UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

SMR.998a - 8

Research Workshop on Condensed Matter Physics
30 June - 22 August 1997
MINIWORKSHOP ON
QUANTUM MONTE CARLO SIMULATIONS OF LIQUIDS AND SOLIDS
30 JUNE - 11 JULY 1997
and
CONFERENCE ON
QUANTUM SOLIDS AND POLARIZED SYSTEMS
3 - 5 JULY 1997

"Path integral monte carlo simulations of atomic and molecular systems"

C. CHAKRAVARTY
Department of Chemistry
Indian Institute of Technology
Hauz Khas
New Delhi 110016
INDIA

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

PATH INTEGRAL MONTE CARLO SIMULATIONS OF ATOMIC AND MOLECULAR SYSTEMS

PATH INTEGRAL MONTE CARLO METHODS

- Finite temperature properties of quantum many-body systems
- Canonical ensemble but can be generalised to other ensembles
- Quantum-classical isomorphism
- Equilibrium static properties
- Exact for distinguishable quantum particles and bosons
- Approximations necessary for fermions
- Extracting dynamical information is problematic
- Monte Carlo, Molecular Dynamics and Langevin Dynamics

- Path Integral Representation of the Density Matrix
- Discretised Path Integral Representation
- Fourier Path Integral Representation
- Identical Particles
- Observables
- Transformation between ensembles
- Molecular Dynamics
- Ab initio Path Integral methods
- Relative efficiencies

PATH INTEGRAL REPRESENTATION OF THE DENSITY MATRIX

Canonical Partition function

$$\begin{aligned} Z &= Tr\{\exp(-\beta\hat{H})\} \\ &= \int dx \langle x|\exp(-\beta\hat{H})|x\rangle \quad , \ \beta = 1/k_B T \end{aligned}$$

Since $\exp(-\beta\hat{H}) = [\exp(-\frac{\beta}{M}\hat{H})]^M$, Inserting $M-1$ complete sets of coordinate states

$$Z = \int \prod_{i=0}^{M-1} dx_i \langle x_i|\exp(-\frac{\beta}{M}\hat{H})|x_{i+1}\rangle \ , \ \hat{H} = \hat{K} + \hat{V}$$

Provided $\epsilon = \beta/M$ is sufficiently small,

$$\exp(-\epsilon\hat{H}) = \exp(-\epsilon\hat{K})\exp(-\epsilon\hat{V}) + \exp(-0.5\epsilon^2[\hat{K},\hat{V}]) + \ldots$$

we obtain the Trotter approximation

$$\exp(-\beta\hat{H}) = \lim_{M\to\infty}[\exp(-\epsilon\hat{K})\exp(-\epsilon\hat{V})]^M$$

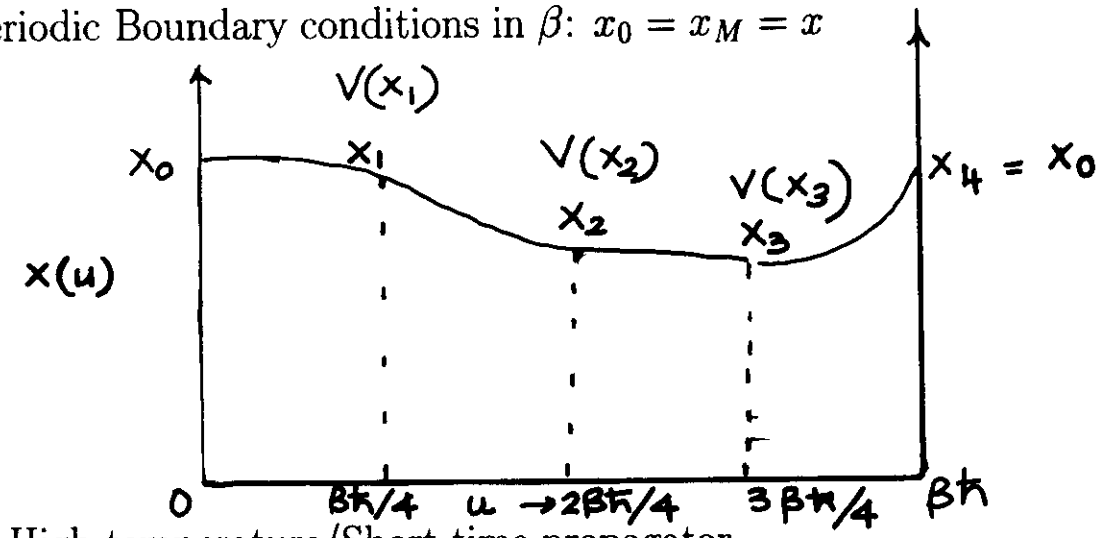
Semiclassical approximation for the high-temperature density matrix elements

