2} + \frac{k}{m} x = 0.
$$

Thermodynamics

- Thermodynamics: phenomenological and empirical.

- A thermodynamic system: any macroscopic system.

- Thermodynamic parameters (state variables): measurable quantities such as pressure P, volume V, temperature T, magnetic field H.

- A thermodynamic state is specified by particular values of $P, V, T, H...$

- An **equation of state**: a functional relation between the state variables. Example: for an ideal gas, $PV = nRT$.

- Other thermodynamic quantities: internal energy E, entropy S, specific heats C_V, C_P (response functions).

Thermodynamics

- At equilibrium, observe **average** behaviour.

- The internal energy E = average total energy of the system : $< \mathcal{H} >$.

- **Intensive** and **Extensive** variables.

- Intensive variables do not depend on the size of the system.
  Examples: pressure P, temperature T, chemical potential μ.

- Extensive variables depend on the size of the system. Examples: the
  total number of particles N, volume V, internal energy E, entropy S.

- The first law of thermodynamics: energy conservation:
  change in internal energy = heat supplied - work done by the system.
  Mathematically:
  $$dE = T\,dS - P\,dV + \mu\,dN\,.$$

Thermodynamics

- T, P, μ are **generalized forces**, intensive. Each associated with an extensive variable, such that
  change in internal energy = generalized force $\times$ change in extensive variable.

- $\{T,S\}$, $\{-P,V\}$, $\{\mu,N\}$ are **conjugate variable pairs.**

- Thermodynamic potentials: analogous to the mechanical potential energy. Energy available to do work – 'free energy'. The free energy is minimized, depending on the conditions.

Thermodynamics

- Helmholtz free energy:

$$
\begin{aligned}
F &= E - TS; \\
dF &= dE - T\,dS - S\,dT \\
&= T\,dS - P\,dV + \mu\,dN - T\,dS - S\,dT \\
dF &= -P\,dV - S\,dT + \mu\,dN.
\end{aligned}
$$

- Like E, the potentials contain all thermodynamic information.

- Equation of state from the free energy – relates state variables:

$$
P(V,T,N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N}.
$$

Kinetic Theory

- A dilute gas of a large number N of molecules in a volume V.

- The temperature T is high, the density is low.

- The molecules interact via collisions.

- An isolated system will always reach equilibrium by minimizing its energy. At equilibrium its energy does not change with time.

- Consider, for each molecule, $\{\mathbf{r}, \mathbf{p}\}$: 3 spatial coordinates, 3 momenta.

- Each particle corresponds to a point in a 6-D phase space. The system as a whole can be represented as N points.

- Not interested in the detailed behaviour of each molecule.

Kinetic Theory – 6-D Phase Space

3 momenta

(px,py,pz)

