

Chapter 1. Introduction

Purpose of Statistical Mechanics:

Studies of macroscopic systems from a microscopic (molecular) point of view

- equilibrium
- non-equilibrium

- molecular interaction not important
- " " " is important

Classical mechanics

Newton's second law:

$$F = ma = m \frac{dv}{dt}$$

Momentum $p = mv$.

$$\frac{dp}{dt} = \dot{p} = F$$

Example 1. Free fall: $F = -mg$

$$x(t) = -\frac{1}{2}gt^2 + v_0 t + x_0$$

Example 2. Simple Harmonic Motion of a spring-mass system

Hooke's Law : $F = -k(x - x_0)$

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k : spring constant

$$x_1 = x - x_0 \rightarrow m \frac{d^2 x_1}{dt^2} = -k x_1$$

Solution $x_1 = c \sin(\omega t + \phi)$

ω : angular frequency

c : amplitude

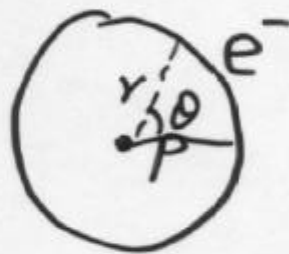
ϕ : phase constant

} determined by initial conditions

Example 3 :

Coulombic Attraction

$$F = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = -\frac{k}{r^2}$$



$$m \ddot{x} = F_x = -\frac{kx}{(x^2 + y^2)^{3/2}}$$

Cartesian coordinates

$$m \ddot{y} = F_y = -\frac{ky}{(x^2 + y^2)^{3/2}}$$

polar coordinates:

$$x = r \cos \theta, \quad y = r \sin \theta$$

$$(1) \left\{ m(\ddot{r} - \dot{\theta}^2 r) + \frac{k}{r^2} \right\} \cos \theta - m(r\ddot{\theta} + 2\dot{\theta}\dot{r}) \sin \theta = 0$$

$$(2) \left\{ m(\ddot{r} - \dot{\theta}^2 r) + \frac{k}{r^2} \right\} \sin \theta + m(r\ddot{\theta} + 2\dot{\theta}\dot{r}) \cos \theta = 0$$

(1) * $\cos\theta +$ (2) * $\sin\theta$ yields: (3)

$$(3) \quad m(\ddot{r} - \dot{\theta}^2 r) + \frac{k}{r} = 0$$

(1) * $\sin\theta -$ (1) * $\cos\theta$ yields:

$$m(r\ddot{\theta} + 2\dot{\theta}\dot{r}) = 0$$

$$(4) \quad \frac{1}{r} \frac{d}{dt} (m r^2 \dot{\theta}) = 0 \quad m r^2 \dot{\theta} = \text{const} = l$$

conservation of angular momentum

plug (4) to (3)

$$m\ddot{r} - \frac{l^2}{m r^3} + \frac{k}{r^2} = 0$$

$$m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{m r^3} \rightarrow \text{centrifugal force}$$

Lagrange's Equation

Kinetic energy $K = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$

Potential energy $m\ddot{x} = -\frac{\partial U}{\partial x}$

Lagrangian function

$$L(x, y, z, \dot{x}, \dot{y}, \dot{z}) = K(\dot{x}, \dot{y}, \dot{z}) - U(x, y, z)$$

$$\frac{\partial L}{\partial \dot{x}} = \frac{\partial K}{\partial \dot{x}} = m\dot{x} \dots, \quad \frac{\partial L}{\partial x} = -\frac{\partial U}{\partial x} \dots$$

(4)

$$\frac{d}{dt} \left(\frac{\partial U}{\partial \dot{x}} \right) = \frac{\partial L}{\partial x} \quad (m\ddot{x} = F)$$

is generalized form, q_1, q_2, q_3 coordinates

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j} \quad (j = 1, 2, 3)$$

Use of it — Example 3 again:

$$K = \frac{m}{2} (\dot{x}^2 + \dot{y}^2) = \frac{m}{2} (\dot{r}^2 + r\dot{\theta}^2)$$

$$U = -\frac{K}{r}$$

$$L(r, \theta, \dot{r}, \dot{\theta}) = K - U = \frac{m}{2} (\dot{r}^2 + r^2 \dot{\theta}^2) + \frac{K}{r}$$

