united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1595 - 12

Joint DEMOCRITOS - ICTP School on
CONTINUUM QUANTUM MONTE CARLO METHODS
12 - 23 January 2004

PATH INTEGRAL MONTE CARLO

(Motivation for Path Integral MC)

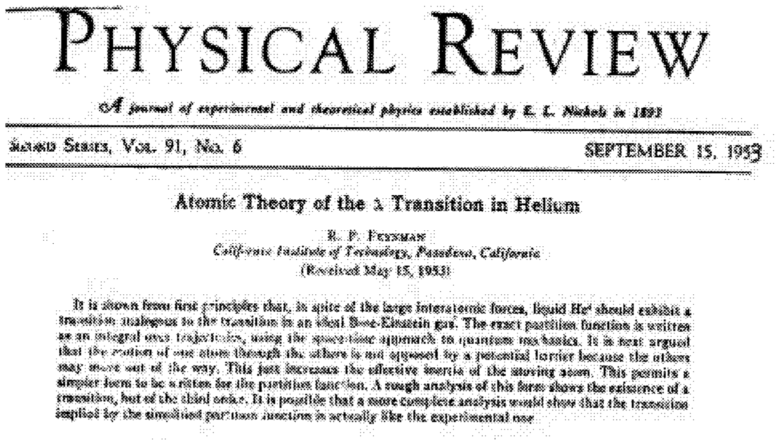
David M. CEPERLEY
Beckman Institute for Advanced Studies & Technology
University of Illinois at Urbana-Champaign - N.C.S.A.
Il-61801 Urbana, U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

Motivation for Path Integral MC

- Problems with VMC and DMC
  - Need to find good trial functions
  - Becomes increasing difficult, especially if one doesn’t know the correct phase.
  - 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,…
- 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
California Institute of Technology, Pasadena, California
(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:

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

$$\beta = 1/(k_B T)$$

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

$$< V >= \frac{1}{Z}\int dR V(R)\rho\left(R;\beta\right)$$

$$\rho\left(R;\beta\right) = \text{diagonal density matrix}$$

- 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 $-\lambda\sum_{i=1}^{N}\nabla_i^2 \quad \text{where } \lambda \equiv \frac{\hbar^2}{2m}$
- 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.

$$\hat{H}\phi_\alpha = E_\alpha \phi_\alpha$$

$$\rho(R;\beta) = \sum_\alpha \left|\phi_\alpha(R)\right|^2 e^{-\beta E_\alpha} \quad \beta = 1/kT$$

$\hat{\rho}_\beta = e^{-\beta \hat{H}}$ operator notation

off-diagonal density matrix:

$$\rho(R,R';\beta) = \sum_\alpha \phi_\alpha^*(R')\phi_\alpha(R)e^{-\beta E_\alpha}$$

$\rho(R,R';\beta) \geq 0$ (without statistics)

$$\rho(R_1,R_2;\beta_1+\beta_2) =$$

$$= \int dR'\, \rho(R_1,R';\beta_1)\rho(R',R_2;\beta_2)$$

or with operators: $e^{-(\beta_1+\beta_2)\hat{H}} = e^{-\beta_1\hat{H}} e^{-\beta_2\hat{H}}$

Trotter's theorem (1959)

- We can use the effects of operators separately as long as we take small enough time steps.
  - n is number of time slices.
  - τ is the "time-step"

$$\hat{\rho} = e^{-\beta(\hat{T}+\hat{V})}$$

$$\hat{\rho} = \lim_{n\to\infty}\left[e^{-\tau\hat{T}}e^{-\tau\hat{V}}\right]^n$$

$$\tau = \beta / n$$

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

Evaluation of kinetic density matrix

$$\left\langle r \middle| e^{-\tau\hat{T}} \middle| r' \right\rangle = \sum_{\alpha} \phi_\alpha^*(r)\phi_\alpha(r')e^{-\tau T_\alpha}$$

In PBC eigenfunctions of $\hat{T} = \frac{1}{\sqrt{\Omega}} e^{-i\vec{k}\vec{r}}$

and eigenvalues are λk^2

$$\left\langle r \middle| e^{-\tau\hat{T}} \middle| r' \right\rangle = \sum_{k} \frac{1}{\Omega} e^{-i\vec{k}\vec{r}} e^{i\vec{k}\vec{r}'} e^{-\tau\lambda k^2}$$

convert to an integral

$$\left\langle r \middle| e^{-\tau\hat{T}} \middle| r' \right\rangle = \frac{1}{(2\pi)^3} \int dk e^{i\vec{k}(\vec{r}'-\vec{r})-\tau\lambda k^2} = (4\pi\lambda\tau)^{-3/2} e^{-(r-r')^2/4\lambda\tau}$$

Danger: makes assumption about boundaries and statistics.

Using this for the density matrix.

