**1929-2**

**Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry**

*21 January - 1 February, 2008*

**PIMC 1 Intro.**

D. Ceperley

*University of Illinois at Urbana-Champaign*

# 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)

## 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 He⁴ 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:

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

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

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

- Hamiltonian $\quad \hat{H} = \hat{T} + \hat{V}$

# The thermal density matrix

- Find exact many-body eigenstates of H.
- Probability of occupying state $\alpha$ is $\exp(-\beta E_\alpha)$

- All equilibrium properties can be calculated in terms of thermal o-d density matrix
- Convolution theorem relates high temperature to lower temperature.

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

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

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

off-diagonal density matrix:

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

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

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

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

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.

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

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

- n is number of time slices.
- $\tau$ is the "time-step"

$$\tau = \beta / n$$

- 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

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

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

and eigenvalues are $\lambda k^2$

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

convert to an integral

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

Danger: makes assumption about boundaries and statistics.

# Generalized Trotter Theorem

- True of any number of operators, as long as they are each bounded below.

$$\hat{\rho} = e^{-\beta(\hat{A}+\hat{B}+\hat{C})}$$

$$\hat{\rho} = \lim_{n\to\infty}\left[ e^{-\tau\hat{A}} e^{-\tau\hat{B}} e^{-\tau\hat{C}} \right]^{n}$$

$$\tau = \beta/n$$

- Interpret $\rho$ as a probability; evolution equation is:

$$-\frac{\partial\hat{\rho}}{\partial\beta} = (\hat{A}+\hat{B}+\hat{C})\hat{\rho} \quad \text{initial value:} \ \hat{\rho}\big|_{\beta=0} = \hat{I}$$

- Discrete-time version:

$$\hat{\rho}(\beta+\tau) \approx e^{-\tau\hat{A}} e^{-\tau\hat{B}} e^{-\tau\hat{C}} \hat{\rho}(\beta)$$

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

# *Using this for the density matrix.*

- We sample the distribution:

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

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

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

- 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.
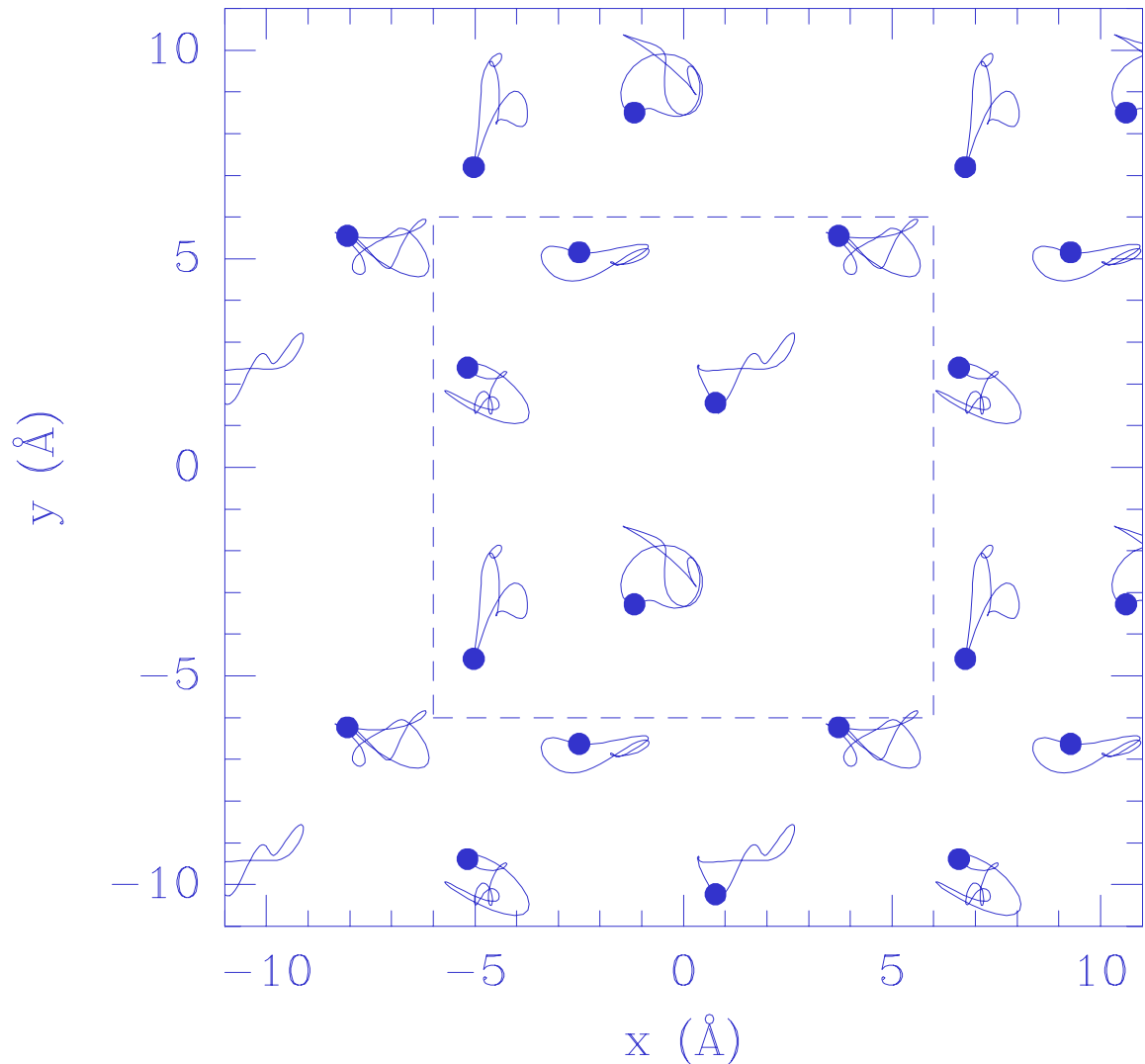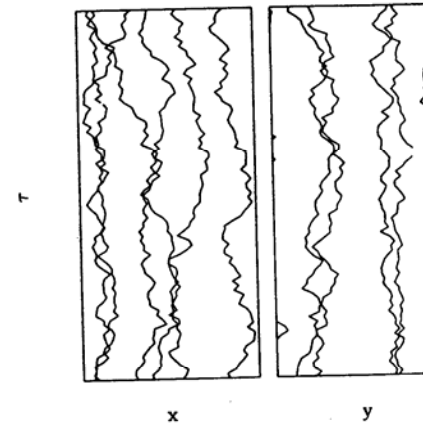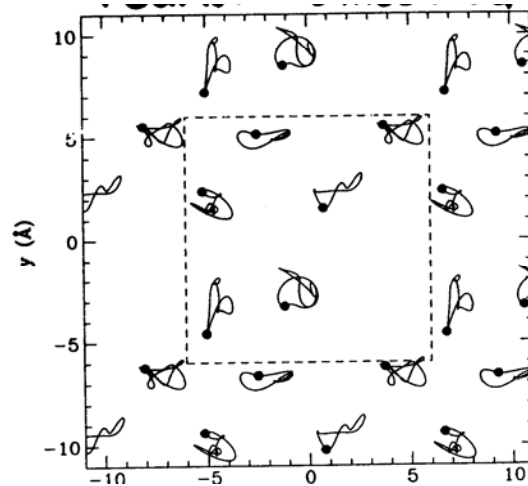
# Different schemes to picture PIs.

