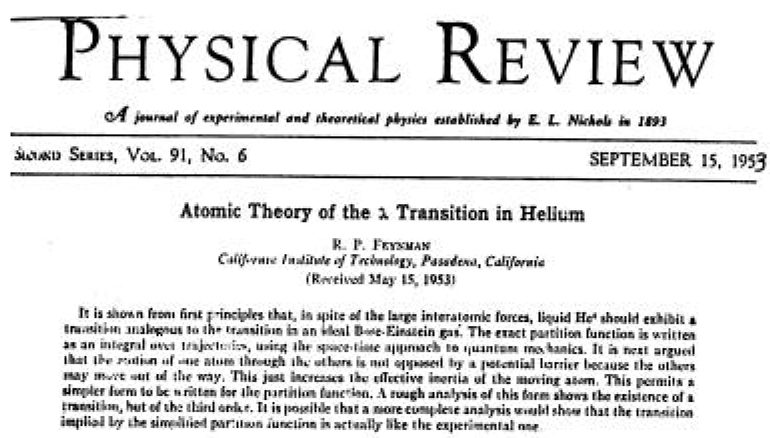
Motivation for Path Integral MC

- There are difficulties with VMC and DMC
  - Need to find good trial functions; this becomes increasing difficult as systems get more complex, especially if one doesn't know the correct physics.
  - Mixed estimator problem for properties other than the energy.
- Temperature is important: e.g. finite temperature phase transitions.
- PIMC makes nice connection with DMC and with other theoretical approaches and leads to concepts such as Reptation MC, understanding of bose condensation, superfluidity, exchange …
- Details given in : RMP **67**, 279 (1995)

Imaginary Time Path Integrals


PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 91, NO. 6 SEPTEMBER 15, 1953

Atomic Theory of the λ Transition in Helium

R. P. FEYNMAN
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(Received May 15, 1953)

It is shown from first principles that, in spite of the large interatomic forces, liquid He[4] should exhibit a transition analogous to the transition in an ideal Bose-Einstein gas. The exact partition function is written as an integral over trajectories, using the space-time approach to quantum mechanics. It is next argued that the motion of one atom through the others is not opposed by a potential barrier because the others may move out of the way. This just increases the effective inertia of the moving atom. This permits a simpler form to be written for the partition function. A rough analysis of this form shows the existence of a transition, but of the third order. It is possible that a more complete analysis would show that the transition implied by the simplified partition function is actually like the experimental one.

PIMC Simulations

- We do Classical Monte Carlo simulations to evaluate averages such as:

$$< V >= \frac{1}{Z}\int dRV(R)e^{-bV(R)}$$

$$b = 1/(k_B T)$$

- Quantum mechanically for T>0, we need both to generate the distribution and do the average:

$$< V >= \frac{1}{Z}\int dRV(R)r\left(R;b\right)$$

$$r\left(R;b\right) = \text{diagonal density matrix}$$

- Simulation is possible since the density matrix is positive.

Notation

- Individual coordinate of a particle r_i
- All 3N coordinates R= $(r_1, r_2, \ldots\ r_N)$
- Total potential energy V(R)
- Kinetic energy $-l\sum_{i=1}^{N}\nabla_i^2$ where $l \equiv \frac{\hbar^2}{2m}$
- Hamiltonian $\hat{H} = \hat{T} + \hat{V}$

The thermal density matrix

- Find exact many-body eigenstates of H.
- Probability of occupying state α is exp(-βE$_\alpha$)
- All equilibrium properties can be calculated in terms of thermal o-d density matrix
- Convolution theorem relates high temperature to lower temperature.

$$\hat{H} f_a = E_a f_a$$

$$r(R;b) = \sum_a |f_a(R)|^2 e^{-bE_a} \quad b = 1/kT$$

$$\hat{r}_b = e^{-b\hat{H}} \quad \text{operator notation}$$

off-diagonal density matrix:

$$r(R,R';b) = \sum_a f_a^*(R') f_a(R) e^{-bE_a}$$

$$r(R,R';b) \geq 0 \quad \text{(without statistics)}$$

$$r(R_1,R_2;b_1+b_2) = \int dR' \, r(R_1,R';b_1) \, r(R',R_2;b_2)$$

or with operators: $e^{-(b_1+b_2)\hat{H}} = e^{-b_1\hat{H}} e^{-b_2\hat{H}}$

Trotter’s theorem (1959)

- We can use the effects of operators separately as long as we take small enough time steps.

$$\hat{r} = e^{-b(\hat{T}+\hat{V})}$$

$$\hat{r} = \lim_{M\to\infty} \left[e^{-t\hat{T}} e^{-t\hat{V}} \right]^M$$

$$t = b/M$$

- n is number of time slices.
- τ is the “time-step”