- We sample the distribution:

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

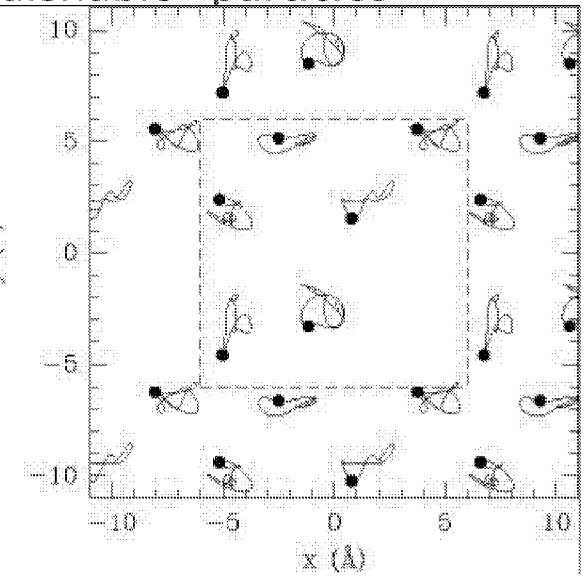
Where the "primitive" link action is:

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

- 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 $R_0 = R_m$ ⇨ closed or ring polymers

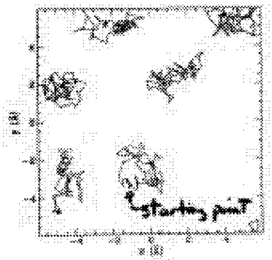
“Distinguishable” particles

- 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.

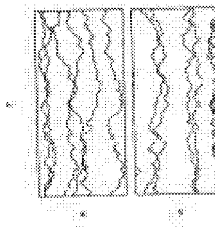


Different schemes to picture PIs.

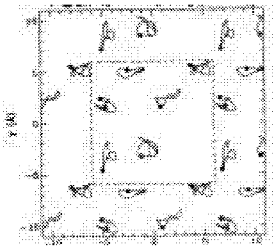
Descretized trace



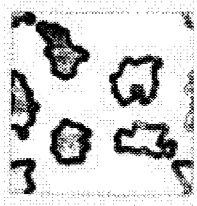
World line picture



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.

Comparison of
DMC with PIMC

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

- Samples the density matrix
- State is 3N*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)

Calculating properties

- Procedure is simple: write down observable:

$$< O >= \frac{\int dR dR' \langle R | \hat{O} | R' \rangle \langle R | e^{-\beta \hat{H}} | R' \rangle}{Z}$$

- Expand density matrix into a "path":

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

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

- 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

$$E = -\frac{dZ}{Z d\beta} = \frac{1}{Z} \int dR e^{-S} \left[\frac{dS}{d\beta} \right] = \left\langle \frac{dS_k}{d\tau} \right\rangle_{path}$$

$$\frac{dS}{d\tau} = \frac{dU}{d\tau} + \frac{dN}{2\tau} - \frac{(R - R')^2}{4\lambda\tau^2}$$

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)

$$E_{virial} = \left\langle \frac{dU}{d\tau} + \frac{dN}{2\beta} + \frac{1}{2\tau}(R_i - C) \cdot \nabla_i U \right\rangle$$

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

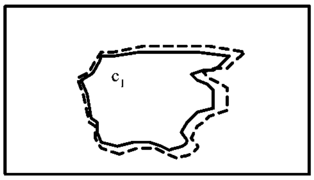
$$\vec{c} = \frac{1}{M}\sum_{i=1}^{M} r_i$$

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

$$\Lambda = \sqrt{4\lambda\tau} \qquad \frac{\partial \ln \Lambda}{\partial \tau} = \frac{1}{2\tau}$$

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

$$E = -\frac{\partial \ln(Z)}{\partial \beta} = \frac{3N}{2\beta} + \int dcd\zeta_j \vec{\nabla} U \cdot (\vec{r} - \vec{c})\tau$$



DANGER with PBC and exchanges

$$E_{virial} = \left\langle \frac{dU}{d\tau} + \frac{dN}{2\beta} + \frac{1}{2\tau}(R_i - C)\cdot\nabla_i U \right\rangle$$

Potential NI-KE deviation from centroid .force

- Can also calculate kinetic energy by differentiating with respect to the mass

$$K = -\frac{mdZ}{\beta Z dm}$$

- Or use the "direct" form:

$$K = \left\langle e^{S}(-\lambda\nabla^2)e^{-S} \right\rangle_{path}$$

- For pressure, differentiate wrt the volume (virial estimator).
- 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.