N points

3 coordinates (x,y,z)
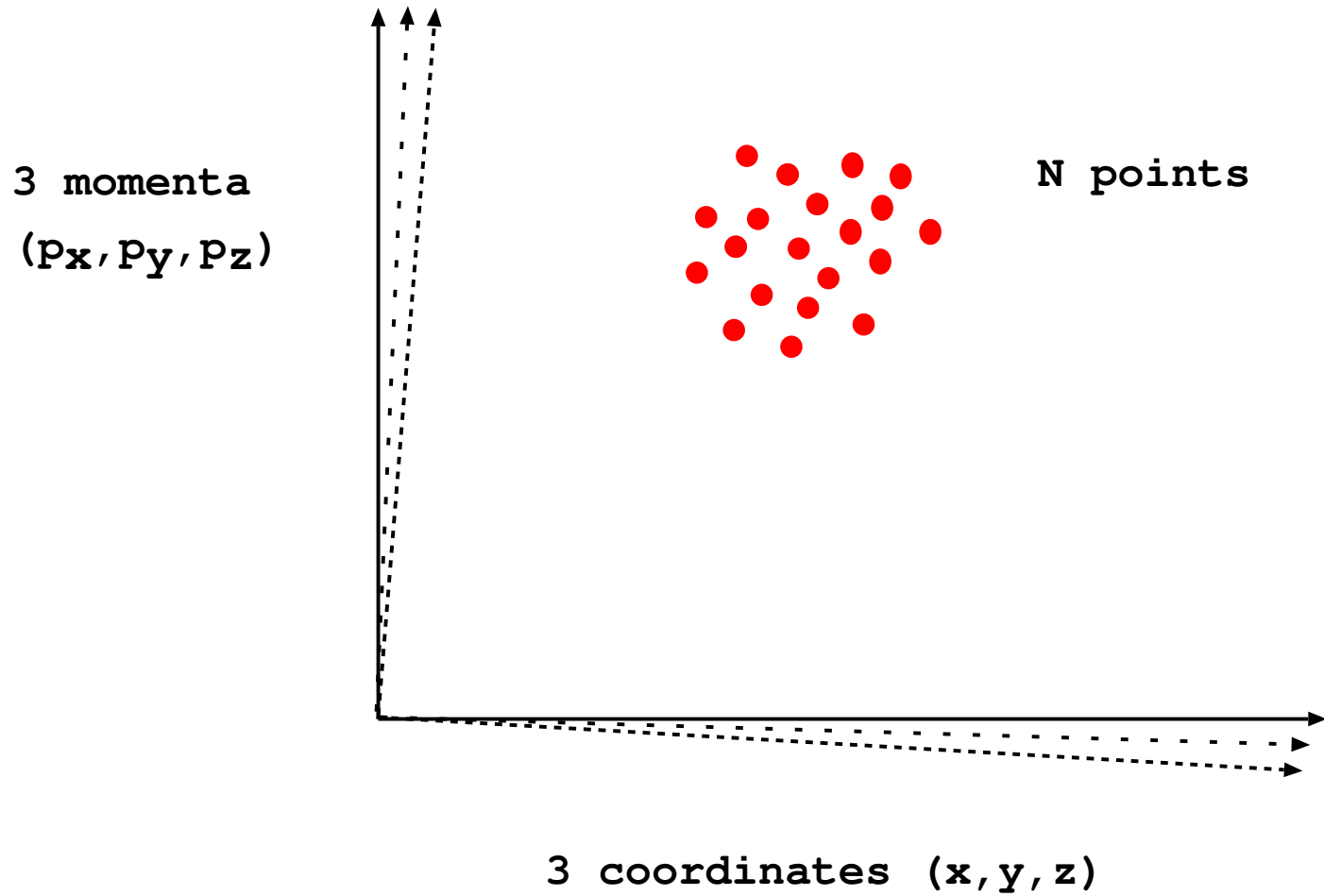
Kinetic Theory

- Define a **distribution function** $f(\mathbf{r}, \mathbf{p}, t)$ so that

$$f(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{r}\, d\mathbf{p}$$

  gives the number of molecules at time t lying within a volume element $d\mathbf{r}$ about $\mathbf{r}$ and with momenta in a momentum-space volume $d\mathbf{p}$ about p.

- $f(\mathbf{r}, \mathbf{p}, t)$ is just the **density of points** in phase space.

- Assume that f is a smoothly varying continuous function, so that:

$$\int f(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{r}\, d\mathbf{p} = N.$$

Kinetic Theory

- Problem of Kinetic Theory: Find f for given kinds of collisions (binary, for example) – can be considered to be a form of interaction.

- Explicit expressions for pressure, temperature; temperature is a measure of the average kinetic energy of the molecules.

- The limiting form of f as $t \to \infty$ will yield all the equilibrium properties for the system, and hence the thermodynamics.

- Maxwell–Boltzmann distribution of speeds for an ideal gas at equilibrium at a given temperature: Gaussian.

- Find the time-evolution equation for f - the equation of motion in phase space.

- Very messy!

Ensembles and Statistical Mechanics

- Gibbs introduced the concept of an ***ensemble***.

- Earlier: N particles in the 6-D phase space.