- We now have to evaluate the density matrix for potential and kinetic matrices by themselves:
- Do by FT’s $$\left\langle r \left| e^{-t\hat{T}} \right| r' \right\rangle = (4p\,l\,t)^{-3/2} e^{-(r-r')^2/4lt}$$
- V is “diagonal” $$\left\langle r \left| e^{-t\hat{V}} \right| r' \right\rangle = d(r-r') e^{-tV(r)}$$
- Error at finite n is roughly: comes from communtator $$e^{-\frac{t^2}{2}[\hat{T},\hat{V}]}$$

Using this for the density matrix.

- We sample the distribution:

$$e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; t)} / Z \quad \text{where} \quad Z = \int dR_1 \ldots dR_M \, e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; t)}$$

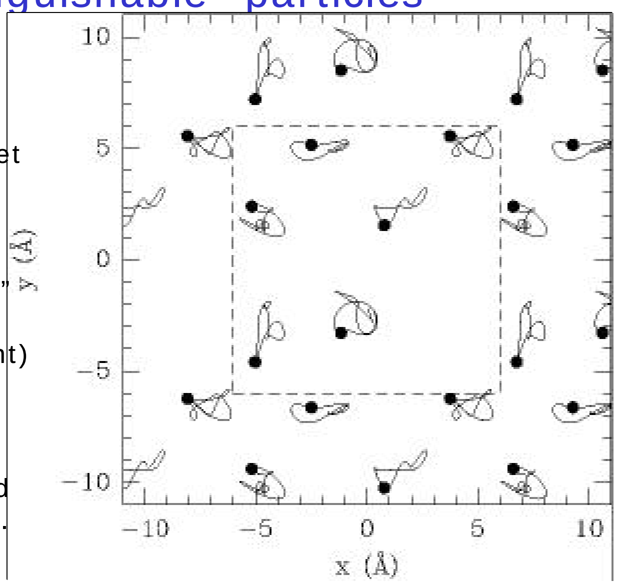
Where the "primitive" <u>link action</u> is:

$$S(R_0, R_1; t) = -\frac{3N}{2}\ln\left(4\pi\lambda t\right) + \frac{(R_0 - R_1)^2}{4\lambda t} + \frac{t}{2}\left[V(R_0) + V(R_1)\right]$$

- Similar to a classical integrand where each particle turns into a "polymer."
  - K.E. is spring term holding polymer together.
  - P.E. is inter-polymer potential.
- Trace implies $R_1 = R_{m+1}$ ⇨ closed or ring polymers

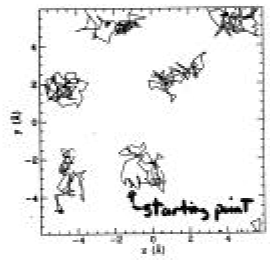
"Distinguishable" particles

- Each atom is a ring polymer; an exact representation of a quantum wavepacket in imaginary time.
- Trace picture of 2D helium. The dots represent the "start" of the path. (but all points are equivalent)
- The lower the real temperature, the longer the "string" and the more spread out the wavepacket.

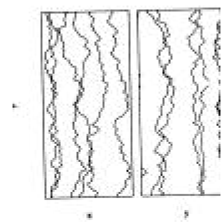


Different schemes to picture PIs.

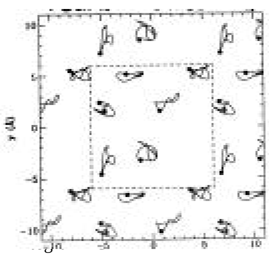
Descretized trace



World line picture



Fourier smoothed trace



Space filling picture

Main Numerical Issues of PIMC

- How to choose the action. We don't have to use the primitive form. Higher order forms cut down on the number of slices by a factor of 10. We can solve the 2-body problem exactly.
- How to sample the paths *and the permutations*. Single slice moves are too slow. We move several slices at once. *Permutation moves are made by exchanging 2 or more endpoints.*
- How to calculate properties. There are often several ways of calculating properties such as the energy.

If you use the simplest algorithm, your code will run 100s or 1000s of times slower than necessary.

Calculations of 3000 He atoms can be done on a workstation-- if you are patient.

Details see: RMP **67**, 279 1995.