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

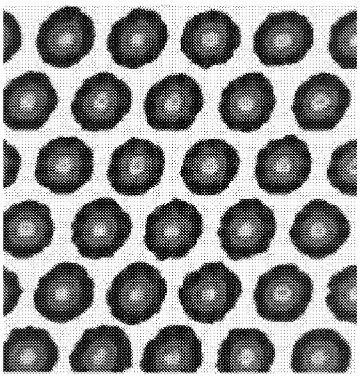
- Solid H_2: work of Marcus Wagner, DMC
- Wigner crystal: 3D Matt Jones, DMC
  2D Ladir Candido, P. Phillips, DMC
- Vortex lattice: Nandini Trivedi, P. Sen and DMC

Example: Solid H_2

Solid molecular hydrogen is a very quantum solid

KE=69K T_t = 13.8K

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



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

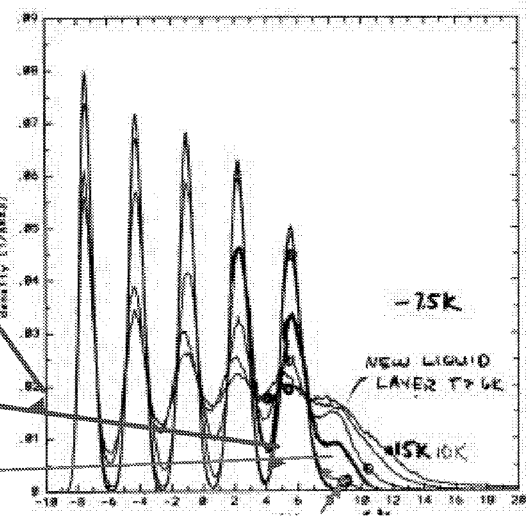
Hard wall on left

Top layer melts around 7K.

Very fluffy top layer.

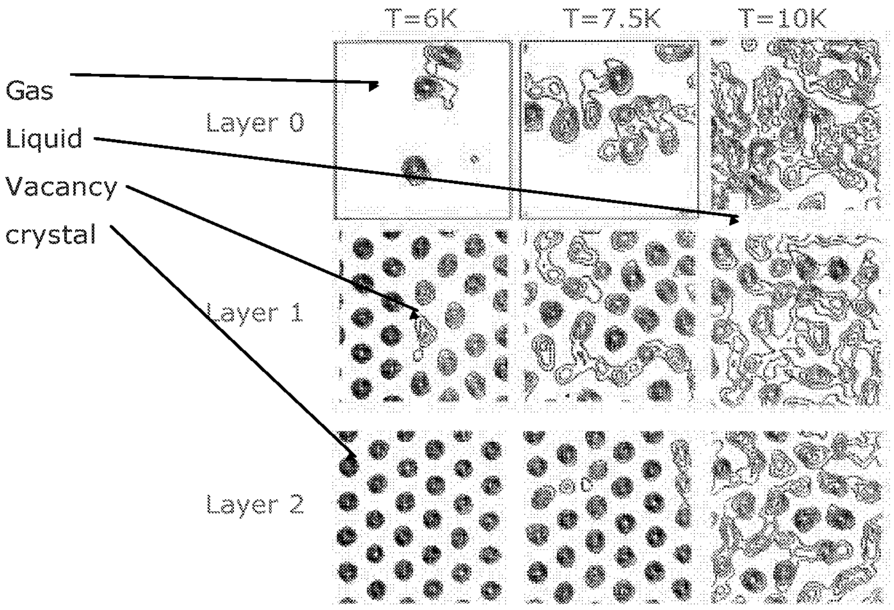
New layer above 6K

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



Z (A)   T=6K

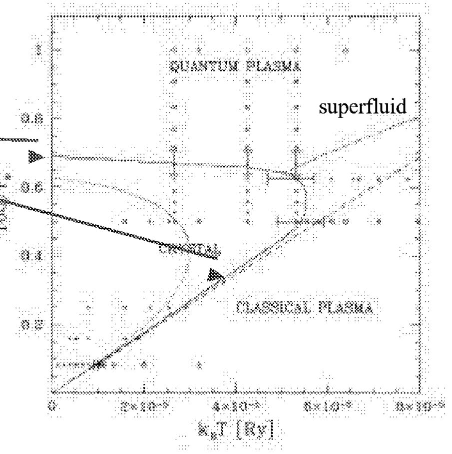
Snapshots of H_2 density



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



Free Energy Computation

$$e^{-F/kT} = e^{-F_0/kT} \int dR e^{-S(R)}$$

•Free energy (and the entropy) is difficult to calculate since ensemble averages are of ratios only.

•Need entropy not only energy.

• Helps to determine phase transitions especially first order.

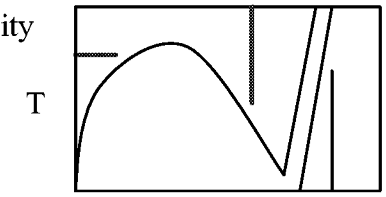
•Metastability makes it difficult--also different size effects in the different phases.