Descretized trace
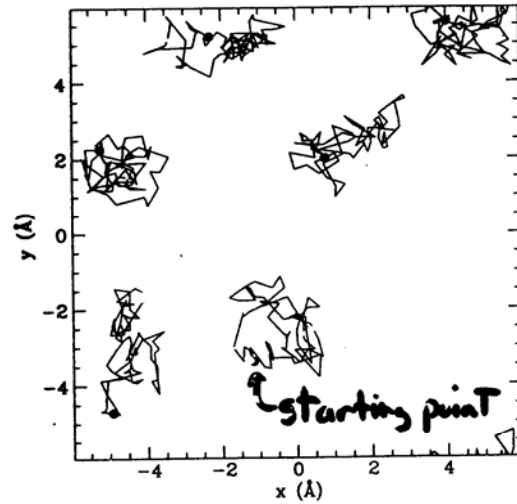
World line picture

Fourier smoothed trace

Space filling picture

11

# 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:

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

- 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

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

$$\frac{dS}{d\tau} = \frac{dU}{d\tau} + \frac{3N}{2\tau} - \frac{(R-R')^2}{4\lambda\tau^2}$$

Potential   n*NI-KE     spring energy

Problem: variance diverges as small time step.

- Virial Estimator: differentiate in "internal coordinates"
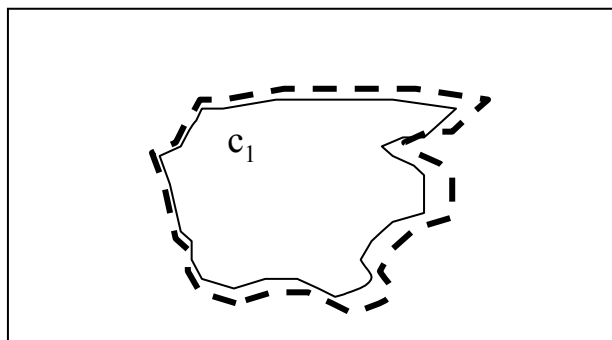  does not diverge at small time steps (Herman, Berne)

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

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



$c_1$

DANGER with PBC and exchanges

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

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

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

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

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

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

Potential    NI-KE    deviation from centroid    .force

15

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

$$K = -\frac{m\,dZ}{\beta Z\,dm}$$

- Or use the "direct" form: $\quad K = \left\langle e^{S}(-\lambda\nabla^{2})e^{-S}\right\rangle_{path}$

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

$$P = \frac{1}{3V}\left[2T - \frac{1}{\tau}\sum_{i<j}\left\langle \mathbf{r}_{ij}\nabla u\left(r_{ij}\right)\right\rangle\right]$$

- 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 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

- 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 $H_2$

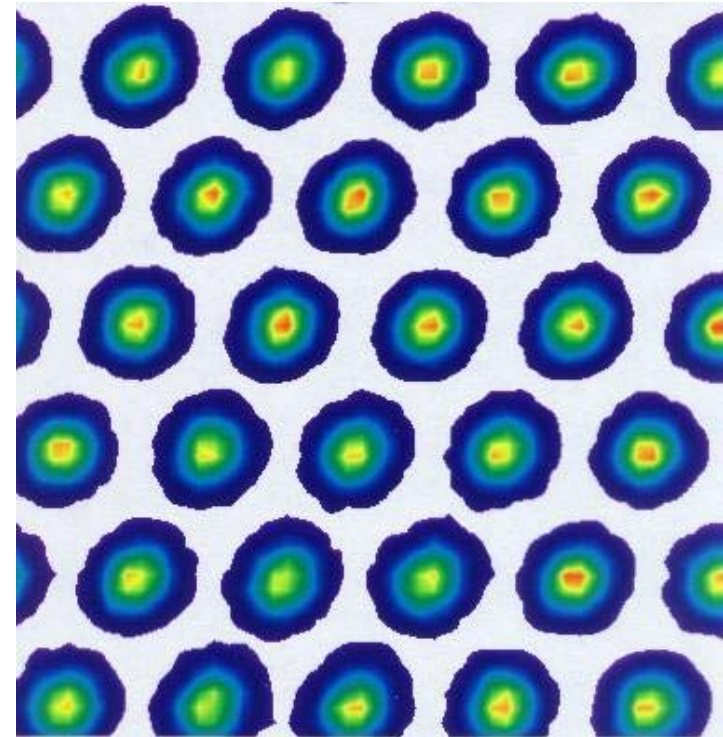Solid molecular hydrogen is a very quantum solid

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 $H_2$
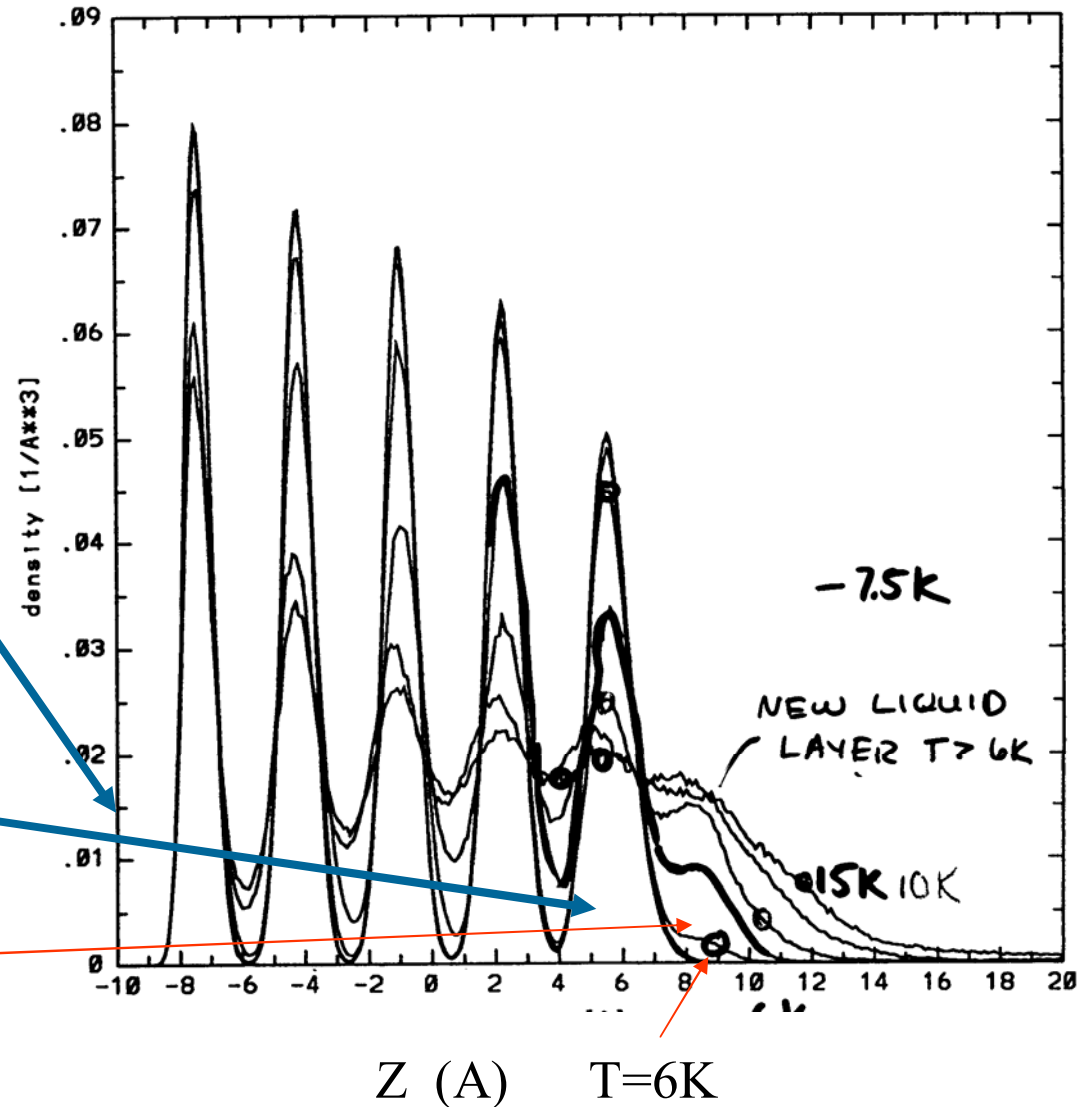
Simulation is of 5 layers