Calculating properties

- Procedure is simple: write down observable:

$$< O >= \frac{\int dRdR' \left\langle R \middle| \hat{O} \middle| R' \right\rangle \left\langle R \middle| e^{-b\hat{H}} \middle| R' \right\rangle}{Z}$$

- Expand density matrix into a "path":

$$< O >= \left\langle \left\langle R \middle| \hat{O} \middle| R' \right\rangle \right\rangle_{\text{path average}}$$

$$< O >= \left\langle \left\langle \hat{O}(R_k) \right\rangle \right\rangle_{\text{path average}} \quad \text{for "diagonal operators}$$

- Density, density-density, …. the potential energy are diagonal operators. Just take average values as you would classically.
- All time slices are the same – can use all for averages.

Calculation of Energy

- Thermodynamic estimator: differentiate partition function

$$E = -\frac{dZ}{Zdb} = \frac{1}{Z}\int dRe^{-S}\left[\frac{dS}{db}\right] = \left\langle \frac{dS_k}{dt} \right\rangle_{path}$$

$$\frac{dS}{dt} = \frac{dU}{dt} + \frac{3N}{2t} - \frac{(R-R')^2}{4lt^2}$$

Potential n*NI-KE spring energy

Problem: variance diverges as small time step.

- Virial Estimator: differentiate in "internal coordinates"

does not diverge at small time steps (Herman, Berne)

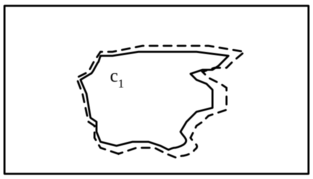
$$E_{virial} = \left\langle \frac{dU}{dt} + \frac{3N}{2b} + \frac{1}{2t}(R_i - C)\cdot\nabla_i U \right\rangle$$

Potential NI-KE deviation from centroid .force

Derivation of Virial Estimator

Write Z as integral over internal scale-free coordinates.

As temperature is changed the path is expanded or contracted



DANGER with PBC and exchanges

$$\vec{c} = \frac{1}{M}\sum_{i=1}^{M} r_i$$

$$\vec{z}_j = \frac{r_i - c}{\Lambda} \qquad 1 \le j \le M-1$$

$$\Lambda = \sqrt{4 l t} \qquad \frac{\partial \ln \Lambda}{\partial t} = \frac{1}{2t}$$

$$Z = \Lambda^{-3N} \int dc dz_j e^{-\sum_j \left(z_j^2 - U(r_j)\right)}$$

$$E = -\frac{\partial \ln(Z)}{\partial b} = \frac{3N}{2b} + \int dc dz_j \vec{\nabla} U \cdot (\vec{r} - \vec{c}) t$$

$$E_{virial} = \left\langle \frac{dU}{dt} + \frac{3N}{2b} + \frac{1}{2t}(R_i - C)\cdot \nabla_i U \right\rangle$$

Potential NI-KE deviation from centroid .force

- Can also calculate kinetic energy by differentiating with respect to the mass
$$K = -\frac{mdZ}{b\, Zdm}$$
- Or use the "direct" form: $K = \left\langle e^{S}(-l\nabla^2)e^{-S} \right\rangle_{path}$
- For pressure, differentiate wrt the volume (virial estimator).
$$P = \frac{1}{3V}\left[2T - \frac{1}{t}\sum_{i<j}\left\langle \mathbf{r}_{ij}\nabla u\left(r_{ij}\right)\right\rangle\right]$$
- In general, one can have different "estimators" having different convergence of systematic (Trotter) or statistical errors.
- Statistical errors require careful estimation.
- Other errors can be bias and finite-size errors.
- Free energy calculated just as in classical simulation, with all the same problems.

Comparison

DMC vs. PIMC

DMC

- DMC uses e^{-tH} as projection
- Branching random walks State is 3N*population.
- Open boundary conditions in time. Single state method.
- Uses importance sampling; mixed estimator problem.
- Iteration corresponds to imaginary time. Dynamics determined and quickly convergent
- Zero variance principle

PIMC

- Samples the density matrix
- State is 3N*#of time steps
- Cyclic BC in time. Finite temperature properties.
- No importance sampling and hence no mixed estimator problem. More "physical."
- Can have slow convergence (ergodic problems)
- Longer time step because of improved actions (bosons)

Dictionary of the Quantum-Classical Isomorphism

Properties of a quantum system are mapped into properties of the fictitious classical polymer system

Attention: *some words have opposite meanings.*

Quantum	**Classical**
Bose condensation	Delocalization of ends
Boson statistics	Joining of polymers
Exchange frequency	Free energy to link polymers
Free energy	Free energy
Imaginary velocity	Bond vector
Kinetic energy	Negative spring energy
Momentum distribution	FT of end-end distribution
Particle	Ring polymer
Potential energy	Iso-time potential
Superfluid state	Macroscopic polymer
Temperature	Polymer length