Thermodynamic Integration

- We can't compute free energies but we can compute its derivatives: $P = -\left.\frac{\partial F}{\partial V}\right|_{NT}$ $E = \left.\frac{\partial(\beta F)}{\partial \beta}\right|_{NV}$
- So pick a path from a known state and integrate to get F.

$$F(T) = F_0(T) + \int_0^{\beta} \frac{dt}{\beta}(E(t) - E_0(t)) = F_0(V_0) + \beta N \int_0^{\rho} \frac{d\rho'}{\rho'}\left(\frac{PV'}{NkT} - 1\right)$$

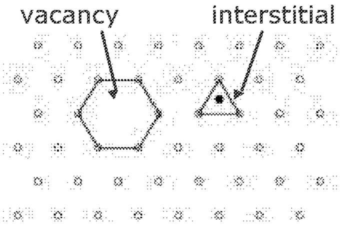
- Find path to known state without crossing phase lines.
- Fluid-go to high T or low density
- Gas-go to low density
- Solid-go to T=0.



Point defects in the 2d Wigner crystal

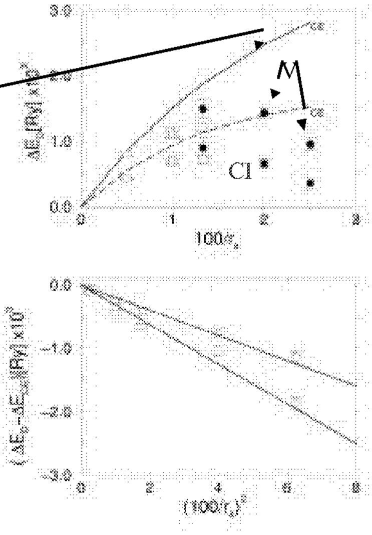
- Add and subtract an electron keeping density fixed. (keep same background density)

  $E_D = [e(N\pm1,\rho) - e(N,\rho)](N\pm1)$
- Box rectangular to allow perfect triangular lattice (55,56,57 electrons)
- Calculate total energy using PIMC
- Hexagonal lattice
- Tethers to keep defects from moving around.
- Restricted paths using a localized picture of the nodes and a ferromagnetic spin arrangement.
- Very weak temperature dependence.



Energy of Defect

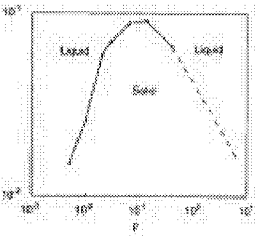
- Interstitials have a lower energy than vacancies!
- Cockayne-Elser determined exact harmonic energy
- Anharmonic terms reduce the defect energy for r_s ~100
- The creation energy for an interstitial vanishes for r_s~35 (for a ferromagnetic crystal)
- This is very close to the melting density r_s~39
- Interstitials and vacancies may be responsible for melting at T=0.



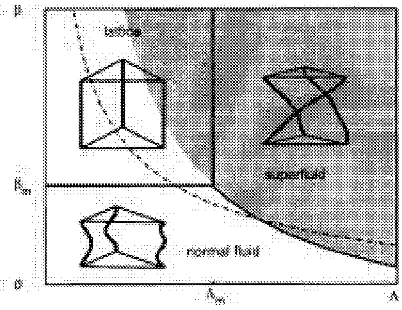
Vortex Models

Sen, Trivedi,DMC PRL 2001.

- PI-bosons are analogous to vortices in superconductors
- Use PIMC to simulate vortices



$$H/\varepsilon_0 = -\Lambda^2 \sum_i \nabla_i^2 + \sum_{i<j} K_0(r_{ij}/\lambda)$$



- Interaction is modified Bessel function.

$$\Lambda^2 = \frac{(kT)^2}{2\varepsilon_1 \lambda^2 \varepsilon_0}$$

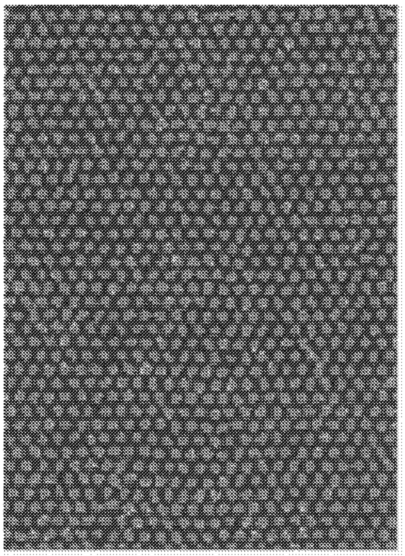
$$\lambda = \text{penetration depth}$$

$$\varepsilon_0 = \frac{\phi_0^2}{8\pi^2\lambda^2}$$

Clean lattice

- Simulation of 1000 vortices near melting
- They form a perfect triangular lattice.
- Fluctuations due to phonons

$$\Lambda = 0.045$$

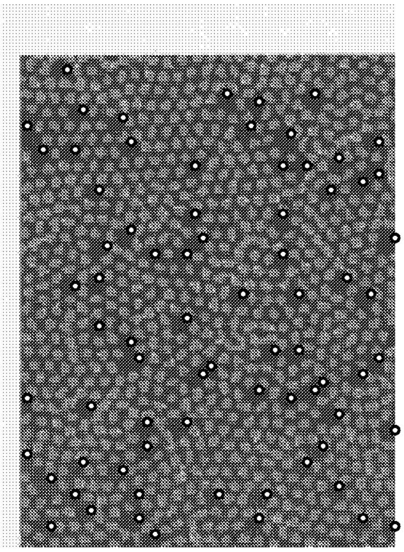


Strongly pinned disorder

- We introduce disorder by taking 10% of the vortices and placing them at random positions and freezing them.

