Discrete path integrals

Now consider $\hat{H} = \hat{T} + \hat{V}$ with the usual kinetic contribution (nonrelativistic, no magnetic field):

$$\hat{T} = \sum_{n=1}^{N} \frac{1}{2m} \hat{p}_n^2 \qquad (\hat{p}_n = -i\hbar \vec{\nabla}_n \text{ in position basis})$$

and the potential contribution $\hat{V} = \int dR\, \underbrace{V(R)}_{=V(\hat{R})} |R\rangle\langle R|$

The fundamental problem in quantum mechanics is that we know eigen basis and density matrix only for either the kinetic or the potential part of the Hamiltonian, not both:

$$e^{-\beta\hat{H}} \neq e^{-\beta\hat{T}}\, e^{-\beta\hat{V}} \qquad \text{(for general } \beta)$$

$e^{-\beta\hat{H}}$: needed, unknown — $e^{-\beta\hat{T}}$: known (see below) — $e^{-\beta\hat{V}}$: known (see below)

But: asymptotic factorization at high temperatures (classical limit), i.e. small β. More generally: good high-T approximations for density matrix!

Notation: imaginary time step $\Delta\tau = \frac{\beta}{M}$ $(M \in \mathbb{N})$

Exact discrete path integral (M equal steps):

$$\rho(R_0, R_M, \beta) = \int dR_1 \int dR_2 \ldots \int dR_{M-1}\, \rho(R_0, R_1; \Delta\tau)\, \rho(R_1, R_2; \Delta\tau) \ldots \rho(R_{M-1}, R_M; \Delta\tau)$$

We will now derive an explicit approximation for this path integral.

Campbell-Baker-Hausdorf formula:

$$\exp\left[-\Delta\tau(\hat{T}+\hat{V})+\underbrace{\tfrac{1}{2}\Delta\tau^2[\hat{T},\hat{V}]+\mathcal{O}(\Delta\tau^3)}\right]=e^{-\Delta\tau\hat{T}}\,e^{-\Delta\tau\hat{V}}$$

negligible in limit of small $\Delta\tau$

$\rightsquigarrow$ Trotter formula

$$e^{-\beta(\hat{T}+\hat{V})}=\lim_{M\to\infty}\left[e^{-\Delta\tau\hat{T}}\,e^{-\Delta\tau\hat{V}}\right]^M;\quad \Delta\tau=\frac{\beta}{M}$$

$$\approx\left[e^{-\Delta\tau\hat{T}}\,e^{-\Delta\tau\hat{V}}\right]^M \text{ for } \Delta\tau \text{ „small"}$$

Primitive approximation in position space for single time step:

$$\rho(R_0,R_2;\Delta\tau)=\int dR_1\,\langle R_0|e^{-\Delta\tau\hat{T}}|R_1\rangle\langle R_1|e^{-\Delta\tau\hat{V}}|R_2\rangle$$

Potential operator is diagonal, therefore:

$$\langle R_1|e^{-\Delta\tau\hat{V}}|R_2\rangle=e^{-\Delta\tau V(R_1)}\,\delta(R_1-R_2)\qquad (*)$$

For kinetic energy operator, introduce eigen function expansion in a cube with side length L and pbc, denoted by integer vector $\vec{n}\in\mathbb{R}^{3N}$:

$$\phi_{\vec{n}}(\vec{R})=\langle\vec{n}|\vec{R}\rangle=L^{-3N/2}\,e^{i\vec{K}_{\vec{n}}\cdot\vec{R}};\quad \vec{K}_{\vec{n}}=\frac{2\pi\vec{n}}{L}$$

plane waves

with eigen values $\quad\frac{\hbar^2}{2m}\vec{K}_{\vec{n}}^2\equiv 2\vec{K}_{\vec{n}}^2$

$$\Rightarrow \langle R_0 | e^{-\Delta\tau \hat{T}} | R_1 \rangle = \sum_{\vec{n}} \langle R_0 | \vec{n} \rangle \langle \vec{n} | e^{-\Delta\tau \hat{T}} | \vec{n} \rangle \langle \vec{n} | R_1 \rangle$$