- Ensemble: A ***single*** point in $6N$-dimensional phase space represents a given configuration.

- A given macrostate with $\{E, T, P, V, \ldots\}$ corresponds to an ensemble of microstates: 'snapshots' of the system at different times.

- Ergodic hypothesis: Given enough time, the system explores all possible points in phase space.

Ensemble Theory – 6N-D Phase Space

3 N momenta

● **1 point**

○ ○ ○ ○ ○ ○ **Ensemble**
○ ○ ○ ○

3 N coordinates
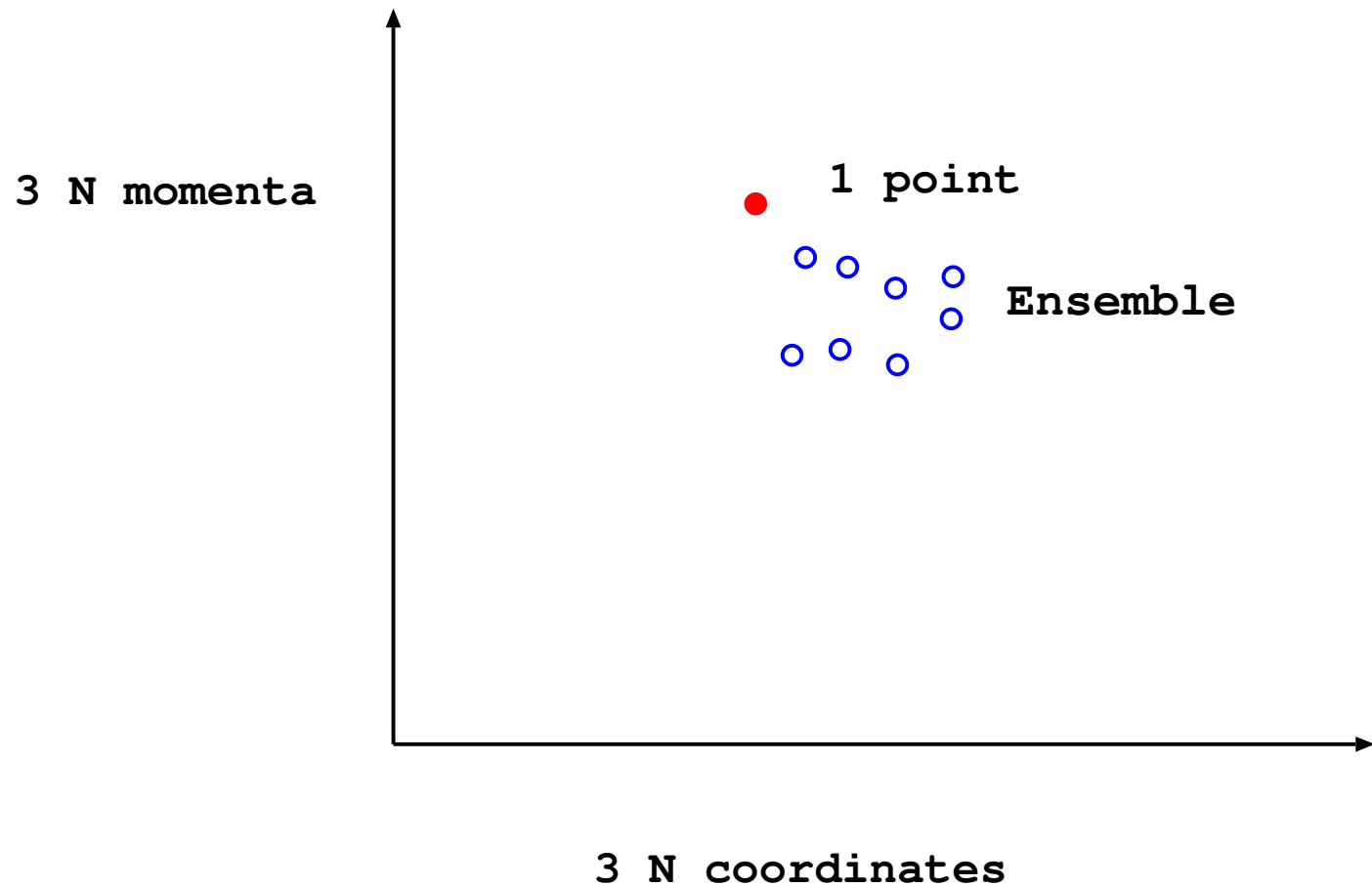
Ensembles and Statistical Mechanics

- Central idea: replace **time averages** by **ensemble averages**.

- Time Average: For any quantity $\phi(\mathbf{r}, \mathbf{p}, t)$:

$$< \phi(\mathbf{r}, \mathbf{p}, t) > = \frac{1}{\tau} \int_0^\tau \phi(\mathbf{r}, \mathbf{p}, t) \, dt.$$

- Ensemble Average: For $\tau \to \infty$:

$$< \phi(\mathbf{r}, \mathbf{p}, t) > = \int \rho(\mathbf{r}, \mathbf{p}) \, \phi(\mathbf{r}, \mathbf{p}, t) \, d\mathbf{r} \, d\mathbf{p}.$$

$$d\mathbf{r} = d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots \ldots d\mathbf{r}_N;$$
$$d\mathbf{p} = d\mathbf{p}_1 \, d\mathbf{p}_2 \ldots \ldots d\mathbf{p}_N.$$

Ensembles

- $\rho(\mathbf{r}, \mathbf{p})$: probability density,

  $\rho(\mathbf{r}, \mathbf{p}) \, d\mathbf{r} \, d\mathbf{p}$: probability of finding the system in a volume element $[d\mathbf{r} \, d\mathbf{p}]$ around $(\mathbf{r}, \mathbf{p})$.

- Different ensembles: **microcanonical**, **canonical** and **grand canonical** ensembles.

- Microcanonical ensemble: isolated systems with fixed energy and number of particles, no exchange of energy or particles with the outside world. Not very useful !