Examples of distinguishable particle calculations

- Solid H_2: work of Marcus Wagner, DMC
- Wigner crystal: 3D Matt Jones, DMC
  2D Ladir Candido, P. Phillips, DMC
- Vortex lattice: Nandini Trivedi, P. Sen and DMC

Example: Solid H_2

Solid molecular hydrogen is a very quantum solid

KE=69K T_t = 13.8K

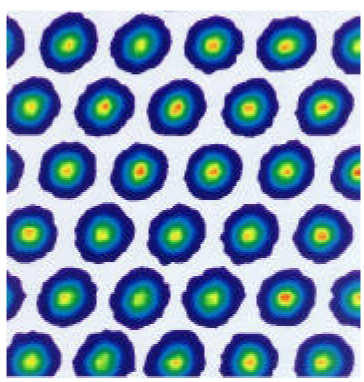
$$\left\langle r^2 \right\rangle^{1/2} = 0.21 r_{NN}$$

Below T_t interface between solid and gas.

Top layer is at a lower density, more delocalized and interesting quantum effects

Normally freezing at surface is depressed by 10%.

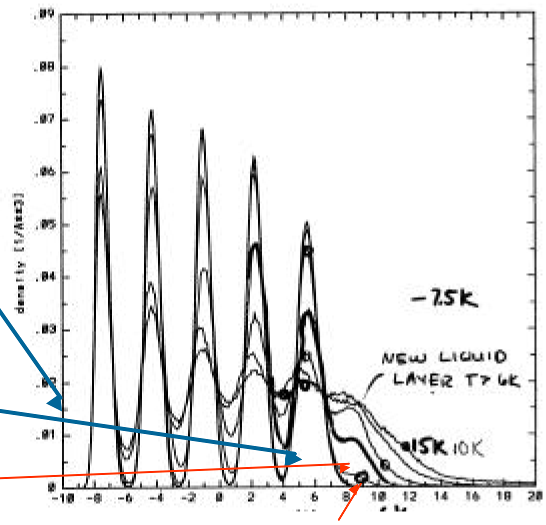
In H_2 it is depressed by 100%.



Layer Structure of Solid H_2

- Simulation is of 5 layers
- Each layer is 30 H_2
- Hard wall on left
- Top layer melts around 7K.
- Very fluffy top layer.
- New layer above 6K

Wagner, DMC, JPTP 102,275 (1996).



Z (A) T=6K

Snapshots of H_2 density

Gas

Liquid

Vacancy

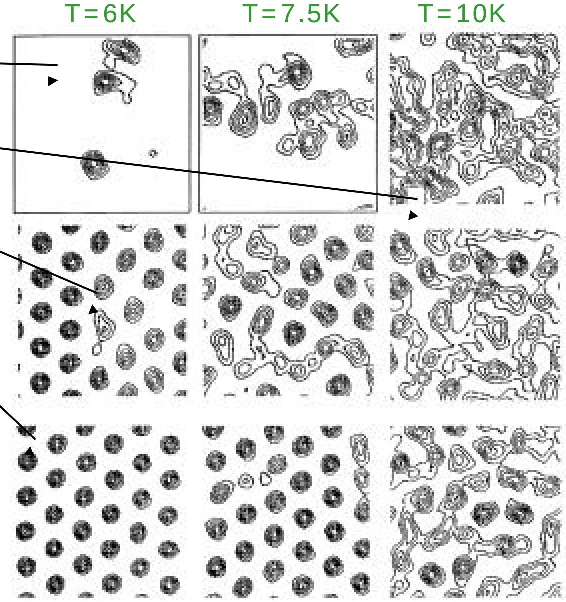
crystal

T=6K T=7.5K T=10K

Layer 0

Layer 1

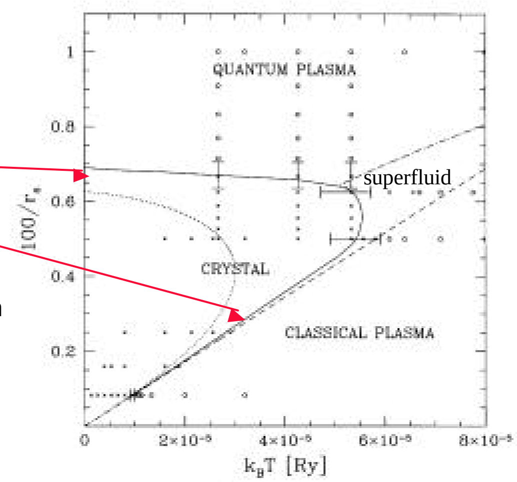
Layer 2



Melting of the 3D Wigner Crystal

- PIMC with Boltzmann statistics
- Phase boundary determined with free energy calculation
- Sudden change from pressure melting to thermal melting.
- Lindemann law is inaccurate
- Melting is first order with no volume change