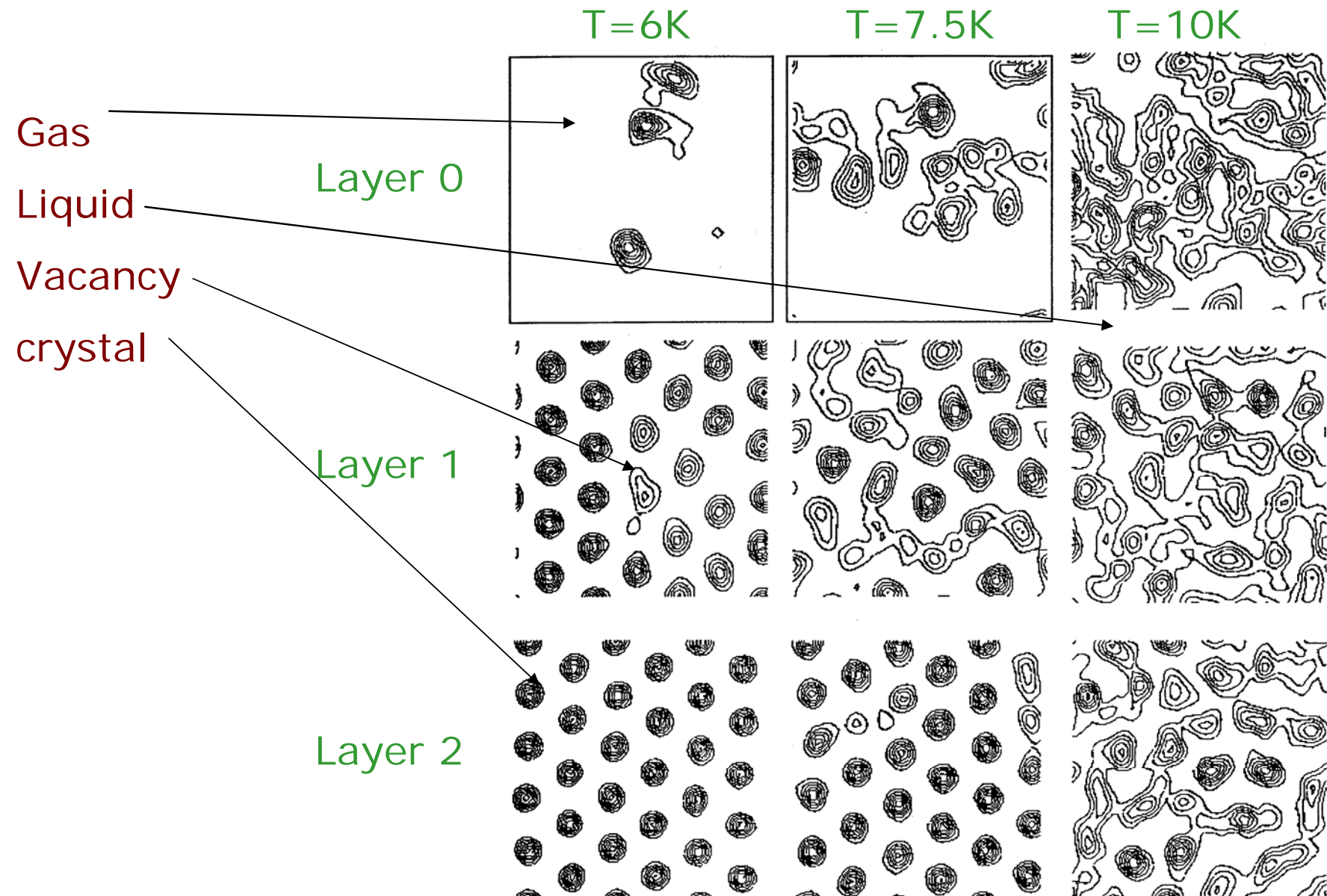Each layer is 30 $H_2$

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

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

Gas

Liquid
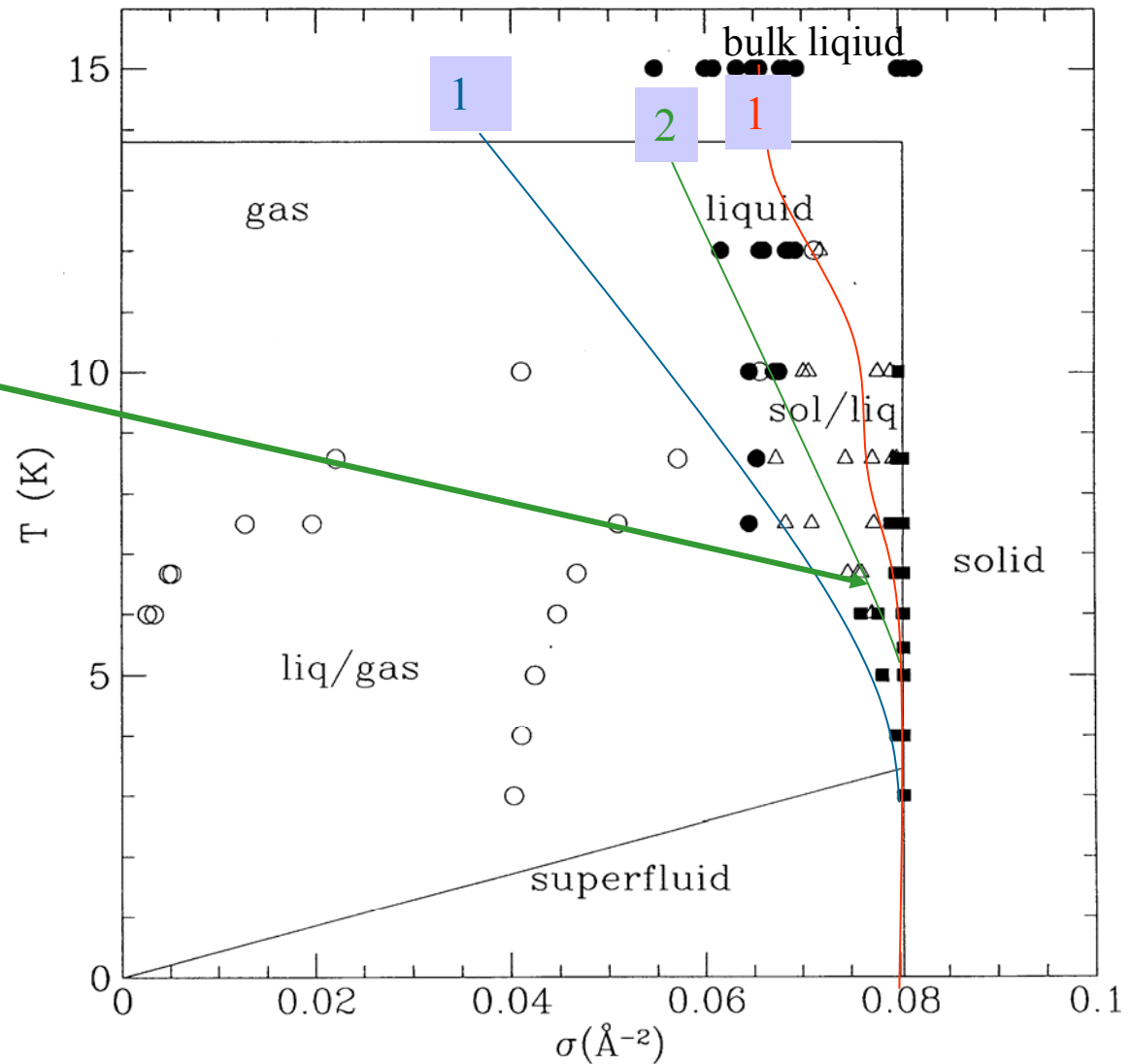
Vacancy

crystal

Layer 0

Layer 1

Layer 2

# "phase diagram of $H_2$"

Each point represents a layer.

