Quantum Statistical Mechanics: the Path-Integral Representation

* in these notes an alternative representation of quantum statistical mechanics is described
* the path-integral representation is in many ways advantageous: it provides an intuitive picture of the difference between quantum vs. classical systems
* here we will develop this representation for a one-dimensional, one particle system

$$H = \frac{p^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

* quantum-mechanical partition function (canonical ensemble)

$$Z_N(T) = \mathrm{Tr}\, e^{-\beta H}$$

* $Z_N(T)$ can be written:

$$Z_N(T) = \mathrm{Tr}\left\{\left[e^{-\frac{\beta}{P}H} \right]^P\right\}$$

$$= \mathrm{Tr}\left\{\left[e^{-\epsilon H} \right]^P\right\} \qquad \epsilon = \beta/P$$

(break-up into P pieces)

$$Z_N(T) = \mathrm{Tr}\left[e^{-\epsilon H}\right]^P$$

* now, insert P identities in the coordinate representation: $\int dx |x\rangle\langle x| = I$

$$Z_N(T) = \int dx_1 \cdots dx_P \prod_{i=1}^{P} \langle x_i | e^{-\epsilon H} | x_{i+1}\rangle$$

where $x_{P+1} = x_1$ (due to the cyclic property of the trace)

for example: if $P = 3$ we have

$$Z_N(T) = \int dx_1 dx_2 dx_3 \langle x_1 | e^{-\epsilon H} | x_2\rangle \cdot \langle x_2 | e^{-\epsilon H} | x_3\rangle \cdot \langle x_3 | e^{-\epsilon H} | x_1\rangle$$

so far we have not made any approximation, $Z_N(T)$ is exact

* we now make an approximation

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) = \hat{T} + \hat{V}$$

$$\underline{e^{-\epsilon \hat{H}} \simeq e^{-\epsilon \hat{T}} e^{-\epsilon \hat{V}}}$$

to what extent is this approximation correct? what is the error?

answer: expand both sides

$$1 - \epsilon \hat{H} + \frac{\epsilon^2}{2}\hat{H}^2 + \dots = \left(1 - \epsilon \hat{T} + \frac{\epsilon^2}{2}\hat{T}^2 + \dots\right)\left(1 - \epsilon \hat{V} + \frac{\epsilon^2}{2}\hat{V}^2 + \dots\right)$$

keep terms on both sides up to second order in ϵ

$$1 - \epsilon \hat{H} + \frac{\epsilon^2}{2}\hat{H}^2 + \dots = 1 - \epsilon(\hat{T} + \hat{V}) + \frac{\epsilon^2}{2}\hat{T}^2 + \frac{\epsilon^2}{2}\hat{V}^2 + \epsilon^2 \hat{T}\hat{V} + \dots$$

$$\epsilon^0: \quad 1 = 1$$

$$\epsilon^1: \quad -\epsilon \hat{H} = -\epsilon(\hat{T} + \hat{V})$$

$$\epsilon^2: \quad \frac{\epsilon^2}{2}\hat{H}^2 \neq \frac{\epsilon^2}{2}\hat{T}^2 + \epsilon^2 \hat{T}\hat{V} + \frac{\epsilon^2}{2}\hat{V}^2$$

ϵ^2 terms do not match

L.H.S.: $\frac{\epsilon^2}{2}(\hat{T} + \hat{V})^2 = \frac{\epsilon^2}{2}\left[\hat{T}^2 + \hat{T}\hat{V} + \hat{V}\hat{T} + \hat{V}^2\right]$