(columnar disorder)

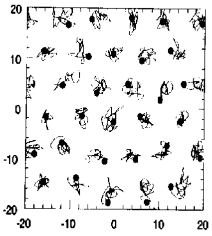
- Perfect crystal is frustrated
- Structure consists of short-ranged crystal with many defects



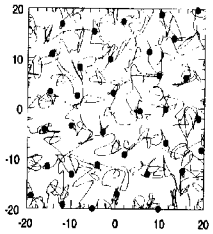
Entangled vortex state

•Structure factor decrease near melting

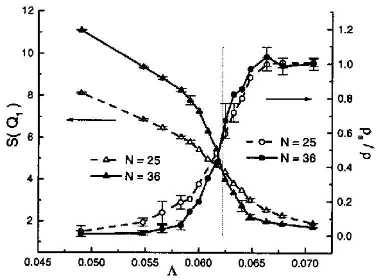
•Superfluid fraction increases.

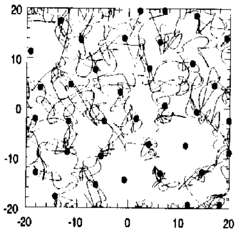


Λ=0.045(clean)



Λ=0.065(clean)





Λ=0.065(with pins)

Improved Actions

- There exists an "exact link action" :

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

$$e^{-\sum_{i=1}^{M} S(\mathrm{R_i},\mathrm{R_{i+1}};\tau)} / Z \quad \text{where} \quad Z = \int d\mathrm{R_1}\ldots d\mathrm{R_M}\, e^{-\sum_{i=1}^{M} S(\mathrm{R_i},\mathrm{R_{i+1}};\tau)}$$

- The "primitive" <u>link action</u> is:

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

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

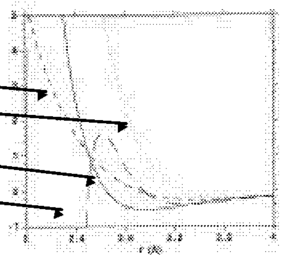
$$U(R_i,R_{i+1};\tau) = S(R_i,R_{i+1};\tau) - S_0(R_i,R_{i+1};\tau)$$

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
- This idea is also used in lattice gauge theory: the "perfect action."

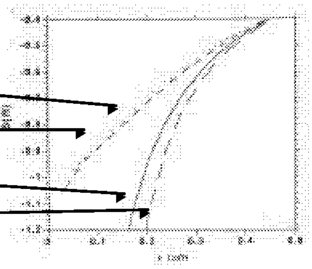
Examples for 2 particles


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 $U(R,R';\beta)=U(R',R;\beta)$
- 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:

$$E_\rho = \rho^{-1}\left[\hat{H}+\frac{\partial}{\partial t}\right]\rho\left(R,R';t\right)\approx 0$$

- Feynman-Kac Formula can be used for insight. Average over all "free particle" bridges from R_0 to R_F. Proof that density matrix is positive.

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

- Also can be used to compute actions (exercise: FKPIMC program)

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.

$$e^{-U(R_0,R_F;\tau)} = \rho(R_0,R_F;\tau)\left\langle \exp\left[-\int_0^\tau dt E_\rho(R(t))\right]\right\rangle_{\rho:RW}$$

$$\frac{dR}{dt} = \eta(t) - \frac{R-R_F}{t} - 2\lambda\nabla U(R;R_F;t)$$

- The density matrix is built into how paths get from R_0 to R_F.
- Gives intuition about how to how to improve it a given action
- Maybe also a way to compute the action better.

Cumulant Approximation

- In FK formula take the average into the exponent

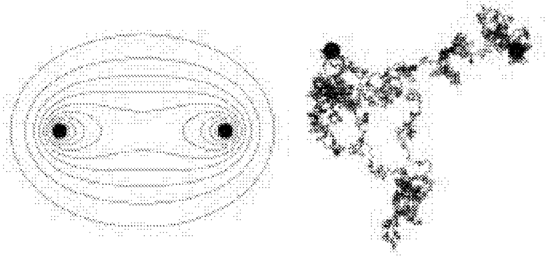
$$e^{-U(R_0,R_F;\tau)} \sim \exp\left[-\left\langle -\int_0^\tau dt V(R(t))\right\rangle_{RW}\right]$$

- It is possible to evaluate the average using fourier transforms.