$$= \sum_{\vec{n}} L^{-3N/2} e^{-i\vec{K}_{\vec{n}} \cdot \vec{R}_0} e^{-\Delta\tau \lambda \vec{K}_{\vec{n}}^2} L^{-3N/2} e^{+i\vec{K}_{\vec{n}} \cdot \vec{R}_1}$$

$$= \sum_{\vec{n}} L^{-3N} \exp\left[-\Delta\tau \lambda \vec{K}_{\vec{n}}^2 - i\vec{K}_{\vec{n}} \cdot (\vec{R}_0 - \vec{R}_1)\right]$$

$$\approx (4\pi\lambda\Delta\tau)^{-3N/2} \exp\left[-\frac{(\vec{R}_0 - \vec{R}_1)^2}{4\lambda\Delta\tau}\right] \qquad (\Delta)$$

$\sum_{\vec{n}} \to \int d^{3N} n$, good for $\lambda\Delta\tau \ll L^2$

then Gauss integral

(exact kinetic density matrix: $\Theta_3(z,q)$ ...)

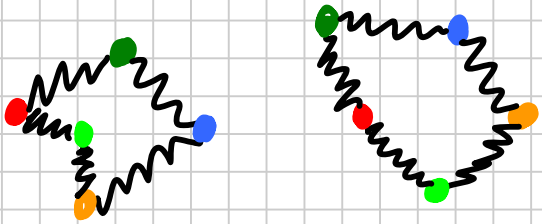
Insert (lowest order) Trotter approximation, using $*$ and Δ, into general discrete path integral:

$$\rho(\vec{R}_0, \vec{R}_M; \beta) = \int d\vec{R}_1 \int d\vec{R}_2 \cdots \int d\vec{R}_{M-1} (4\pi\lambda\Delta\tau)^{-3NM/2}$$

$$\exp\left[-\sum_{m=1}^{M} \left(\frac{(\vec{R}_{m-1} - \vec{R}_m)^2}{4\lambda\Delta\tau} + \Delta\tau V(\vec{R}_m) \right)\right] \geq 0$$

primitive approximation for density matrix

$Z = \int d\vec{R}\, \rho(\vec{R}, \vec{R}; \beta)$ corresponds to classical partition function of ring polymers with ideal springs within each polymer and interpolymer interaction only at equal times ($\cong$ color).



More explicitly: position-dependent part of Z

for pair interactions $V(\vec{R}_m) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} v\left(\vec{r}_i(\tau_m) - \vec{r}_j(\tau_m)\right)$

is $\int d\vec{R}_1 \int d\vec{R}_2 \dots \int d\vec{R}_M \; e^{-\beta \tilde{V}(\{\vec{R}\})}$

with

$$\tilde{V}(\{R\}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{M} \sum_{m=1}^{M} v\left(\vec{r}_i(\tau_m) - \vec{r}_j(\tau_m)\right) + \sum_{i=1}^{N} \underbrace{\frac{M}{4\pi\lambda\beta^2}}_{k/2} \sum_{m=1}^{M} \left(\vec{r}_i(\tau_{m-1}) - \vec{r}_i(\tau_m)\right)^2$$

Fractal nature

In the case of a smooth imaginary-time path $\vec{r}(\tau)$ we would expect $|\vec{r}(\tau_i) - \vec{r}(\tau_j)|^2 \le v_{max}^2 |\tau_i - \tau_j|^2$

however, in the noninteracting limit $V \to 0$ we get

$$\langle |\vec{r}_i(\tau_m) - \vec{r}_i(\tau_{m-1})|^2 \rangle = 3(2\lambda\Delta\tau)$$

$\rightsquigarrow$ in the limit $\Delta\tau \to 0$, each polymer acquires infinite length!

(smoothing + shading)

Role of temperature

In the polymer model, the finite size of each polymer is an entropic effect: for fixed spring constant k, the size would vanish for $T \to 0$.