Lagrangian equations (2 of 3)

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}} \right) = \frac{\partial L}{\partial r} \rightarrow \frac{d}{dt} (m\dot{r}) = m r \dot{\theta}^2 - \frac{K}{r^2}$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\theta}} \right) = \frac{\partial L}{\partial \theta} \rightarrow \frac{d}{dt} (m r^2 \dot{\theta}) = 0$$

we need six initial conditions
to solve complete Lagrangian equations

Hamiltonian Equations

generalized momentum $P_j = \frac{\partial L}{\partial \dot{q}_j}$ conjugate to q_j
e.g. $P_x = m\dot{x}$

$$H(P_1, P_2, P_3, q_1, q_2, q_3) = \sum_{j=1}^3 P_j \dot{q}_j - L$$

$$K = \sum a_j \dot{q}_j^2 \quad (5)$$

$$p_j = \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial K}{\partial \dot{q}_j} = 2a_j \dot{q}_j$$

$$H = K + U = \text{total energy} \quad \frac{dH}{dt} = 0$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \quad \frac{\partial H}{\partial p_j} = \dot{q}_j \quad j=1, 2, \dots, 3N$$

Quantum Mechanics

In small scales the position of an electron in an atom (for example) is not certain. So the wave function $\psi(q, t)$ is introduced to describe the probability =

$$\psi^* \psi \, dq_1 \, dq_2 \, \dots \, dq_{3N}$$

$$\int \psi^* \psi \, dq = 1 \quad \text{normalization}$$

ψ is given by solving Schrödinger's equation

$$\mathcal{H} \psi = E \psi$$

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z)$$

$$\hbar = \frac{h}{2\pi}$$

h : Planck constant
 $6.62 \times 10^{-34} \text{ J}\cdot\text{s}$

\mathcal{H} : Hamiltonian operator

For given boundary conditions, there are many solutions to Schrödinger's equation

$$\mathcal{H} \psi_j = E_j \psi_j \quad j = 1, 2, \dots$$

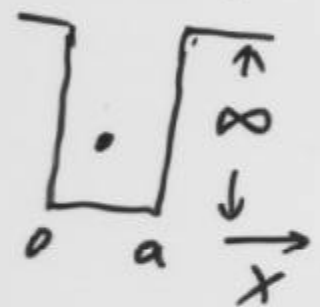
ψ_j : eigen function

E_j : eigen energy

Example 1. one-dimensional infinite well

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

$$E_n = \frac{\hbar^2 n^2}{8ma^2} \quad n=1, 2, \dots$$



Example 2. Simple harmonic oscillator

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} K x^2$$

$$E_n = (n + \frac{1}{2}) \hbar \omega \quad \omega = (\frac{K}{m})^{\frac{1}{2}}, \quad n=0, 1, 2, \dots$$

Example 3. rigid rotator.

$$\mathcal{H} = -\frac{\hbar^2}{2I} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\}$$

$$E_J = \frac{J(J+1) \hbar^2}{2I} \quad J = 0, 1, 2, \dots$$

Degeneracy w : number of different ψ which have the same E

Example 1. rigid rotator

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$$W_J = 2J + 1.$$

$$J_z = 0, \pm 1, \dots, \pm J.$$

Example 2. 1-D infinite well.

$$W_n = 1$$

Example 3. 3-D infinite well (const

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) = \epsilon n$$

n=1.	n_x	n_y	n_z	n=2	n_x	n_y	n_z
$w=3$	0	0	1	$w=3$	1	0	1
	0	1	0		1	1	0
	1	0	0		0	1	1