R.H.S.: $\frac{\epsilon^2}{2}\hat{T}^2 + \epsilon^2 \hat{T}\hat{V} + \frac{\epsilon^2}{2}\hat{V}^2$

$$\left[e^{-\epsilon\hat{H}} - e^{-\epsilon\hat{T}} e^{-\epsilon\hat{V}}\right] \simeq \frac{\epsilon^2}{2}[\hat{V},\hat{T}] + O(\epsilon^3)$$

error in approximation is second order in ϵ

$\Downarrow$ $\Downarrow$ $\Downarrow$ $\Downarrow$ $\Downarrow$

$$Z_N(T) = \int dx_1 \cdots dx_P \prod_{i=1}^{P} \langle x_i | e^{-\epsilon\hat{T}} e^{-\epsilon\hat{V}} | x_{i+1}\rangle$$

since $\hat{V}(\hat{x})|x_i\rangle = \hat{V}(x_i)|x_i\rangle$ ($\hat{V}(\hat{x})$ is diagonal in the coordinate representation)

$\Downarrow$

$$Z_N(T) = \int \ldots \int dx_1 \cdots dx_P \prod_{i=1}^{P} \langle x_i | e^{-\epsilon\hat{T}} | x_{i+1}\rangle e^{-\epsilon V(x_{i+1})}$$

it remains to evaluate $\langle x_i | e^{-\epsilon\hat{T}} | x_{i+1}\rangle$

we do this by inserting a momentum space identity:

$$\langle x_i | e^{-\epsilon\hat{T}} | x_{i+1}\rangle = \int dp \langle x_i | p\rangle \langle p | e^{-\epsilon\hat{T}} | x_{i+1}\rangle$$

$\hat{T}$ - kinetic energy operator/diagonal

$\hat{T}$. in momentum representation

$\Downarrow$

$$\hat{T}|p\rangle = \frac{p^2}{2m}|p\rangle$$

$$\langle x_i | e^{-\epsilon \hat{T}} | x_{i+1} \rangle = \int dp \, \langle x_i | p \rangle \langle p | x_{i+1} \rangle \, e^{-\frac{\epsilon p^2}{2m}}$$

(5)

now use the fact that $\langle x_i | p \rangle = \frac{e^{ipx_i}}{\sqrt{2\pi}}$

($\langle x_i | p \rangle$ is the eigenstate of the momentum in the coordinate representation or vice versa)

$$\langle x_i | e^{-\epsilon \hat{T}} | x_{i+1} \rangle = \frac{1}{2\pi} \int dp \, e^{ip(x_i - x_{i+1})} \, e^{-\frac{\epsilon p^2}{2m}}$$

Gaussian integral / evaluates to

$$\langle x_i | e^{-\epsilon \hat{T}} | x_{i+1} \rangle = \frac{1}{2\pi} \left(\frac{2m\pi}{\epsilon} \right)^{1/2} e^{-\frac{m}{2\epsilon}(x_i - x_{i+1})^2}$$

$$\boxed{\begin{aligned} Z_N(T) &\simeq \int \ldots \int dx_1 \ldots dx_p \prod_{i=1}^{p} e^{-\frac{m}{2\epsilon}(x_i - x_{i+1})^2} \, e^{-\epsilon V(x_i)} \\ &\simeq \int \ldots \int dx_1 \ldots dx_p \, e^{-\epsilon \sum_{i=1}^{p} \left[\frac{m}{2\epsilon^2}(x_i - x_{i+1})^2 + \epsilon V(x_i) \right]} \end{aligned}}$$

* $Z_N(T)$ is now expressed approximately up to an error of ϵ^2

INTERPRETATION:

* we started with a one-particle one-dimensional system
* classically the partition function would be

$$Z_N^{(c)}(T) = \frac{1}{h} \int dp\, dx\, e^{-\beta\left(\frac{p^2}{2m} + V(x)\right)}$$

depends on two coordinates p, x

- can integrate out p

$$\boxed{Z_N^{(c)}(T) = \left(\frac{2\pi m}{h^2 \beta}\right)^{1/2} \int dx\, e^{-\beta V(x)}}$$

depends only on one variable x

* quantum partition function for same system

$$Z_N^{(q)}(T) = \lim_{p\to\infty} \int dx_1 \dots dx_p\, e^{-\epsilon\left[\frac{m}{2\epsilon^2}(x_i - x_{i-1})^2 + V(x_i)\right]}$$

depends on p variables $x_i \quad i = 1, \dots, p$

(becomes exact as $p \to \infty$)