Jones & DMC PRL 1996



Improved Actions

- There exists an "exact link action" :

$$S(R_i, R_{i+1}; \tau) = -\ln\left(\left\langle R_i \middle| e^{-\tau\hat{H}} \middle| R_{i+1} \right\rangle\right)$$

$$e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; \tau)} / Z \quad \text{where} \quad Z = \int dR_1 \ldots dR_M\, e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; \tau)}$$

- The "primitive" link action is:

$$S(R_0, R_1; t) = -\frac{3N}{2}\ln\left(4\pi\lambda\tau\right) + \frac{(R_0 - R_1)^2}{4\lambda\tau} + \frac{t}{2}\left[V(R_0) + V(R_1)\right]$$

- We often define the exact "inter-action" as:

$$U(R_i, R_{i+1}; \tau) = S(R_i, R_{i+1}; \tau) - S_0(R_i, R_{i+1}; \tau)$$

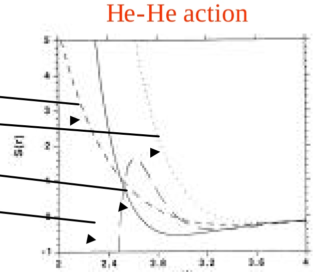
potential term = total - kinetic term (topological)

Improved Action

- If we make better actions, we can drastically cut down on the number of time slices.
- This saves lots of time, because the number of variables to integrate over is reduced
- but also because the correlation time of the walk is reduced since “polymers” are less entangled
- Possible approaches to better actions:
  - Harmonic approximation
  - Semi-classical approximation (WKB)
  - Cumulant approximation
  - Pair-product approximation
- Improved actions are also used in lattice gauge theory: the “perfect action.”

Examples for 2 particles

He-He action

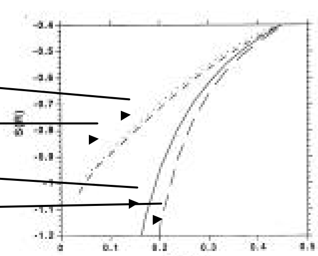


- Exact action
- Cumulant action
- Primitive action
- WKB

Exact action is smoother than the primitive form

WKB does not converge

Hydrogen atom



- Exact action
- Cumulant action
- Primitive action
- WKB

Properties of the action

- Positivity (U is real)
- Hermitian property $$U(R,R';b)=U(R',R;b)$$
- Cusp condition (i.e. behavior when two particles get close together)
- Semiclassical behavior: expansion as mass goes to infinity.
- Defining property. Residual energy should be small:
$$E_r = r^{-1}\left[\hat{H}+\frac{\partial}{\partial t}\right] r\left(R,\, R';t\right) \approx 0$$
- Feynman-Kac Formula can be used for insight. Average over all "free particle" bridges from R_O to R_F. Proof that density matrix is positive.
$$e^{-U(R_0,R_F;t)} = \left\langle \exp\left[-\int_0^t dt V(R(t))\right]\right\rangle_{RW}$$

Generalized Feynman-Kacs

- We can generalize the FK formula to find the correction to any density matrix just like with the trial function.
- Usual formula is the correction to the free particle density matrix.
$$e^{-U(R_0,R_F;t)} = r(R_0,R_F;t)\left\langle \exp\left[-\int_0^t dt E_r(R(t))\right]\right\rangle_{r:RW}$$
$$\frac{dR}{dt} = h(t) - \frac{R-R_F}{t} - 2l\nabla U(R;R_F;t)$$
- The density matrix is average over paths from R_O to R_F.
- Gives intuition about how to how to improve it a given action
- Can be used to compute the action. FKPIMC code

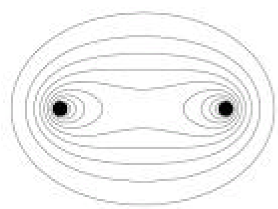
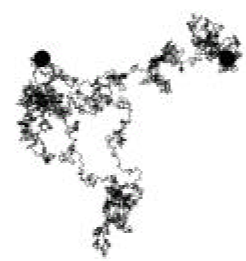
Cumulant Approximation

- In FK formula take the average into the exponent
- It is possible to evaluate the average using fourier transforms.
- Very accurate for Coulomb problems
- However the CA does not exist for non-integrable potentials.