$$\begin{aligned} \rho(x_i, x_{i+1}; \epsilon) &= \langle x_i|\exp(-\epsilon\hat{H})|x_{i+1}\rangle \\ &= \langle x_i|\exp(-\epsilon\hat{K})|x_{i+1}\rangle \exp(-\epsilon V(x_{i+1})) \\ &= \sqrt{\frac{m}{2\pi\epsilon\hbar}}\exp(-\frac{m(x_i - x_{i+1})^2}{2\epsilon\hbar^2})\exp(-\epsilon V(x_{i+1})) \end{aligned}$$

PARTITION FUNCTION

$$Z = \left(\frac{m}{2\pi\epsilon\hbar}\right) \int \prod_{i=0}^{M-1} \exp\left(-\frac{m}{2\epsilon\hbar^2} \sum_{i=0}^{M-1} (x_i - x_{i+1})^2 - \epsilon \sum_{i=0}^{M-1} V(x_i)\right) dx_0 \ldots dx_{M-1}$$

Periodic Boundary conditions in β: $x_0 = x_M = x$



High-temperature/Short-time propagator

$$\begin{aligned}
& \langle x_i | \exp(-(\beta/M)\hat{H}) | x_{i+1} \rangle \\
= \; & \langle x_i | \exp(-it\hat{H}/\hbar) | x_{i+1} \rangle, \qquad t = -i\beta\hbar \\
= \; & \sqrt{\frac{mM}{2\pi\beta\hbar}} \exp\left(-\frac{mM(x_i - x_{i+1})^2}{2\beta\hbar^2}\right) \exp(-(\beta/M)V(x_{i+1})) \\
= \; & \sqrt{\frac{mM}{2\pi\beta\hbar}} \exp\left\{\frac{-\beta}{M}\left(\frac{m}{2}\left(\frac{\Delta x}{\Delta u}\right)^2 + V(x_i)\right)\right\}
\end{aligned}$$

When $\Delta u \to 0$,

$$\begin{aligned}
Z &= \int \mathcal{D}(x(u)) \exp\left((-1/\hbar) \int_0^{\beta\hbar} \left(\frac{m}{2}\left[\frac{dx}{du}\right]^2 + V(x(u))\right) du\right) \\
&= \int \mathcal{D}(x(u)) \exp(-S(x(u)))
\end{aligned}$$

THE DISCRETISED PATH APROACH

Each path is represented by a set of coordinates $\{\mathbf{x}_0, \mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_M\}$ at equispaced points in imaginary time between 0 and $\beta\hbar$

PRIMITIVE APPROXIMATION

Simplest form of the high-temperature propagator

$$\exp(-\epsilon\hat{H}) \approx \exp(-\epsilon\hat{K})\exp(-\epsilon\hat{V})$$

has an error of the order ϵ^2.

The symmetrised form

$$\exp(-\epsilon\hat{H}) \approx \exp(-0.5\epsilon\hat{V})\exp(-\epsilon\hat{K})\exp(-0.5\epsilon\hat{V})$$

has an error of the order of ϵ^3.