Surface melting.

Low density liquid is unstable to separation into a fully filled layer and a gas.
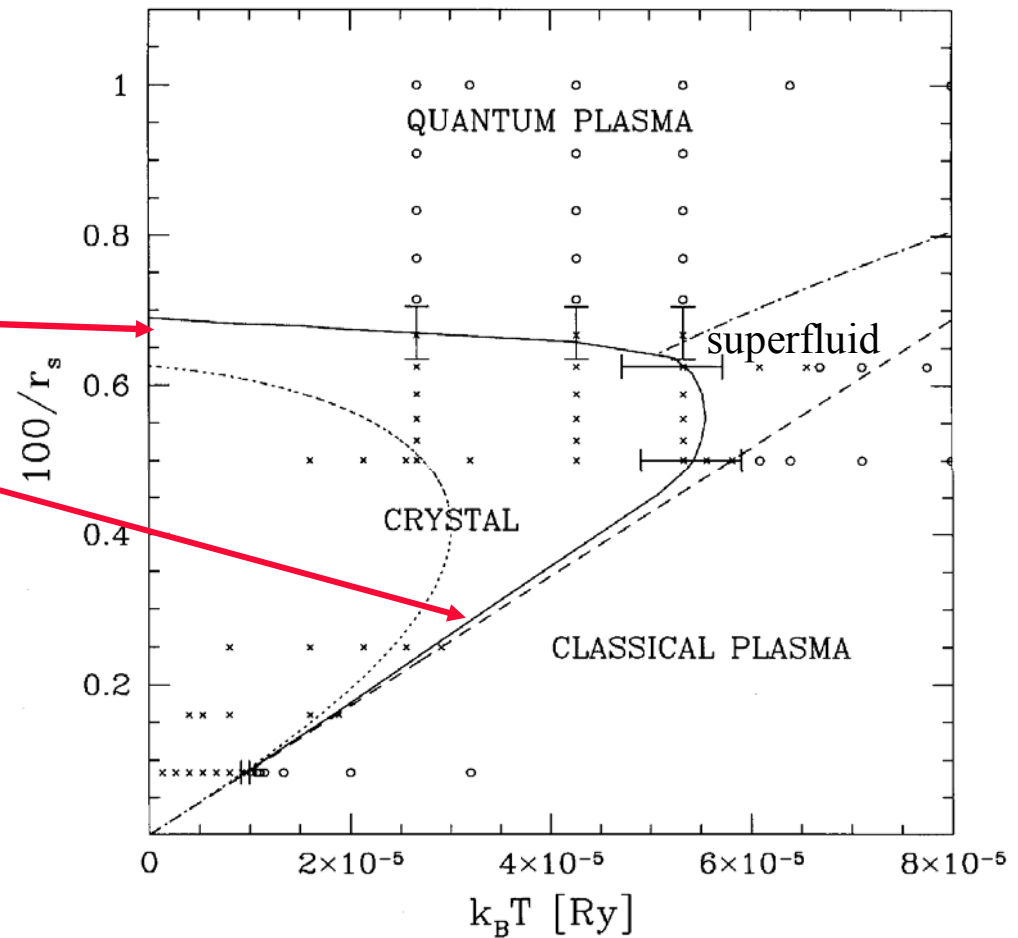
# Melting of the 3D Wigner Crystal

- 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" :

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

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

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

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

- 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."

# Differences between lattice and continuum PIMC

- For lattice models the Hamiltonian is bounded. commutator expansion are a way of getting smaller time step errors.

- Potentials for continuum problems are unbounded. Much more care needed to treat singular parts of the potential. Watch out for expansions.

- Detailed comparison with experiment for all properties is possible for continuum models. Not just exponents. Numerical convergence is important for this.

- Deadlocks do not arise. Paths can always wiggle out but it may take a long time.

- Paths are truly distinguishable. First quantitized description is more natural. Allows fixed-node fermion methods.

# Higher Order Methods?

- Comparison of MD integration algorithms
- Higher order does not always mean better
- Problem is that potentials are not analytic
- Systematic error
- **Usually one tries to balance all sources of errors**

*Berendsen 86*

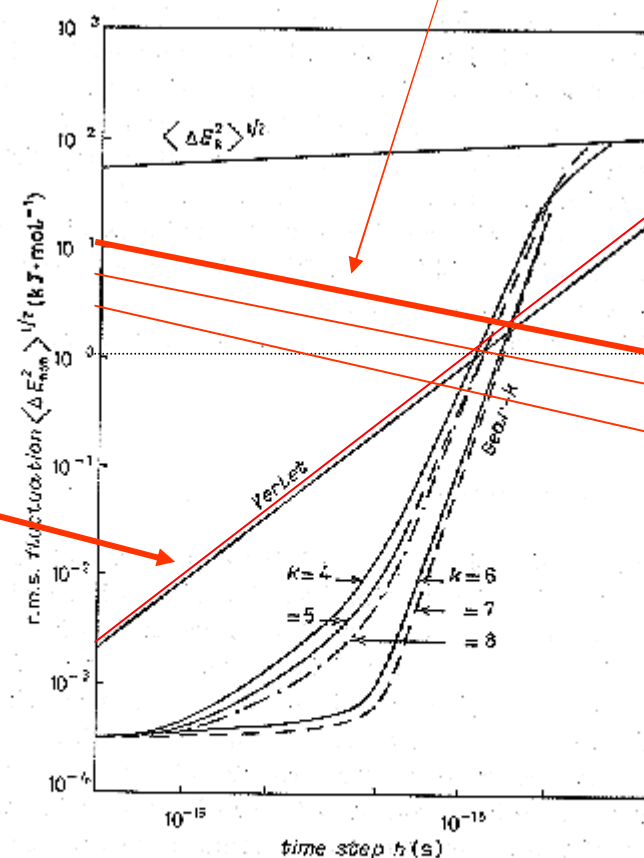*Statistical error for fixed CPU time.*



Fig. 4. – R.m.s. fluctuation of the total energy over 100 steps in a molecular-dynamics simulation of the protein BPTI (458 atoms). Verlet and Gear algorithms are compared. The fluctuation in the total kinetic energy is indicated as a reference (from ref. [15]).