$$e^{-U(R_0,R_F;t)} \sim \exp\left[-\left\langle -\int_0^t dt V(R(t))\right\rangle_{RW}\right]$$

$$U_C(R_0,R_F;t)=\int_0^t dt V_s\left[R_0+t\left(R_F-R_0\right), s_t\right]$$

$$V_S(r,s)=\int dk e^{-ikr-\frac{sk^2}{2}} v_k \qquad s=\frac{2lt(t-t)}{t}$$

Harmonic Approximation

- We can exactly calculate the action for a harmonic oscillator. It is just a shifted Gaussian.
- In the neighborhood of (R,R') let's approximate the potential by a harmonic one.
- Reasonable if the potential is really harmonic within a thermal wavelength. (for example in the high temperature limit)

$$U_H(R_O,R_F;t)=tV(R^*)+\tfrac{t^2 l}{6}\nabla^2 V(R^*)-\tfrac{t^3 l}{12}\left[\nabla V(R^*)\right]^2$$
$$-\tfrac{t}{12}\left(R_F-R_O\right)\nabla\nabla V(R^*)\left(R_F-R_O\right)$$

for LJ $r^{-5} = r^{-12}+r^{-14}+r^{-26}+r^{-14}+\ldots$

- R^* is an arbitrary place to evaluate the potential. If we choose it to be one of the end-points we get the Wigner-Kirkwood approximation.
- Bad idea for realistic potentials because expansion does not converge uniformly. Problem is at small r. Look at derivatives.

Cluster action

- For spherically symmetric pair potentials.
- Find the action for a reduced subset of particles exactly and put together to get a many-body action.

$$e^{-U(R_0,R_F;t)} = \left\langle \exp\left[-\int_0^t dt \sum_{i<j} v(r_{ij}(t))\right]\right\rangle_{RW}$$

$$= \left\langle \prod_{i<j} \exp\left[-\int_0^t dt v(r_{ij}(t))\right]\right\rangle_{RW}$$

$$\approx \prod_{i<j} \left\langle \exp\left[-\int_0^t dt v(r_{ij}(t))\right]\right\rangle_{RW}$$

- take the uncorrelated average:
- This is now a 2 particle problem.

- Generalization of T=0 of the Jastrow wavefunction to finite temperatures.
- At finite T, it is the off-diagonal terms that are important.

Exact pair action from "SQUARER"

How to determine the exact density matrix for a pair of atoms.

1. Use relative coordinates.
2. Go into spherical coordinates. Angles become trivial
3. Result is a 1-d problem for each angular momentum
4. Solve 1-d problem by matrix squaring. Iterate:

$$r_{\ell}(r,r';2t) = \int_0^{\infty} dr'' r_{\ell}(r,r'';t)\, r_{\ell}(r'',r';t)$$

5. Complete density matrix is:

$$r(\vec{r},\vec{r}';t) = \sum_{\ell} r_{\ell}(r,r';t) P_{\ell}(\cos(q))$$

6. Fit to a form easy-to-compute during the PIMC run.

PIMC representation of pair density matrix

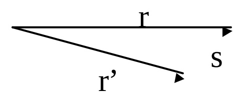
- In bare form it is 3d+time.
- But as normally used
  - Time is discrete (fixed)
  - 2 other variables are small (expand in them)

$$q = \frac{1}{2}\left[|\vec{r}| + |\vec{r}\,'|\right]$$

$$\left.\begin{aligned} s &= |\vec{r} - \vec{r}\,'| \\ z &= |\vec{r}| - |\vec{r}\,'| \end{aligned}\right\} \text{small and symmetric}$$

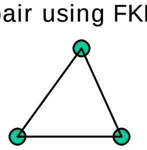
$$u(r, r') = \frac{1}{2}\left[u_0(r) + u_0(r')\right] + \sum_{j<k} u_{kj}(q) z^{2j} s^{2(k-j)}$$

- k is the "order". Typically we use k=1 or k=2.
- This will take only 2-3 times longer to compute action than the pair potential (bare Trotter formula).
- But with fewer time slices.



Compare pair action for 3 He atoms

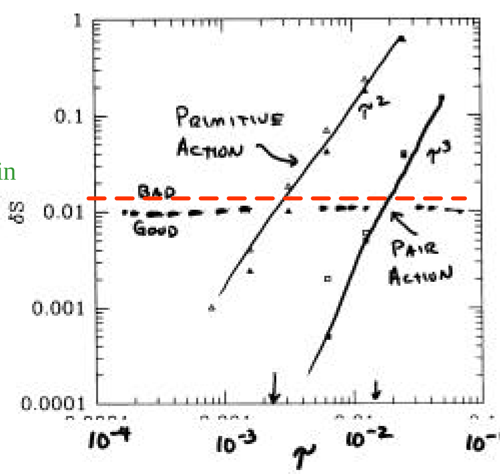
- Compute exact action for each pair using FKPIMC



3A

- How good is it for the triangle?
- Pair action will have 1/6 the number of time slices.