However: for fixed M, $k \propto T^2 \Rightarrow |\vec{r}_i(\tau_{m-1}) - \vec{r}(\tau_i)|^2 \propto T^{-1} \to \infty$

for fixed τ: $k \propto T \Rightarrow |\vec{r}_i(\tau_{m-1}) - \vec{r}(\tau_m)|^2 \propto T^0 \to \text{const}$

and $M \to \infty$!

in both cases: polymer diameter $\propto \sqrt{\lambda\beta} \to \infty$

Connection to Feynman-Kac path integral

For simplicity, write only for Z (analogous for ρ):

$$Z = \left\langle (4\pi\lambda\Delta\tau)^{-3NM/2} \prod_{m=1}^{M} e^{-\frac{|\vec{R}_{m-1} - \vec{R}_m|^2}{4\lambda\Delta\tau}} e^{-\Delta\tau V(\vec{R}_m)} \right\rangle_{\text{uniform}}$$

$$= Z_{\text{free}} \left\langle \prod_{m=1}^{M} e^{-\Delta\tau V(\vec{R}_m)} \right\rangle_{\text{free}}$$

$\{R_m\}$ generated according to Z for $V=0$

$$= Z_{\text{free}} \left\langle \exp\left[-\sum_{m=1}^{M} \Delta\tau\, V(\vec{R}_m) \right] \right\rangle_{\text{free}}$$

$$\xrightarrow{M \to \infty} Z_{\text{free}} \left\langle \exp\left[-\int_0^\beta V(\vec{R}(\tau))\, d\tau \right] \right\rangle_{\text{free}}$$

$$\boxed{e^{-\beta(F - F_{\text{free}})} = \frac{Z}{Z_{\text{free}}} = \left\langle \exp\left[-\int_0^\beta V(\vec{R}(\tau))\, d\tau \right] \right\rangle_{\text{free}}}$$

Monte Carlo sampling of the partition function

Not possible: naive simple sampling (take all $r_i(\tau_m)$ as independent random variables in L^3)

1) single-particle displacement moves (~ classical atoms)

a) select particle i

b) draw displacement $\vec{\delta}$ from uniform distribution inside cube $[-\frac{\Delta}{2}, \frac{\Delta}{2}]^3$

c) propose move $\vec{r}_i(\tau_m) \to \vec{r}_i(\tau_m) + \vec{\delta}$ for all m

d) accept with propability $p = \min\{1, e^{-\beta \Delta V}\}$

- These moves are only useful for not too low T
- Δ is adjusted for acceptance probability of 25% - 75%

2) single-partirle single-slice moves

a) select particle i and slice m

(i) classic rule

b) random displacement $\vec{\delta}$ uniformly from cube $[-\frac{\Delta}{2}, \frac{\Delta}{2}]^3$

c) propose move $\vec{r}_i(\tau_m) \to \vec{r}_i(\tau_m) + \vec{\delta}$ for single m

d) accept with prob. $p = \min\{1, e^{-\beta \Delta \tilde{V}}\}$

- now also kinetic contributions to $\Delta \tilde{V}$
- adjust $\Delta \approx \sqrt{\lambda \Delta \tau}$ to ~ 50% acceptance prob.

(ii) free-particle sampling

In general, the probability density for position vector $\vec{R}_m$ at fixed $\vec{R}_i$ for $i \neq m$ can be written as

$$P[\vec{R}_m] \propto \rho(\vec{R}_{m-1}, \vec{R}_m; \Delta\tau)\, \rho(\vec{R}_m, \vec{R}_{m+1}; \Delta\tau)$$

specifically for $\hat{V} = 0$ we have

$$P[\vec{R}_m] \propto \exp\left[-\frac{|\vec{R}_{m-1} - \vec{R}_m|^2}{4\lambda\Delta\tau}\right] \exp\left[-\frac{|\vec{R}_m - \vec{R}_{m+1}|^2}{4\lambda\Delta\tau}\right]$$