# Examples for 2 particles

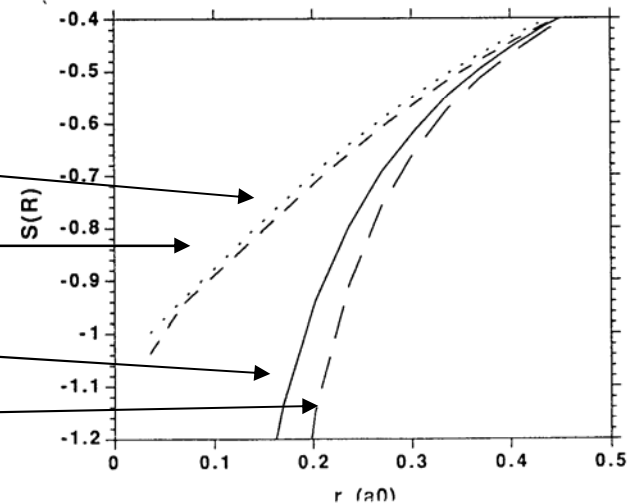- Exact action
- Cumulant action
- Primitive action
- WKB

Exact action is <u>smoother</u> than the primitive form

WKB does not converge
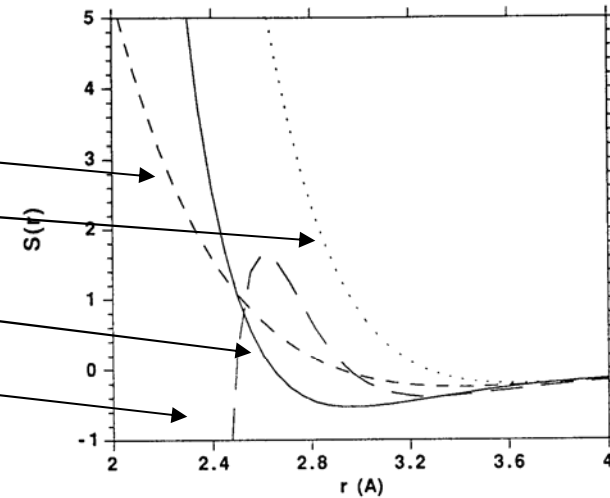
Hydrogen atom

•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:

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

- 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.

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



30

# 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 average over paths from $R_O$ to $R_F$.
- Gives intuition about how to how to improve it a given action
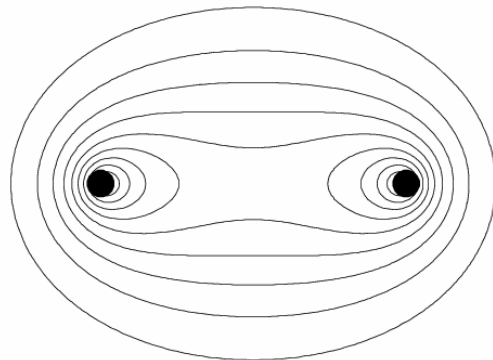- Can be used to compute the action. FKPIMC code

# 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.

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

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

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

# 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)

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

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

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

- $R^*$ is an arbitrary place to evaluate the potential. If we choose it to be one of the end-points we get the <u>Wigner-Kirkwood</u> 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.

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

• take the uncorrelated average:

• This is now a 2 particle problem.

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

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

- 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:

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

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)

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

$$\left.\begin{array}{l} s = |\vec{r} - \vec{r}\,'| \\[1.2em] z = |\vec{r}| - |\vec{r}\,'| \end{array}\right\} \text{small and symmetric}$$
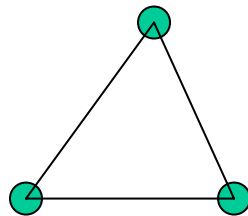
$$u(r, r') = \frac{1}{2}\left[u_0(r) + u_0(r')\right] + \sum_{j<k} u_{kj}(q) z^{2j} s^{2(k-j)}$$

- 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.
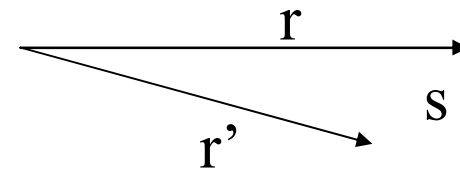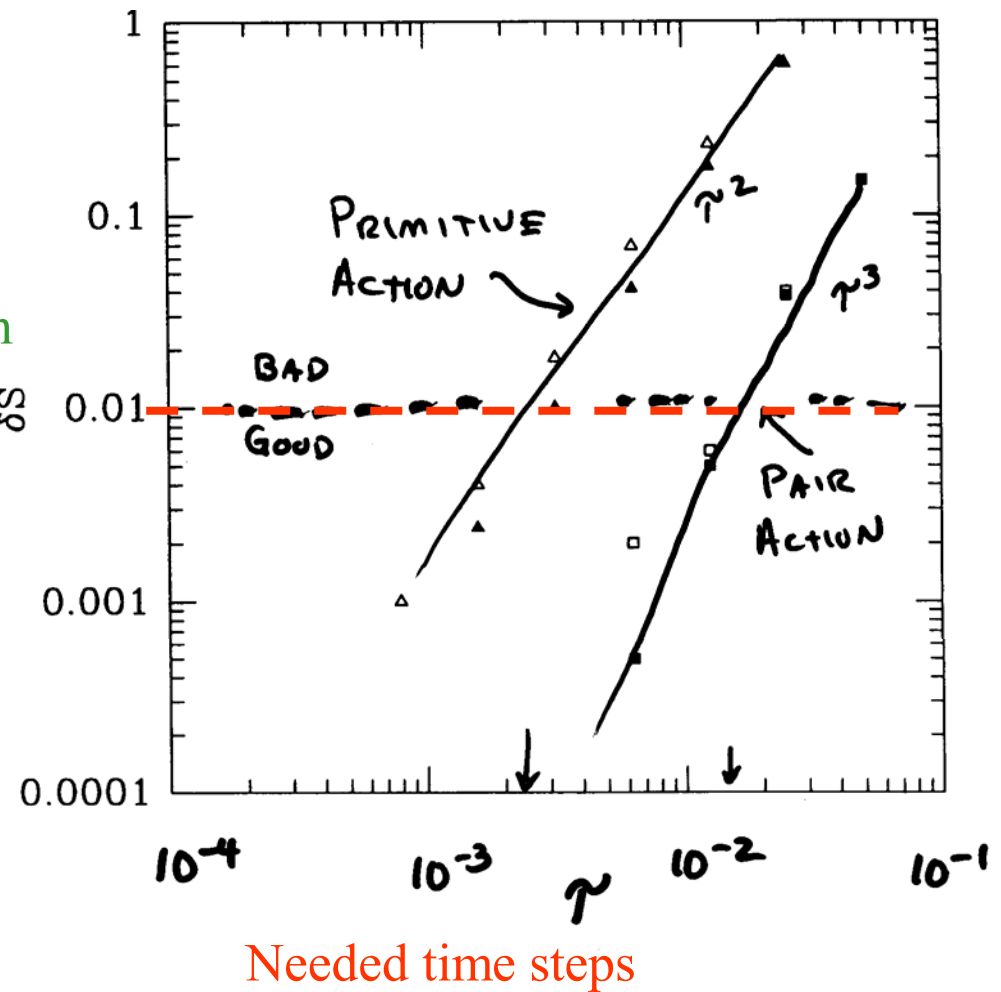
# Compare pair action
# for 3 He atoms