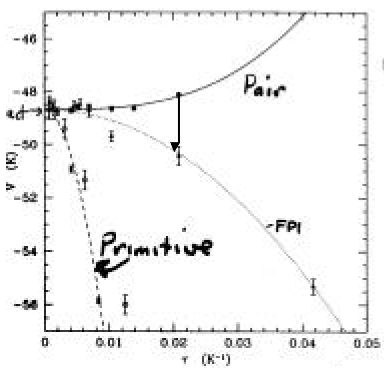
Error in action



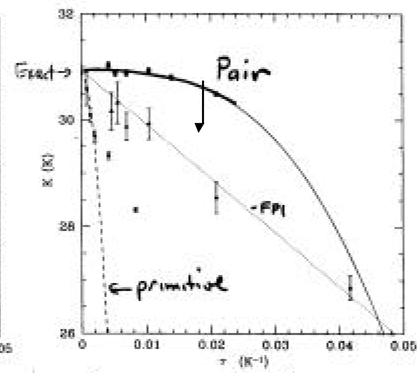
Needed time steps

Convergence on an $(H_2)_{22}$ cluster

Potential energy



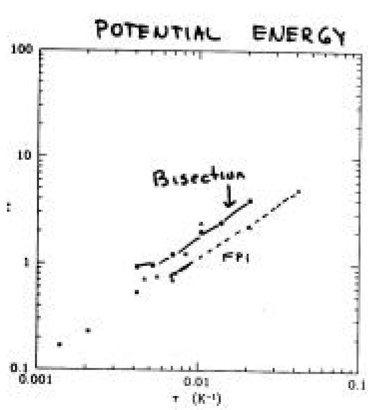
Kinetic energy

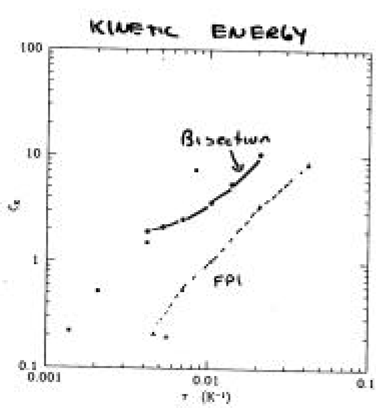


Potential converges much faster than the kinetic energy

Speed of calculation for 22 H_2 molecules

Efficiency (CPU time for a given error) versus time step.





Special Potentials

Coulomb

- Coulomb: eigenfunctions are hydrogen atom wavefunctions and hypergeometric function
- lots of analytic formulas, asymptotic formulas.
- Can use super-symmetry to get rid of one variable: simplifies making tables.
- Gets rid of the infinity in the attractive Coulomb singularity.
- Describes hydrogen atom exactly.

Hard Sphere

- Expansion in partial waves simple: spherical bessel functions+phase shifts
- Various analytic approximations

Harmonic Oscillator

- First rotate to diagonal representation to get a product of 1D density matrices
- Can do analytically

Path Integral Sampling Methods

- We need to perform integrals over the distribution:

$$e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; t)} / Z$$

- Where the exact link action is kinetic and potential energy:

$$S(R_0, R_1; t) = -\frac{3N}{2} \ln\left(4p l t\right) + \frac{(R_0 - R_1)^2}{4?t} + U(R_0, R_1)$$

- Similar to a classical collection of ring “polymers”.
- 3NM degrees of freedom. 64 He atoms*40 slices=2560 classical particles
- Available classical methods are Monte Carlo or Molecular Dynamics. (in fact many different MC methods)

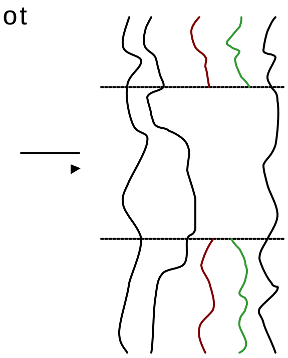
Multi-level sampling

We need to sample several links at once. Why?

- Polymers move slowly as number of links increase.
- Maximum moving distance is order: $\sqrt{lt}$
- Calculate how much CPU time it takes the centroid of a single particle's path to move a given distance
- Scales as M^3 . Hence doubling the number of time slices will slow down code by a factor of 8! Eventually you get into trouble.
- (also shows why good actions help)
- Permutations/windings will not get accepted easily because pair permutations need to have the path move as well.