* for classical system x experiences only the classical potential $V(x)$
* for quantum system x_i $(i = 1, \dots, p)$ experiences a harmonic potential plus the scaled potential $\epsilon V(x_i)$

$$Z_N^{(a)}(T) \cong \int dx_1 \ldots dx_p \exp\Big[-\epsilon\Big(\underbrace{\sum_{i=1}^{p} \frac{m}{2\epsilon^2}(x_{i+1}-x_i)^2}_{\text{harmonic spring potential between coordinates } x_i} + \underbrace{V(x_i)}_{\text{potential multiplied by } \epsilon}\Big)\Big] \quad (7)$$

* ~~a on~~ note: $Z_N^{(a)}(T)$ is the partition function of a <u>one-particle</u> <u>one-dimensional</u> <u>quantum</u> system (approximately)

BUT it is isomorphic to a <u>classical</u> <u>system</u>, <u>one-dimensional</u>, <u>p particle</u>

the p classical particles interact via harmonic springs (originating from the quantum kinetic energy), and the attenuated original potential $\epsilon V(x_i)$

* this isomorphism is very useful
  - mapping to a classical system based on this isomorphism allows applying classical Monte Carlo methods in calculating the properties of quantum systems

* now, to the path-integral representation

$$Z_N^{(q)}(T) = \int\cdots\int dx_1 \cdots dx_p \, e^{-\epsilon \sum_{i=1}^{p}\left[\frac{m}{2\epsilon^2}(x_i - x_{i+1})^2 + V(x_i)\right]}$$

consider: $\beta = \epsilon P$, associate with x_i a continuous function $x(\tau)$

$$x_i = x(i\epsilon) \qquad (\tau = i\epsilon)$$

points x_i are the discrete representation of $x(\tau)$

$$x_1 = x(\epsilon)$$
$$x_2 = x(2\epsilon)$$
$$\vdots$$
$$x_p = x(p\epsilon) = x(\beta)$$

can also associate: $\dfrac{x_{i+1} - x_i}{\epsilon} = \dfrac{x((i+1)\epsilon) - x(i\epsilon)}{\epsilon}$

$$= \frac{x(i\epsilon + \epsilon) + x(i\epsilon)}{\epsilon} = \frac{dx(i\epsilon)}{d\tau} = v(i\epsilon)$$

in other words $v(i\epsilon)$ is the "velocity" associated with $x(i\epsilon)$ [or $x(\tau)$]

* rewrite partition function

$$Z_N^{(q)}(T) \simeq \int\cdots\int dx_1 \cdots dx_p \, e^{-\epsilon \sum_{i=1}^{p}\left[\frac{M}{2} v^2(i\epsilon) + V(x(i\epsilon))\right]}$$

the argument of the exponential is

$$\sum_{i=1}^{P} \left[\frac{m}{2} v^2(i\epsilon) + V(x(i\epsilon)) \right] \epsilon$$

in general $\lim_{P\to\infty} \sum_{i=1}^{P} f(i\epsilon)\,\epsilon = \int_0^L d\tau\, f(\tau)$

where $L = \epsilon P$

thus: $$\lim_{P\to\infty} \sum_{i=1}^{P} \left[\frac{m}{2} v^2(i\epsilon) + V(x(i\epsilon)) \right] \epsilon =$$