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

$$V_S\left(r,\sigma\right) = \int dk e^{-ikr-\frac{\sigma k^2}{2}} v_k \qquad \sigma = \frac{2\lambda t\left(\tau - t\right)}{\tau}$$

- Very accurate for Coulomb problems
- However the CA does not exist for non-integrable potentials.



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)

$$U_H(R_O,R_F;\tau)=\tau V(R^*)+\frac{\tau^2\lambda}{6}\nabla^2V(R^*)-\frac{\tau^3\lambda}{12}\left[\nabla V(R^*)\right]^2$$

$$-\frac{\tau}{12}\left(R_F-R_O\right)\nabla\nabla V(R^*)\left(R_F-R_O\right)$$

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

- 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.

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

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

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

- 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

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

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:

$$\rho_\ell(r,r';2\tau)=\int_0^\infty dr''\rho_\ell(r,r'';\tau)\rho_\ell(r'',r';\tau)$$

5. Complete density matrix is:

$$\rho(\vec{r},\vec{r}';\tau)=\sum_\ell \rho_\ell(r,r';\tau)P_\ell(\cos(\theta))$$

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

PIMC representation of pair density matrix

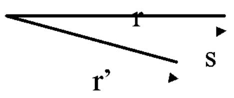
- In bare form it is 3d+time.
- But as normally used
  - Time is discrete (fixed)
  - 2 other variables are small (expand in them)

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

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

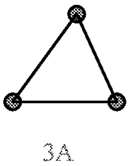
$$u(r,r')=u_0(r)+u_0(r)+\sum_{j<k}u_{kj}(q)z^{2j}s^{2(k-j)}$$

- 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 fewer time slices….

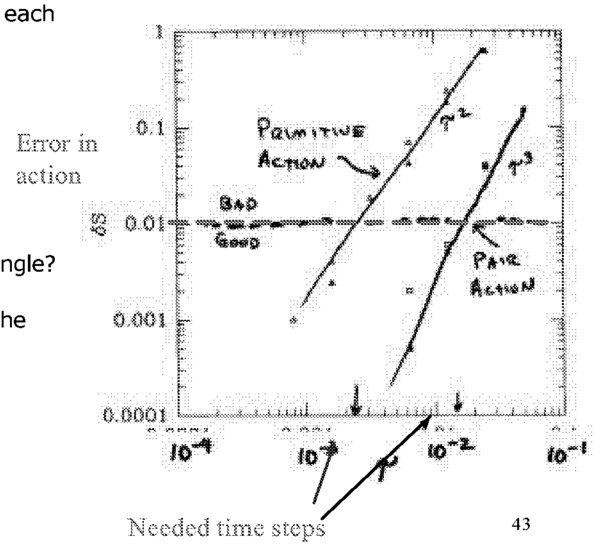


Compare pair action
3 He atoms

- Compute exact action for each pair using FKPIMC

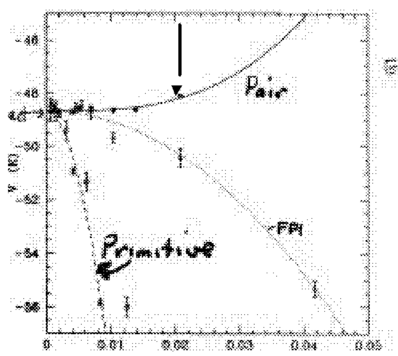


- How good is it for the triangle?
- Pair action will have 1/6 the number of time slices.

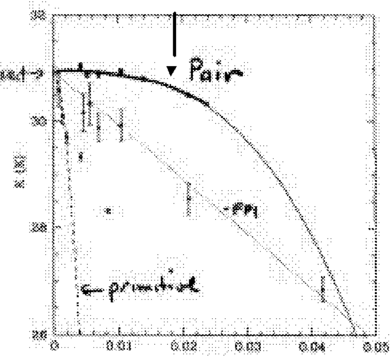


Convergence on an $(H_2)_{22}$ cluster

Potential energy



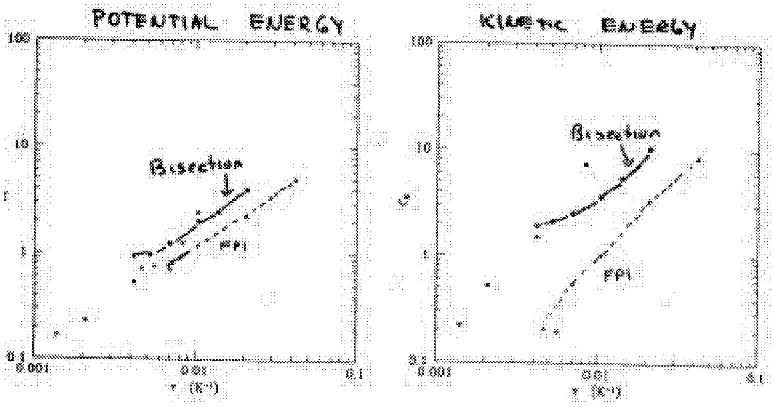
Kinetic energy



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.