PIMC Sampling considerations

- Metropolis Monte Carlo that moves a single variable is too slow and will not generate permutations.
- We need to move many time slices together
- Key concept of sampling is how to sample a "bridge": construct a path starting at R_0 and ending at R_t.
- How do we sample $R_{t/2}$? GUIDING RULE. Probability is:



$$P(R_{t/2}) = \frac{\left\langle R_0 \middle| e^{-tH/2} \middle| R_{t/2} \right\rangle \left\langle R_{t/2} \middle| e^{-tH/2} \middle| R_t \right\rangle}{\left\langle R_0 \middle| e^{-tH} \middle| R_t \right\rangle}$$

- Do an entire path by recursion from this formula.
- Related method: fourier path sampling.

How to sample a single slice.

- pdf of the midpoint of the bridge: (a pdf because it is positive, and integrates to 1)
- For free particles this is easy-a Gaussian distribution

PROVE: product of 2 Gaussians is a Gaussian.

- Interaction reduces P(R) in regions where spectator atoms are.
- Better is correlated sampling: we add a bias given by derivatives of the potential (for justification see RMP pg 326)
- Sampling potential U_s is a smoothed version of the pair action.

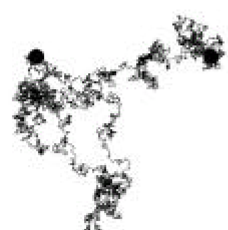
$$P(R_{t/2}) = \frac{\langle R_0 | e^{-tH/2} | R_{t/2} \rangle \langle R_{t/2} | e^{-tH/2} | R_t \rangle}{\langle R_0 | e^{-tH} | R_t \rangle}$$

$$\boxed{\begin{aligned} R_{t/2} &= \frac{1}{2}(R_0 + R_t) + h \\ s^2 &= l t/2 = \langle h^2 \rangle \end{aligned}}$$

$$\boxed{\begin{aligned} R_{t/2} &= \frac{1}{2}(R_0 + R_t) + l t \nabla U_s(R^0_{t/2}) + h \\ \overline{\overline{s}}^2 &= l t/2\overline{\overline{I}} + (l\, t)^2 \overleftarrow{\nabla}\vec{\nabla} U_s(R^0_{t/2}) = \langle \vec{h}\vec{h} \rangle \\ U_s(R) &= \text{sampling potential} \end{aligned}}$$

Lévy construction

- How to generate a random walk by starting in the middle.
- So you don't fall into Zeno's paradox.
- Construct a whole path by recursively sampling bridges
  - Midpoint
  - Midpoint of midpoints
  - Etc.
  - Stop when you are at the desired level of precision.



$$P(R_{t/2}) = \frac{\langle R_0 | e^{-tH/2} | R_{t/2} \rangle \langle R_{t/2} | e^{-tH/2} | R_t \rangle}{\langle R_0 | e^{-tH} | R_t \rangle}$$

$$R_{t/2} = \frac{1}{2}(R_0 + R_t) + h$$

$$s_t^2 = l t/2 = \langle h^2 \rangle$$

Bisection method

1. Select time slices

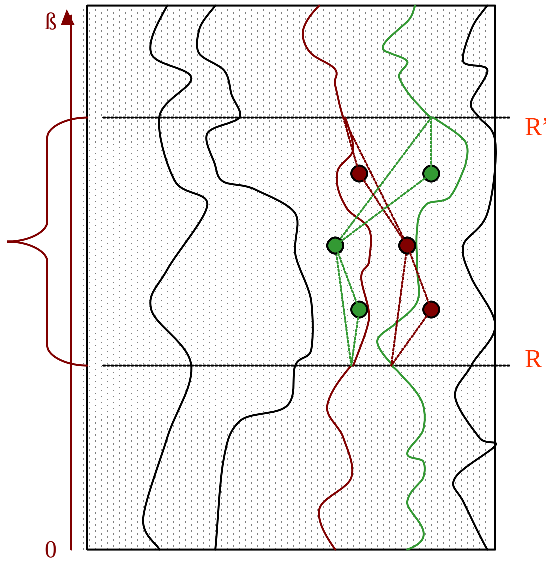
2. Select permutation
   from possible pairs,
   triplets, from:

   $r(R, PR'; 4t)$

3. Sample midpoints

4. Bisect again, until
   lowest level

5. Accept or reject entire
   move



Multilevel Metropolis/ Bisection

• Introduce an approximate level action and sampling.

• Satisfy detailed balance at each level with rejections (PROVE)

$$A_k(s \to s') = \min\left[1, \frac{T_k(s' \to s)p_k(s')p_{k-1}(s)}{T_k(s \to s')p_k(s)p_{k-1}(s')}\right]$$

• Only accept if move is accepted at all levels.

• Allows one not to waste time on moves that fail from the start (first bisection).