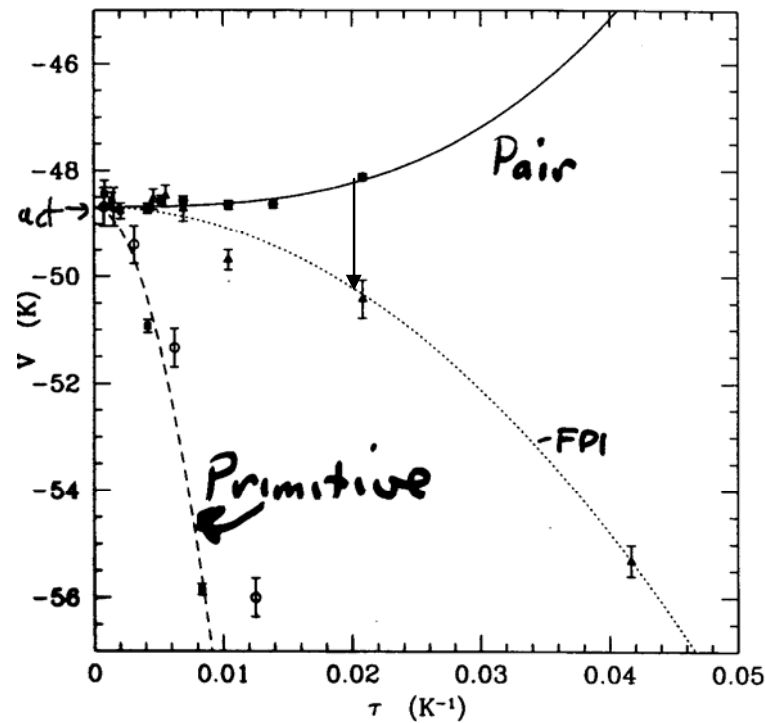- Compute exact action for each pair using FKPIMC

3A

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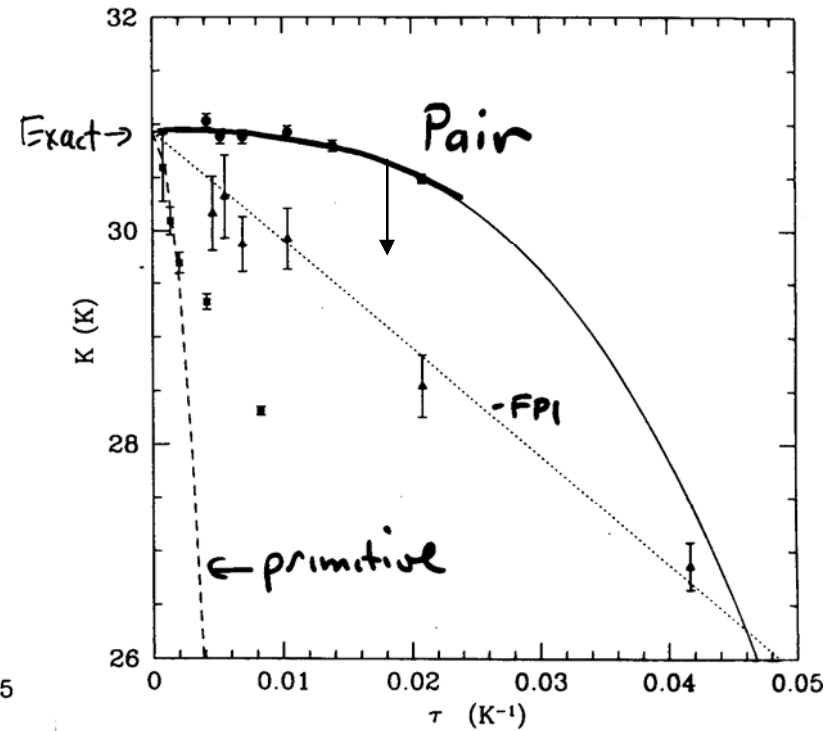- Pair action will have 1/6 the number of time slices.

Error in action

Needed time steps

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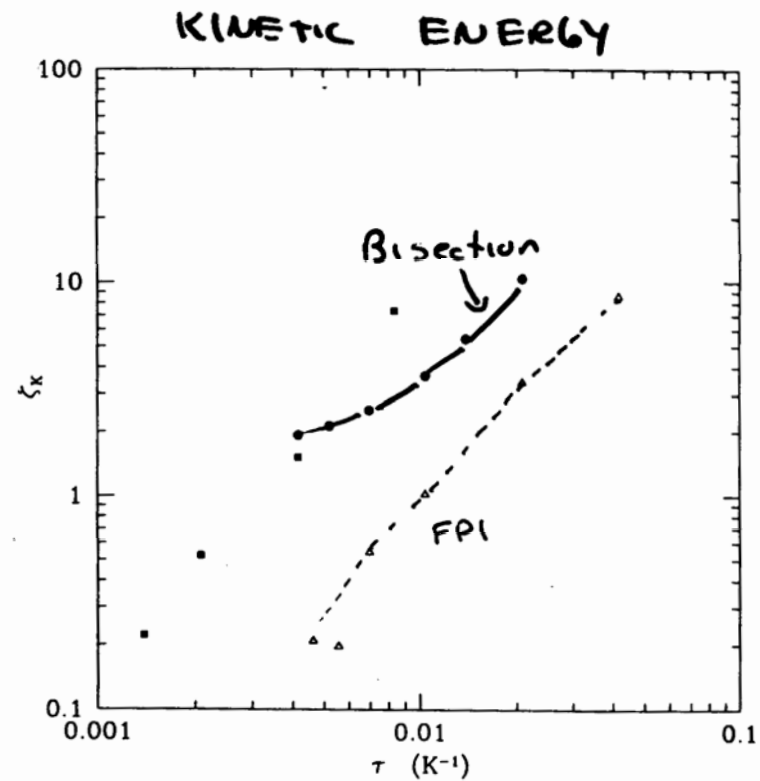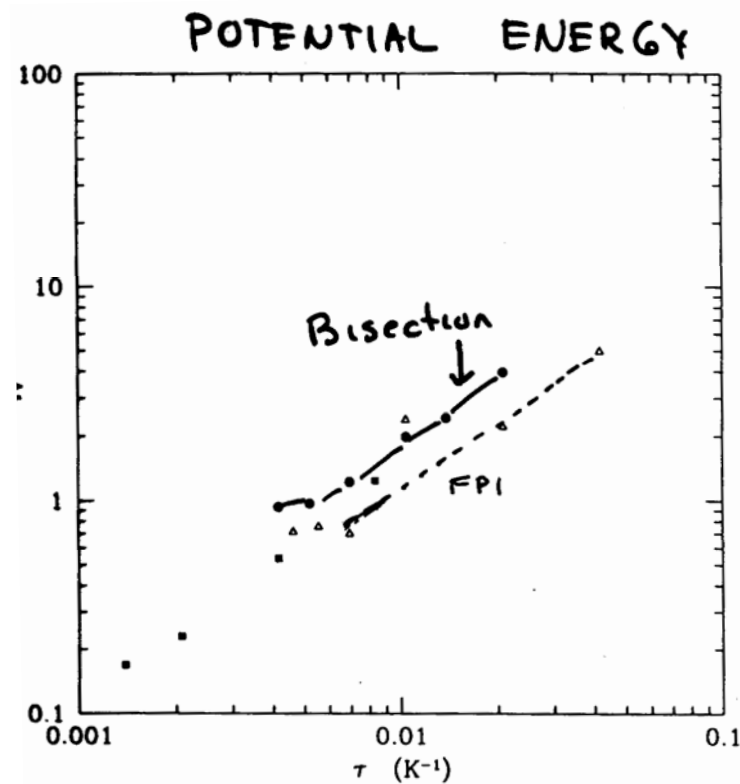


Potential converges much faster than the kinetic energy

# 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 $\tau$ then the residual energy has to be order $\tau^2$ and by the GFK the corrections must be $\tau^3$.
- Since $u \sim r^{-5}$ 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.