$$(x-a)^2 + (x-b)^2 = 2x^2 - 2x(a+b) + a^2 + b^2$$
$$= 2\left[x^2 - 2x\frac{a+b}{2} + \left(\frac{a+b}{2}\right)^2\right] + \frac{(a-b)^2}{2}$$

$$\Rightarrow P[\vec{R}_m] \propto \exp\left[-\frac{|\vec{R}_m - \vec{R}_{av}|^2}{2\lambda\Delta\tau}\right]; \quad \vec{R}_{av} = \frac{\vec{R}_{m-1} + \vec{R}_{m+1}}{2}$$

in case of single-particle move:

$$P[\vec{r}_i(\tau_m)] \propto \exp\left[-\frac{|\vec{r}_i(\tau_m) - \vec{r}_i^{\,av}|^2}{2\lambda\Delta\tau}\right]; \quad \vec{r}_i^{\,av} = \frac{\vec{r}_i(\tau_{m+1}) + \vec{r}_i(\tau_{m-1})}{2}$$

This can be sampled directly (diffusion step)

b) draw $\vec{\delta}$ from Gaussian distribution with width $\sqrt{\lambda\Delta\tau}$ (in each dimension)

c) propose move $\vec{r}_i(\tau_m) \to \frac{\vec{r}_i(\tau_{m-1}) + \vec{r}_i(\tau_{m+1})}{2} + \vec{\delta}$

d) accept with probability $\min\{1, e^{-\beta\Delta V}\}$

(this expression is valid for primitive approximation; generalize for better actions)

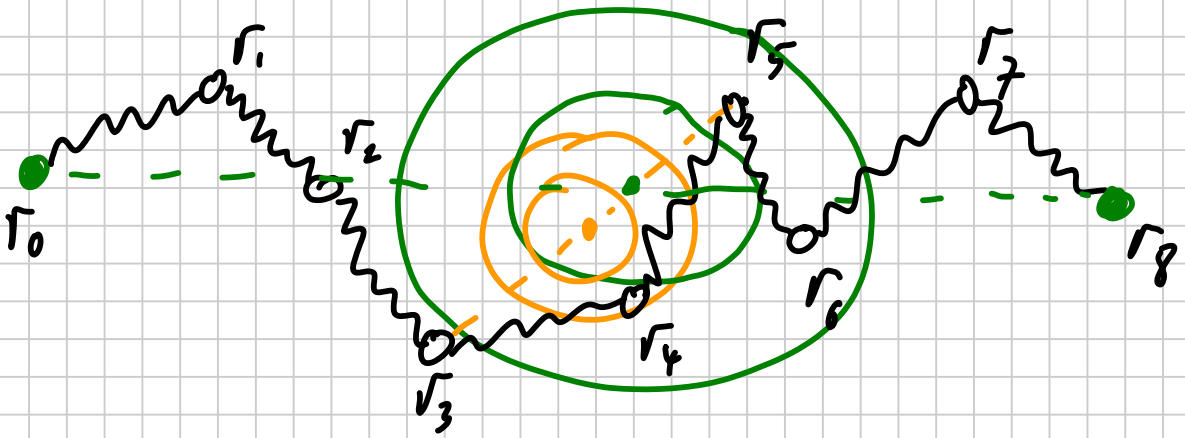
procedure analogous to diffusion Monte Carlo

$$|0\rangle = \lim_{\beta\to\infty} e^{-\beta\hat{H}}|\Psi_0\rangle \approx \prod_{m=1}^{M}\left(e^{-\Delta\tau\hat{V}}e^{-\Delta\tau\hat{T}}\right)|\Psi_0\rangle$$

$e^{-\Delta\tau\hat{V}}$: birth/death of „walkers" | $e^{-\Delta\tau\hat{T}}$: diffusion of „walkers"

1) and 2) are in principle sufficient for distinguishable particles. However: single-slice moves inefficient for large M