A Brief Introduction to Statistical Mechanics

Ensembles

- Canonical ensemble: Energy is not fixed, can exchange E with a reservoir; N fixed.

- Grand canonical ensemble: Both energy and N can vary.

- In the canonical ensemble, the probability of a given configuration with energy E (corresponding to Hamiltonian $\mathcal{H}$) :

$$p_c = \frac{e^{-\beta \mathcal{H}(\mathbf{r},\mathbf{p})}}{Z_N(V,T)} \, .$$

- $\beta = 1/k_B T, \quad k_B$: Boltzmann constant $= R/N_A$.

- $e^{-\beta \mathcal{H}(\mathbf{r},\mathbf{p})}$: Boltzmann factor or Boltzmann weight.

The Canonical Partition Function

$$Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int d\mathbf{r}\, d\mathbf{p}\, e^{-\beta\mathcal{H}(\mathbf{r},\mathbf{p})}$$

h: Planck's constant.

- Z_N : phase space volume, each volume element weighted with the Boltzmann factor.

- From Z_N, we can calculate various thermodynamic quantities.

The Canonical Partition Function

- For example: internal energy E is given by the ensemble average $<\mathcal{H}>$ of the Hamiltonian:

$$
\begin{aligned}
E &= <\mathcal{H}> \\
&= \frac{1}{Z_N(V,T)} \int d\mathbf{r}\, d\mathbf{p}\; \mathcal{H}\; e^{-\beta \mathcal{H}(\mathbf{r},\mathbf{p})}
\end{aligned}
$$

- Also, more conveniently,

$$
E = - \left. \frac{\partial \ln Z_N(V,T)}{\partial \beta} \right|_{N,V}.
$$

The Canonical Partition Function

Can show that it is related to the Helmholtz free energy F:

$$F = E - TS$$

$$Z_N(V,T) = e^{-\beta F}$$

$$F = -k_B T \ln Z_N(V,T).$$

Example: The Ideal Gas

- One of the simplest statistical systems: a gas of N non-interacting particles, each of mass m, in a volume V at temperature T.