If energy is given by ϵ

$$n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2\epsilon}{h^2} = R^2$$

Total number of states inside a ball

with a radius of R is $\phi = \frac{1}{8} \frac{4}{3} \pi R^3$

(because only positive numbers are counted)

$$\phi = \frac{\pi}{6} \left(\frac{8ma^2\epsilon}{h^2} \right)^{3/2}$$

number of states between ϵ & $\epsilon + \Delta\epsilon$

$$W(\epsilon, \Delta\epsilon) = \frac{d\phi}{d\epsilon} \Delta\epsilon = \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} \epsilon^{1/2} \Delta\epsilon$$

If $\epsilon = \frac{3}{2} kT$, $T = 300^\circ K$, $m = 10^{-22} g$, $a = 10 cm$, $\Delta\epsilon = 0.01 \epsilon$

$\Omega(E, \Delta E)$ is in the order of 10^{28}

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For N -particle system

$$\bar{E} = \frac{h^2}{8ma^2} \sum_{j=1}^N (n_{x_j}^2 + n_{y_j}^2 + n_{z_j}^2)$$

total states with E

$$\bar{\Omega}(E) = \frac{1}{\Gamma(N+1) \Gamma\left(\frac{3N}{2} + 1\right)} \left(\frac{2\pi ma^2 E}{h^2} \right)^{3N/2}$$

$$\Gamma(x) = \int_0^{\infty} e^{-t} t^{x-1} dt$$

For many body system: if no interaction

$$\mathcal{H} = \mathcal{H}_\alpha + \mathcal{H}_\beta + \mathcal{H}_\gamma + \dots$$

$$\psi = \psi_\alpha \psi_\beta \psi_\gamma \dots$$

Symmetry of wave function

$$\begin{aligned} P_{12} \psi(1, 2, 3, \dots, N) &= \psi(2, 1, 3, \dots, N) \\ &= \pm \psi(1, 2, 3, \dots, N) \end{aligned}$$

+ symmetric — bosons

- antisymmetric — fermions

Thermodynamics

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1st law $\Delta E = E_B - E_A = Q - W$

ΔE internal energy

$Q = \int_A^B \delta Q$: heat absorbed

$W = \int_A^B p dV$ work done by the system

2nd law entropy increases

reversible process $\Delta S = \int_A^B \frac{dQ_{rev}}{T}$

All other process $\Delta S > \int_A^B \frac{dQ_{rev}}{T}$

3rd Law

perfect crystalline substances

$T=0 \text{ K}$ $S_0 = 0$

other use-ful equations

$dE = T ds - p dV$ $(\frac{\partial E}{\partial s})_V = T$, $(\frac{\partial E}{\partial V})_s = -P$

$dE = [T(\frac{\partial P}{\partial T})_V - P] dV + C_V dT$

$C_p - C_V = [P + (\frac{\partial E}{\partial V})_T] (\frac{\partial V}{\partial T})_P$

Legendre Transformation

consider a function $y = y(x)$

slope $p = p(x)$, intercepts y at $\phi(p)$

The $p = \frac{y - \phi}{x - 0}$, $\phi(p) = y - px$

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Helmholtz Free Energy: A

$$dE = Tds - pdv \quad E = E(S, V)$$

$$T = \left(\frac{\partial E}{\partial S} \right)_V \rightarrow \text{slope}$$

$$\phi = A(T, V) = E - TS$$

$$dA = -SdT - pdV$$

similarly, $p = -\left(\frac{\partial E}{\partial V} \right)_S$

enthalpy $H = E + pV$ $dH = Tds + vdp$

generalized Legendre Transformation

$$\phi(p) = y - \sum P_j x_j \quad P_j = \frac{\partial y}{\partial x_j}$$

Gibb's Free Energy $G = E - TS + pV$

$$dG = -SdT + vdp$$

Multi-component system:

$$dE = Tds - pdv + \sum_j \mu_j dN_j$$

$$dH = Tds + vdp + \sum_j \mu_j dN_j$$

$$dA = -SdT - pdv + \sum_j \mu_j dN_j$$

$$dG = -SdT + vdp + \sum_j \mu_j dN_j$$

$$\mu_j = \left(\frac{\partial E}{\partial N_j} \right)_{S, V, \dots} = \left(\frac{\partial H}{\partial N_j} \right)_{S, P, \dots} \dots \text{Chemical potential}$$