$$= \int_0^L d\tau \left[\frac{m}{2} v^2(\tau) + V(x(\tau)) \right]$$

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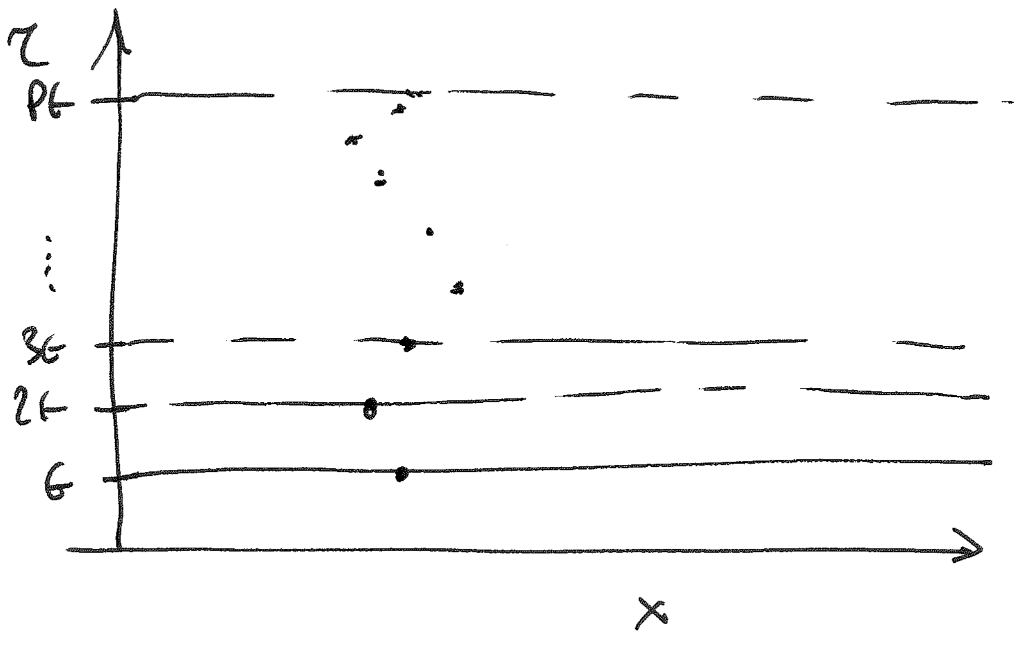
as $P \to \infty$ what happens to the integration measure?

$$\int \cdots \int dx_1 \cdots dx_P \to \; ?$$

we associated x_i with a continuous function

$x(\tau)$ $\quad [x(i\epsilon) = x_i]$

can plot each $x(i\epsilon) = x_i$



- in a usual integral $\int dx$ x is a set of numbers
- for quantum partition function

$$\int \dots \int dx_1 \dots dx_p$$

integrating over a set of numbers

$$x_1, \dots, x_p \qquad (x(\epsilon), x(2\epsilon), \dots, x(p\epsilon))$$

- ~~as~~ looking back at the figure, one realisation of $x_1, \dots, x_p$ is a set of numbers for each x_i

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can think of it as the discrete representation of a path

- as $p \to \infty \Rightarrow$ becomes a path $x(\tau)$
- due to cyclic nature of the trace the path must be cyclic: $x(\tau)$: $\boxed{x(0) = x(\beta)}$
- symbolically we write:

$$Z_N^{(a)}(T) = \int dx_0 \int_{x(0)=x_0}^{x(\beta)=x_0} D[x(\tau)]\, e^{-\int_0^\beta d\tau \left[\frac{m}{2} v^2(\tau) + V(x(\tau))\right]}$$

Interpretation

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$$Z_N^{(\omega)}(T) = \int dx_0 \int_{x(0)=x_0}^{x(\beta)=x_0} D[x(\tau)]\, e^{-\int_0^\beta d\tau \left[\frac{m}{2} v^2(\tau) + V(x(\tau))\right]}$$

~~in~~ $\int dx_0$ means integrate over all points x_0

$\int_{x(0)=x_0}^{x(\beta)=x_0} D[x(\tau)]$ means integrate over all paths $(x(\tau))$ which start at x_0 $(x(0)=x_0)$ and end at x_0 $(x(\beta)=x_0)$