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

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

## Harmonic Oscillator

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

# 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 $H_o$. We want the "left-over" part to be smooth so commutator is small.

# 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:

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

- 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. <span style="color:orange">Why?</span>

- Polymers move slowly as number of <u>links</u> 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.

# Metropolis algorithm

Three key concepts:
1. Sample by using an ergodic random walk.
2. Determine equilibrium state by using detailed balance
3. Achieve detailed balance by using rejections.

**Detailed balance**: $\pi (s) P(s \rightarrow s') = \pi (s')P (s' \rightarrow s )$.

*Rate balance from s to s'.*

Put $\pi (s)$ into the master equation.

$$\sum_{s}\pi(s)P(s \rightarrow s') = \sum_{s}\pi(s')P(s' \rightarrow s) = \pi(s')\sum_{s}P(s' \rightarrow s) = \pi(s')$$

- Hence $\pi(s)$ is an eigenfunction.
- If $P(s \Rightarrow s')$ is ergodic then $\pi (s)$ is the unique steady state solution.

# General Metropolis MC

Metropolis achieves detailed balance by *rejecting* moves.

Break up transition probability into sampling and acceptance:

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

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

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

The optimal acceptance probability that gives detailed balance is:

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

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 "<u>bridge</u>": construct a path starting at $R_0$ and ending at $R_t$.
- How do we sample $R_{t/2}$?  GUIDING RULE. Probability is:

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

- Do an entire path by recursion from this formula.
- Related method: fourier path sampling.
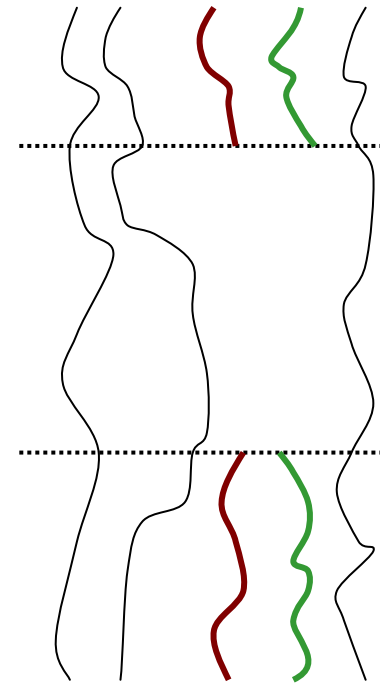
# How to sample a single slice.

- 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.

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

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

$$\sigma^2 = \lambda t / 2 = \left\langle \eta^2 \right\rangle$$

$$R_{t/2} = \frac{1}{2}\left(R_0 + R_t\right) + \lambda t \nabla U_s(R_{t/2}^0) + \eta$$

$$\overline{\overline{\sigma}}^2 = \lambda t / 2 \overline{\overline{I}} + (\lambda t)^2 \overleftarrow{\nabla} \overrightarrow{\nabla} U_s(R_{t/2}^0) = \left\langle \vec{\eta}\vec{\eta} \right\rangle$$

$$U_s(R) = \text{sampling potential}$$

# How to sample a Normal distribution
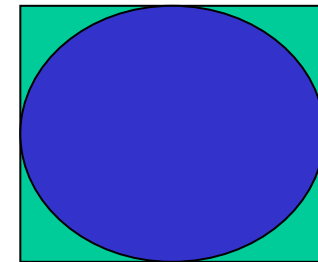
- Trick: generate 2 ndrn at a time: r=(x,y)

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

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

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

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

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

# Example of code to sample normal distribution

Normal distribution $\langle x \rangle = x_0$ and $\langle (x-x_0)^2 \rangle = \sigma^2$

```
1       x=sprng()-0.5
        y=sprng()-0.5
        r2=x*x+y*y
        if (r2>0.25) go to 1
        radius= sigma*sqrt (-2*ln(sprng())/r2)
        xnormal=x0+x*radius
        ynormal=y0+y*radius
```

- No trig functions
- Mixes up regularity of random numbers
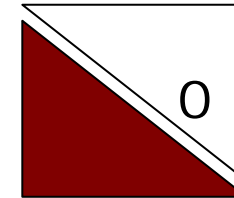- Efficiency of angle generation is $4/\pi$.
- Can get 2 ndrn's each time.

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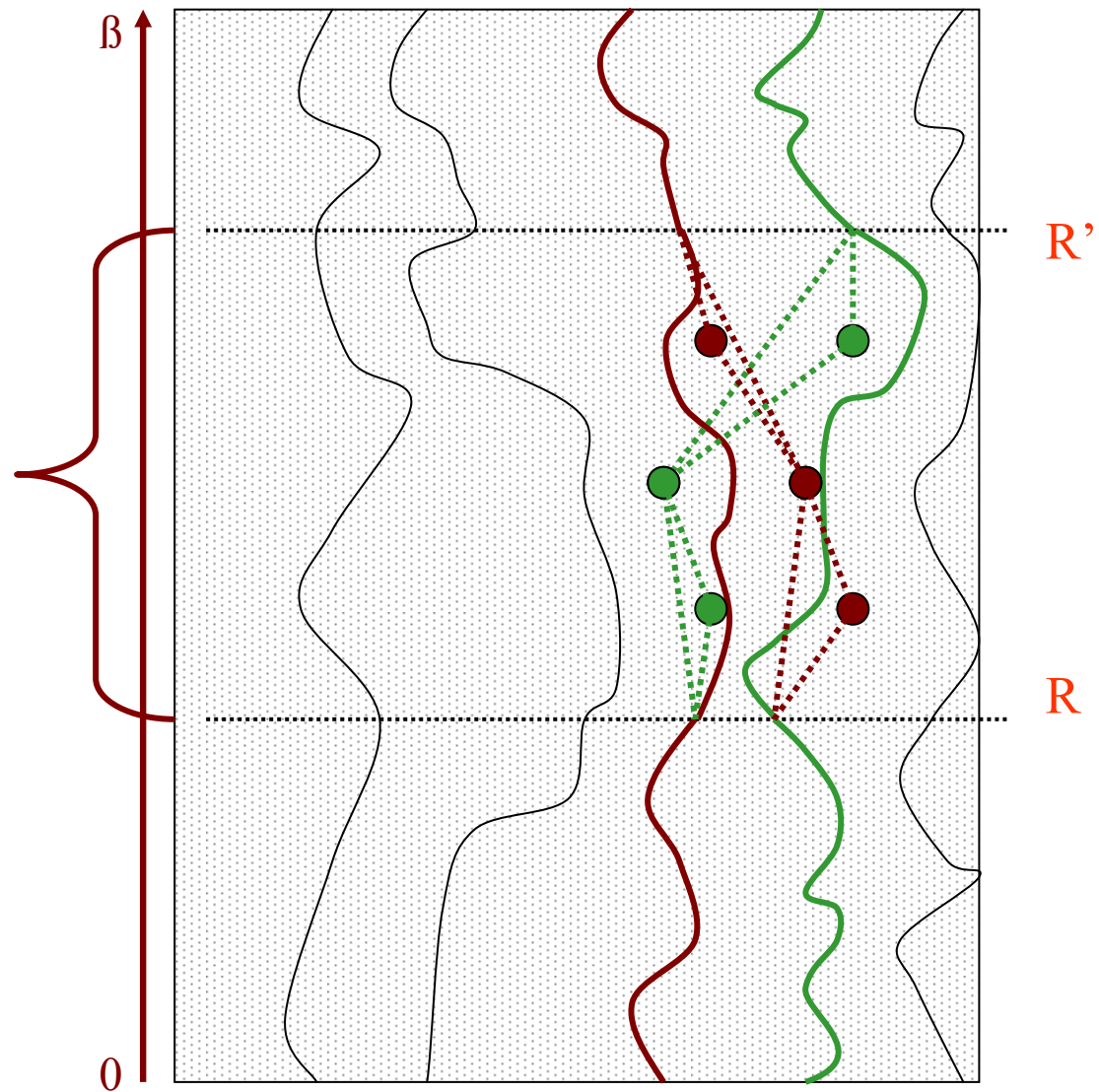  - Stop when you are at the desired level of precision.
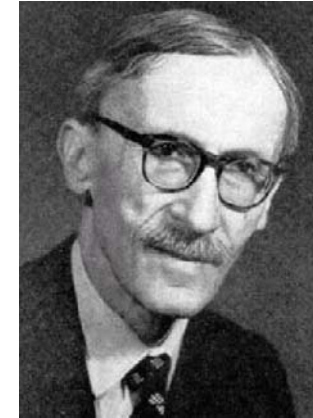