Mathematics

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Probability Distributions

M discrete values u_1, u_2, \dots, u_M
corresponding probabilities p_1, p_2, \dots, p_M

mean $\bar{u} = \frac{\sum_1^M u_j p_j}{\sum p_j = 1}$

$$f(\bar{u}) = \frac{\sum f(u_j) p_j}{\sum p_j} = \sum_{j=1}^M f(u_j) p_j$$

$f(u) = u^m$ m-th moment

$f(u) = (u - \bar{u})^m$ m-th central moment

$(u - \bar{u})^2$ variance

$\sqrt{(u - \bar{u})^2}$ standard deviation

Poisson Distribution

$$P(m) = \frac{a^m e^{-a}}{m!} \quad m=0, 1, 2, \dots$$

for continuous distribution

$$f(\bar{u}) = \int f(u) p(u) du$$

Gaussian Distribution

$$P(x) = \frac{1}{(\sqrt{2\pi}\sigma)^2} e^{-\left\{\frac{(x-\bar{x})^2}{2\sigma^2}\right\}} \quad -\infty < x < \infty$$

Stirling's Approximation

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factorials $N! = N(N-1)\dots 2 \cdot (1)$

$$\ln N! = \sum_{m=1}^N \ln m = \int_1^N \ln x dx$$

$$= N \ln N - N$$

Binomial Distribution

Divide N into sub systems n_1, n_2, \dots
 $n_1 + n_2 + \dots = N$

number of different arrangement
 $N(N-1)(N-2)\dots = N!$

Divide N into two groups N_1 & N_2

binomial coefficient $\frac{N!}{N_1! N_2!} = \frac{N!}{N_1! (N-N_1)!}$

$$(x+y)^N = \sum_{n_1, n_2} \frac{N! x^{N_1} y^{N_2}}{N_1! N_2!} \quad \boxed{N_1 + N_2 = N}$$

Multinomial coefficient

$$\frac{N!}{N_1! N_2! \dots N_r!} = \frac{N!}{\prod_{j=1}^r N_j!} \quad \boxed{N_1 + N_2 + \dots + N_r = N}$$

$$(x_1 + x_2 + \dots + x_r)^N = \sum_{N_1=0}^N \sum_{N_2=0}^N \dots \sum_{N_r=0}^N \frac{N! x_1^{N_1} \dots x_r^{N_r}}{\prod_{j=1}^r N_j!}$$

Method of Lagrange undetermined multipliers

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consider function $f(x_1, x_2 \dots x_r)$

maximum (or minimum) would satisfy

$$\delta f = \sum \frac{\partial f}{\partial x_j} \delta x_j = 0 \rightarrow \frac{\partial f}{\partial x_j} = 0$$

But, if $g(x_1, x_2 \dots) = 0$

$$\sum_{j=1}^r \left(\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} \right) \delta x_j = 0$$

$$\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} = 0$$

Conversion of Binomial to Gaussian distributions
use stirling equation

Taylor expansion $N_i^* = \frac{N}{2}$ $\frac{N!}{N_i!(N-N_i)!}$ gets maximum

$$\ln f(N_i) = \ln f(N_i^*) + \frac{1}{2} \left(\frac{d^2 \ln f(N_i)}{dN_i^2} \right)_{N_i=N_i^*} (N_i - N_i^*)^2 + \dots$$

$$f(N_i) = f(N_i^*) \exp \left\{ - \frac{2(N_i - N_i^*)^2}{N} \right\}$$

$$f(x) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}} \exp \left\{ - \frac{(x - x^*)^2}{2\sigma^2} \right\}$$