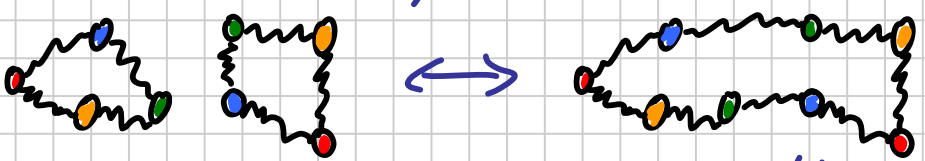
2') Multilevel-sampling



On fine grid: $\vec{r}_4$ cannot move very far

idea:
- consider coarse grid with $\tilde{\Delta\tau} = 4\Delta\tau$ first
- construct move iteratively
- keep track of intermediate proposal prob.
- correct everything in final acceptance rule

3) Exchange moves: for distinguishable particles, we must allow exchanges (discrete move - not possible in MD)



In practice: combine with multilevel moves.

Observables

- density, pair correlation function, structure factor: directly from $\{R_m\}$

- already the energy is non trivial

(i) „direct" or „Hamiltonian" estimator:

$$E_H = \frac{Tr\left(\hat{H} e^{-\beta \hat{H}}\right)}{Tr\left(e^{-\beta \hat{H}}\right)} = \ldots.$$

(ii) thermodynamic estimator

$$E_T = -\frac{1}{Z}\frac{dZ}{d\beta}$$

$$= \frac{1}{N}\sum_{m=1}^{N} \left\langle \frac{3N}{2\Delta\tau} - \frac{|\vec{R}_m - \vec{R}_{m-1}|^2}{4\lambda\Delta\tau^2} + V(\vec{R}_m) \right\rangle$$

(iii) virial estimator

$$E_V = \left\langle \ldots - \frac{1}{2} F^m \Delta_m \ldots \right\rangle$$

Δ_m: deviation from center of mass

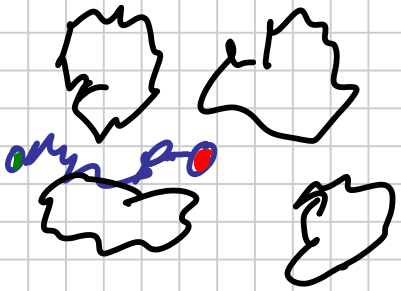
F^m: generalized force

- condensate fraction

insert two free ends $\vec{r}_0, \vec{r}_t$

measure prob $(\vec{r}_0 - \vec{r}_t|$

no exchange:

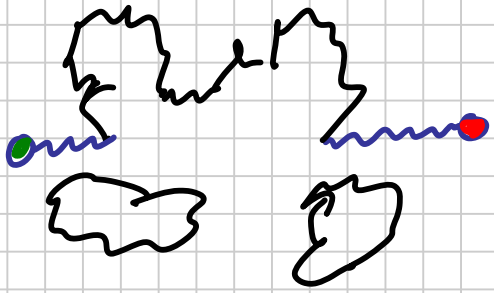


$$p \propto e^{-a|\vec{r}_0 - \vec{r}_t|^2}$$

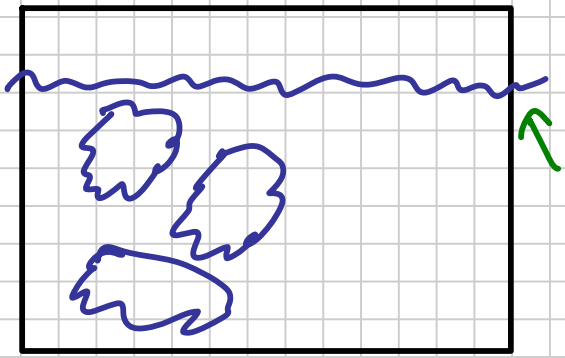
with exchange:

$P \xrightarrow{T \to 0} \text{const.}$

i.e. $\vec{k} = 0$



- superfluid density



Application to vacancies in solid ^4He

see slides: http://komet337.physik.uni-mainz.de/Bluemer/Talks/DPG98HE.pdf