$$P(R_{t/2}) = \frac{\langle R_0 | e^{-tH/2} | R_{t/2} \rangle \langle R_{t/2} | e^{-tH/2} | R_t \rangle}{\langle R_0 | e^{-tH} | R_t \rangle}$$

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

$$\sigma_t^2 = \lambda t/2 = \langle \eta^2 \rangle$$

# 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
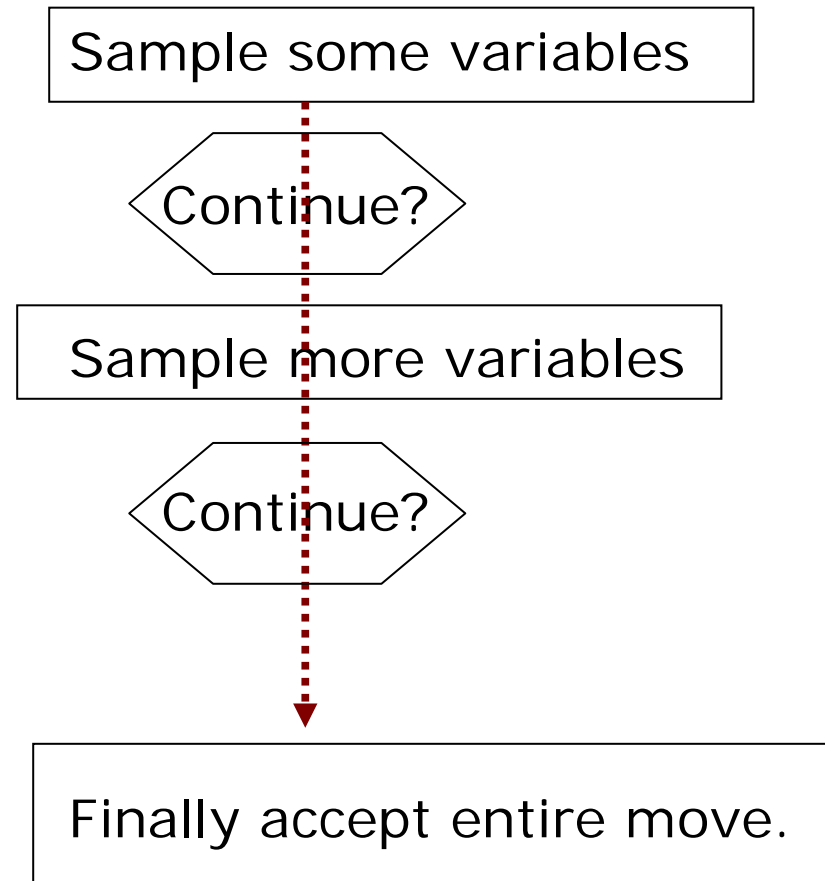
5. Accept or reject entire
   move

# Multilevel Metropolis/ Bisection

- Introduce an approximate level action and sampling.

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

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

- Only accept if move is accepted at all levels.

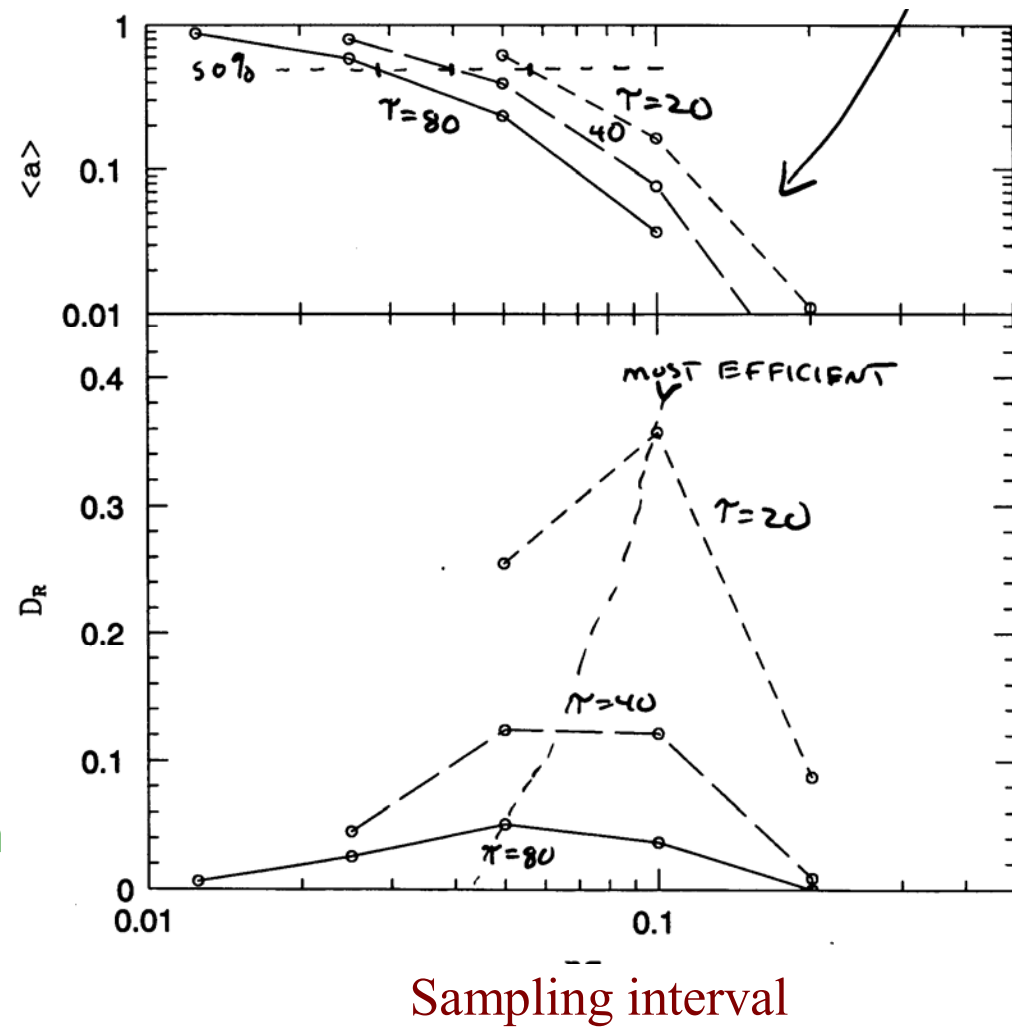- Allows one not to waste time on moves that fail from the start (first bisection).

| 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**



Sampling interval

# 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.*

- Development of "worm algorithms" for lattice systems.