- The Hamiltonian $\mathcal{H}$ = Kinetic Energy:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} = \sum_{i=1}^{N} \frac{p_i^2}{2m}. \tag{1}$$

- The canonical partition function:

$$Z_N(V,T) = \frac{1}{N!\, h^{3N}} \int d\mathbf{r}\, d\mathbf{p}\; e^{-\beta \mathcal{H}(\mathbf{r},\mathbf{p})}$$

$$Z_N(V,T) = \frac{1}{N!\, h^{3N}} \int d\mathbf{r}\, d\mathbf{p}\; \exp\left(-\sum_{i=1}^{N} \frac{p_i^2}{2m} \right).$$

Example: The Ideal Gas

$$Z_N = \frac{V^N}{N!\,h^{3N}} \left(\int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m} \right)^{3N}$$

$$Z_N = \frac{V^N}{N!\,h^{3N}} \left(\sqrt{2\pi m/\beta} \right)^{3N}$$

$$= \frac{V^N}{N!\,h^{3N}} \left(2\pi m k_B T \right)^{3N/2}$$

$$\ln Z_N = N \ln V + \frac{3}{2} N \left[\ln(2\pi m) - \ln \beta \right] - \ln N! - 3N \ln h .$$

The Ideal Gas

- Can calculate macroscopic thermodynamical quantities.

- Average (kinetic) energy of the gas:

$$E = -\frac{\partial \ln Z_N}{\partial \beta}$$

$$= -\frac{\partial(-\frac{3}{2} N \ln \beta)}{\partial \beta}$$

$$= \frac{3}{2} \frac{N}{\beta}$$

$$E = \frac{3}{2} N k_B T.$$

- Average (kinetic) energy per particle: $\frac{E}{N} = \frac{3}{2} k_B T$.

The Ideal Gas

$$\ln Z_N = N \ln V + \frac{3}{2} N \left[\ln(2\pi m) - \ln \beta \right] - \ln N! - 3N \ln h.$$

The Helmholtz free energy:

$$F = - k_B T \ln Z_N.$$

The ideal gas equation of state:

$$P(V,T,N) = - \left. \frac{\partial F}{\partial V} \right|_{T,N}.$$

The Ideal Gas

Equation of state:

$$P = -\frac{\partial(-k_B T N \ln V)}{\partial V}$$

$$= \frac{N k_B T}{V}$$

$$PV = n N_A k_B T$$

$$PV = n R T$$

The Partition Function

- The partition function approach is very important because of its success.

- A whole range of equilibrium phenomena can be understood this way.

- Recipe: Write down the Hamiltonian - mostly interested in the potential energy term:
$$V = V_{ext} + V_{int}$$

- The V_{int} term includes all the interactions: two-body, three-body . . .

- Get the free energy from the partition function.

- Minimize the free energy: the equilibrium 'ground state' of the system.

Extensions ?

- The Hamiltonian can be either discrete or continuous.

- Continuous systems: concept of *fields* (example: density field, magnetization field, field of interactions).

- When dealing with fields, the Hamiltonian, and the free energy, become **functionals** :

$$\mathcal{H} = \mathcal{H}\left[\phi(\mathbf{r},t)\right]$$

.

- Use field theory techniques and variational calculus.

- Non-equilibrium: time-dependent Hamiltonian, dissipation $\Longrightarrow$ transport properties; failure of equilibrium statistical mechanics.

- Deal with time-dependent probabilities: stochastic equations.

Concluding Remarks

- What has all this to do with research at MSDL ?

- Look for **universal** features and quantify them: symmetry properties; conservation laws ?

- Equivalent concepts to: generalized coordinates, energy, energy minimization.

- Typical scales in a problem: length and time. Approximations based on this.

- Map one problem onto another: reduce it to something you know (SHO) .

- Apply the statistical mechanical approach to agents.