Beyond Pair product
Residual energy for pair product

- Will vanish for 2 particles.
- Since u is of order τ then the residual energy has to be order τ^2 and by the GFK the corrections must be τ^3.

- Since u ~ r^{-5} for LJ potential at small r, then the residual energy goes as r^{-6}
- But errors will depend on density, since 3 particles must be involved.

$$E_p = -2\sum_{i<j<k} \lambda \nabla_i u(r_{i,j}) \nabla_i u(r_{i,k})$$

This is the analytic form to use for an action beyond the pair form.

Called the "polarization action" or 3-body term in ground state calculations because it can be written:

$$U_P = -\lambda\tau \sum_i \left[\sum_j \vec{\nabla}_i \tilde{u}(\vec{r}_{ij}) \right]^2 + \text{pair terms}$$

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

How do we treat an arbitrary potential?

- Can do harmonic, cumulant or WK but not guaranteed to be good if strong forces are present.
- Harmonic approximation just fixes the "easy" part.
- Basic idea is to remove a reference potential that we can treat exactly and the rest is treated with primitive approximation

$$H = H_0 + \Delta V(R)$$

$$S(R,R';\tau) = S_0(R,R';\tau) + \frac{\tau}{2}\left[\Delta V(R) + \Delta V(R')\right]$$

- Errors are due to the commutator: $\tau^2 \left[H_0, \Delta V(R)\right]$
- Put the fast varying parts into H_0. We want the "left-over" part to be smooth so commutator is small.

Differences between lattice and continuum PIMC

- Potential is unbounded. Much more care needed to treat singular parts of the potential. Watch out for expansions.
- Deadlocks do not arise. Paths can always wiggle out but it may take a long time.
- Detailed comparison with experiment is possible. Numerical convergence is important.
- Paths are truly distinguishable. First quantitized description is more natural. Allows fixed-node fermion methods.

Path Integral Sampling Methods

- We need to perform integrals over the distribution:

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

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

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

- 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.

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: $\sqrt{\lambda\tau}$
- 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.

General Metropolis MC

Metropolis achieves detailed balance by *rejecting* moves.

Break up transition probability into sampling and acceptance:

$$P(s \to s') = T(s \to s') A(s \to s')$$

$$T(s \to s') = \text{sampling probability}$$

$$A(s \to s') = \text{acceptance probability}$$

The optimal acceptance probability that gives detailed balance is:

$$A(s \to s') = \min\left[1, \frac{T(s' \to s)\pi(s')}{T(s \to s')\pi(s)}\right]$$

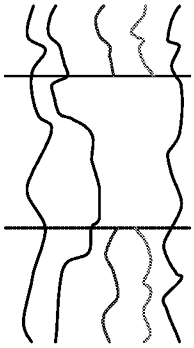
Note that normalization of $\pi(s)$ is not needed or used!

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:

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

- 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.

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

$$\boxed{\begin{aligned} R_{t/2} &= \frac{1}{2}(R_0 + R_t) \\ \sigma^2 &= \lambda t / 2 \end{aligned}}$$

$$\boxed{\begin{aligned} R_{t/2} &= \frac{1}{2}(R_0 + R_t) + \lambda t \nabla U_s(R^0_{t/2}) \\ \sigma^2 &= \lambda t / 2 + (\lambda t)^2 \nabla\nabla U_s(R^0_{t/2}) \\ U_s(R) &= \text{sampling potential} \end{aligned}}$$

How to sample a Normal distribution

- Trick: generate 2 ndrn at a time: r=(x,y)

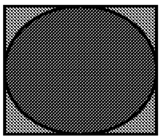
$$p(x,y)dxdy = (2\pi)^{-1}\exp(-\frac{r^2}{2}) = p(r)rdrd\theta$$

$$p(v)dv = \frac{1}{2}e^{-v/2} \text{ with } v = r^2$$

$$x = \sqrt{-2\ln(u_1)}\cos(2\pi u_2)$$

$$y = \sqrt{-2\ln(u_1)}\sin(2\pi u_2)$$

- Or sample angle using rejection technique:
  - Sample (x,y) in square
  - Accept if $x^2+y^2 < 1$
  - Normalize to get the correct r.