$e^{-\int_0^\beta d\tau \left[\frac{m}{2} v^2(\tau) + V(x(\tau))\right]}$ means for each path, evaluate $x(\tau) \to v(\tau)$, using $x(\tau), v(\tau)$ evaluate integral

$$\int_0^\beta d\tau \left[\frac{m}{2} v^2(\tau) + V(x(\tau))\right] = S[x(\tau)]$$

which gives a <u>number</u> for each path, using this number evaluate $e^{-S[x(\tau)]}$ as the ~~argument of~~ integrand

- in summary: $Z_N^{(c)}(T)$ consists of the integral over all cyclic paths $x(\tau)$ with the integrand being $e^{-S[x(\tau)]}$

* the path-integral representation is symbolic
  * in numerical applications we use the discretized version

$$Z_N^{(a)}(T) \simeq \int dx_1 \dots dx_P \, e^{-\sum_{i=1}^{P}\left[\frac{m}{2}\frac{(x_{i+1}-x_i)^2}{\varepsilon^2}+V(x_i)\right]\varepsilon}$$

  * but it makes some things easier to see

For example: consider the following Hamiltonian

$$H = \frac{p^2}{2m} + V(x) + Ex$$

- classical partition function:

$$Z_N^{(c)}(T) = \int dp \, e^{-\frac{\beta p^2}{2m}} \int dx \, e^{-\beta V(x) - \beta E x}$$

$$-\frac{1}{\beta}\frac{\partial \ln Z_N^{(c)}(T)}{\partial E} = \langle x \rangle$$

$$+\frac{1}{\beta^2}\frac{\partial \ln Z_N^{(c)}(T)}{\partial E^2} = \langle x^2 \rangle - \langle x \rangle^2$$

- for the quantum case:

$$Z_N^{(q)}(T) = \int dx_0 \int_{x(0)=x_0}^{x(\beta)=x_0} D[x(\tau)]\, e^{-\int_0^\beta \left[\frac{m}{2} v^2(\tau) + V(x(\tau)) + E x(\tau)\right]}$$

$$-\frac{1}{\beta}\frac{\partial \ln Z_N^{(q)}(T)}{\partial E} = \frac{1}{\beta}\frac{1}{Z_N^{(c)}(T)}(-1)\int dx_0 \int D[x(\tau)]\, e^{-S_0[x(\tau)]}\left[-\int_0^\beta x(\tau)\right]$$

since paths are cyclic we can write

$$-\frac{1}{\beta}\frac{\partial \ln Z_N^{(q)}(T)}{\partial E} = \frac{\cancel{\beta}}{\cancel{\beta} Z_N^{(c)}(T)}\int dx_0 \int D[x(\tau)]\, e^{-S_0[x(\tau)]}\, x(0)$$

$$= \langle x \rangle$$ (same as the classical case)

- but the second derivative $-\frac{1}{\beta^2}\frac{\partial}{\partial E^2}\ln Z$ will not be the same

$$+\frac{1}{\beta^2}\frac{\partial \ln Z_N^{(q)}(T)}{\partial E^2} = \frac{\int dx_0 \int D[x(\tau)]\, e^{-S_0[x(\tau)]}\int_0^\beta x(0)\,x(\tau)}{\beta^2 Z_N^{(c)}(T)} - \langle x\rangle^2$$

$$= \frac{1}{\beta}\int_0^\beta \langle (x(0)-\langle x\rangle)(x(\tau)-\langle x\rangle)\rangle\, d\tau$$

$$= \frac{1}{\beta}\langle x(0)\,x(\tau)\rangle - \langle x\rangle^2 \Rightarrow$$

- susceptibility expressions differ for the quantum and classical expressions
  - in classical case it corresponds to ~~the~~ spread of quantity coupled to field E
  - in quantum case it corresponds to an integrated imaginary time correlation function

$$\langle x(0)\, x(\tau) \rangle \rightarrow \text{known as imaginary time correlation function}$$

- reason: we approximated $e^{-\beta H}$

in QM $e^{-iHt} \rightarrow$ real time propagator

$e^{-\beta H} \rightarrow$ imaginary time propagator