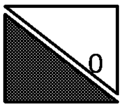
Multivariate normal distributions

How to sample a correlated Gaussian? (say with D components)

- Assume we want $<x_i x_j> = T_{ij}$
- Make Choleski decomposition of T, its square root. (see Numerical Recipes)

$$SS^t = T$$

by assuming S is a triangular matrix



- Generate D normally distributed numbers y.
- Transform to correlated random distribution

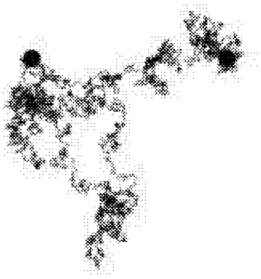
$$X = Sy$$

Lévy construction

- How to generate a random walk by starting in the middle. So you don’t fall into Zeno’s paradox.

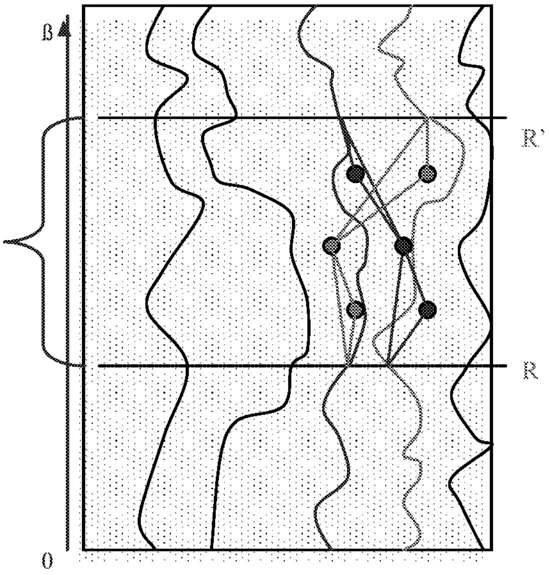
$$P(R_{t/2}) = \frac{\left\langle R_0 \middle| e^{-tH/2} \middle| R_{t/2} \right\rangle \left\langle R_{t/2} \middle| e^{-tH/2} \middle| R_t \right\rangle}{\left\langle R_0 \middle| e^{-tH} \middle| R_t \right\rangle}$$

- Construct a whole path by recursively sampling bridges
  - Midpoint
  - Midpoint of midpoints
  - Etc.
- Stop when you are at the desired level of precision.



Bisection method

1. Select time slices
2. Select permutation from possible pairs, triplets, from:
   $\rho(R, PR'; 4\tau)$
3. Sample midpoints
4. Bisect again, until lowest level
5. Accept or reject entire move

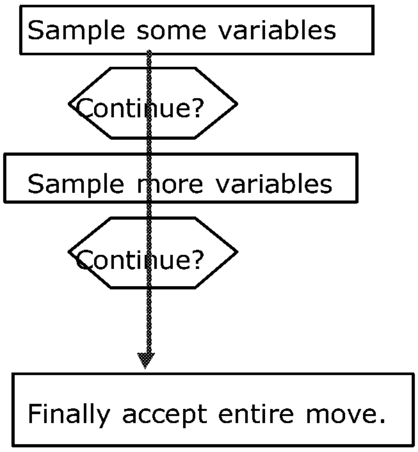


Multilevel Metropolis/ Bisection

- Introduce an approximate level action and sampling.
- Satisfy detailed balance at each level with rejections (PROVE)

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

- Only accept if move is accepted at all levels.
- Allows one not to waste time on moves that fail from the start (first bisection).



Sample some variables

Continue?

Sample more variables

Continue?

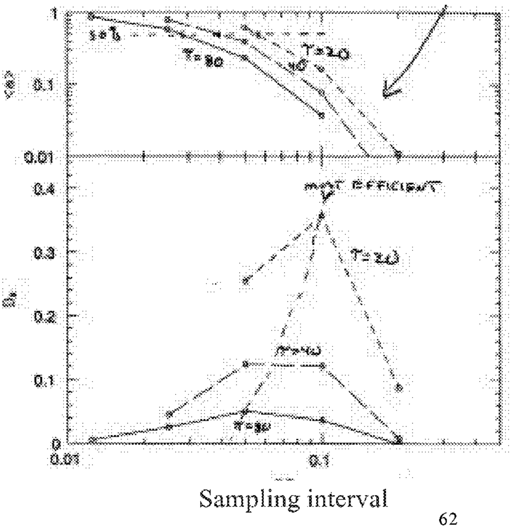
Finally accept entire move.

Efficiency for number of links moved

Total acceptance ratio

Best sampling is of 4-8 slices at once.

Center of mass diffusion



MC versus MD sampling

- MD can be used BUT basic algorithm is not ergodic because spring terms do not exchange "pseudoenergy" with the other degrees of freedom.

(in Fermi-Ulam-Pasta experiment, slightly anharmonic chains never come into equilibrium.)

- Coupled themostats are introduced to solve this problem--but requires some detailed tinkering to make it work in many cases.
- Basic problem with MD-cannot do discrete moves needed for bose/fermi statistics
- An advantage of MD is that multiparticle moves are natural-allows fast computation of energy and forces within LDA.
- *Little systematic comparison for a realistic systems.*