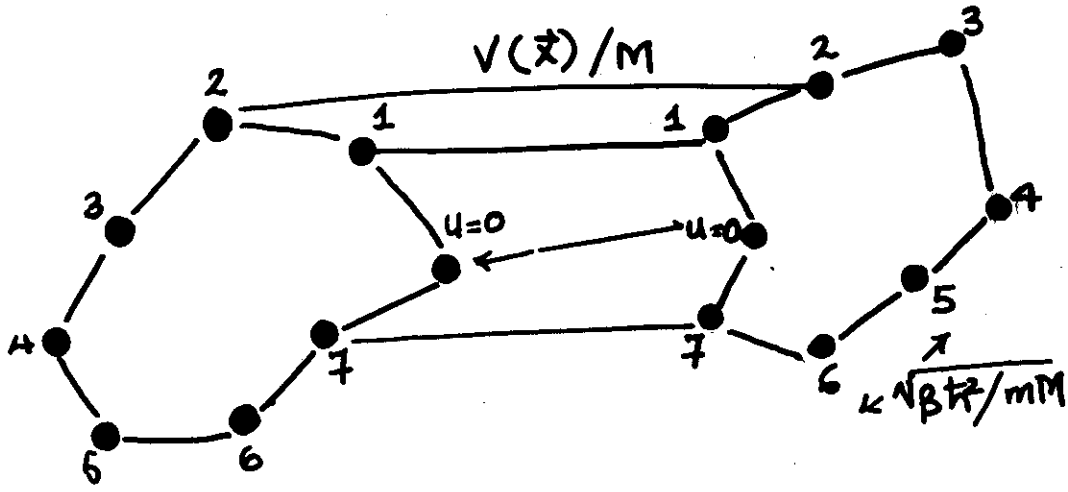
Partition function

$$Tr\{\exp(-\epsilon M(\hat{K}+\hat{V}))\} = Tr\{[\exp(-\epsilon\hat{K})\exp(-\epsilon\hat{V})]^M\} + \mathcal{O}(M\epsilon^3)$$

QUANTUM-CLASSICAL ISOMORPHISM

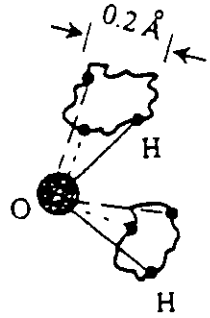
System of N interacting, distinguishable quantum particles is transformed to a classical, NM-particle system.

$$Z_{NM} = \left(\frac{m}{2\pi\epsilon\hbar}\right)^{3NM/2} \int \left(\prod_{i=0}^{M-1} d\mathbf{x}_i\right) \exp\left[\frac{-m}{2\epsilon\hbar^2}\sum_{i=0}^{M-1}(\mathbf{x}_i - \mathbf{x}_{i+1})^2 - \epsilon\sum_{i=0}^{M-1} V(\mathbf{x}_i)\right]$$

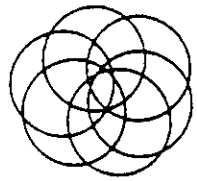


Quantum Particle	≡	Polymer chain
Position in imaginary time	≡	Bead
Thermal de Broglie wavelength $\sqrt{\beta\hbar^2/m}$	≡	Average radius of polymer chain

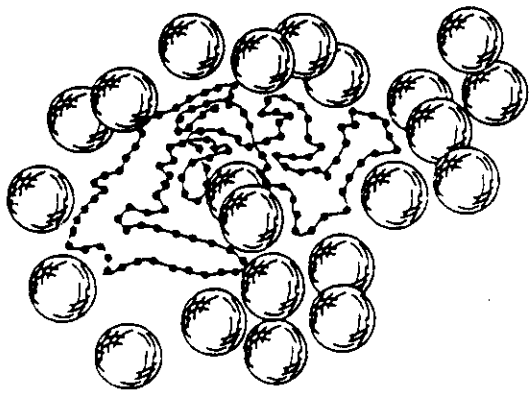
- Beads on different polymer chains can interact if they are on the same time slice i.e. the same point in imaginary time.
- Beads on the same chain can interact with adjacent beads by a harmonic interaction with force constant $\frac{Mm}{\beta\hbar^2}$



Water isomorph. The uncertainty in proton positions correspond to quantal librations at room temperature.



Typical configuration of the isomorphic He atom at 10 K with P = 6.



Typical configuration of e^- in liquid Xe.

Fig. 3. Isomorphic polymers representing quantum particles.

Barker, J.C.P, 1979
D. Chandler & P. Wolynes
J.C.P., 1981

HIGHER-ORDER PROPAGATORS

$$Tr\{\exp(-\epsilon M(\hat{K}+\hat{V}))\} = Tr\{[\exp(-\epsilon\hat{K})\exp(-\epsilon\hat{V}_{eff})]^M\} + \mathcal{O}(M\epsilon^5)$$

where $\hat{V}_{eff} = \hat{V} + (\beta/24M)[\hat{V},[\hat{K},\hat{V}]]$.

In the coordinate representation,

$$\hat{V}_{eff}(\mathbf{x}) = V(\mathbf{x}) + (\beta^2\hbar^2/24mM^2)\sum_{i=1}^{N}(\frac{\partial V}{\partial x_i})^2$$

where the second term is a quantum correction to the bare potential $V(\mathbf{x})$.

Trotter scaling: M/β must be of the order of the characteristic frequencies of the system.

Systematic errors $\propto 1/M^2$ primitive approximation

$\propto 1/M^4$ first-order approximation

Takahashi & Imada
J. Phys. Soc. Jpn, '84

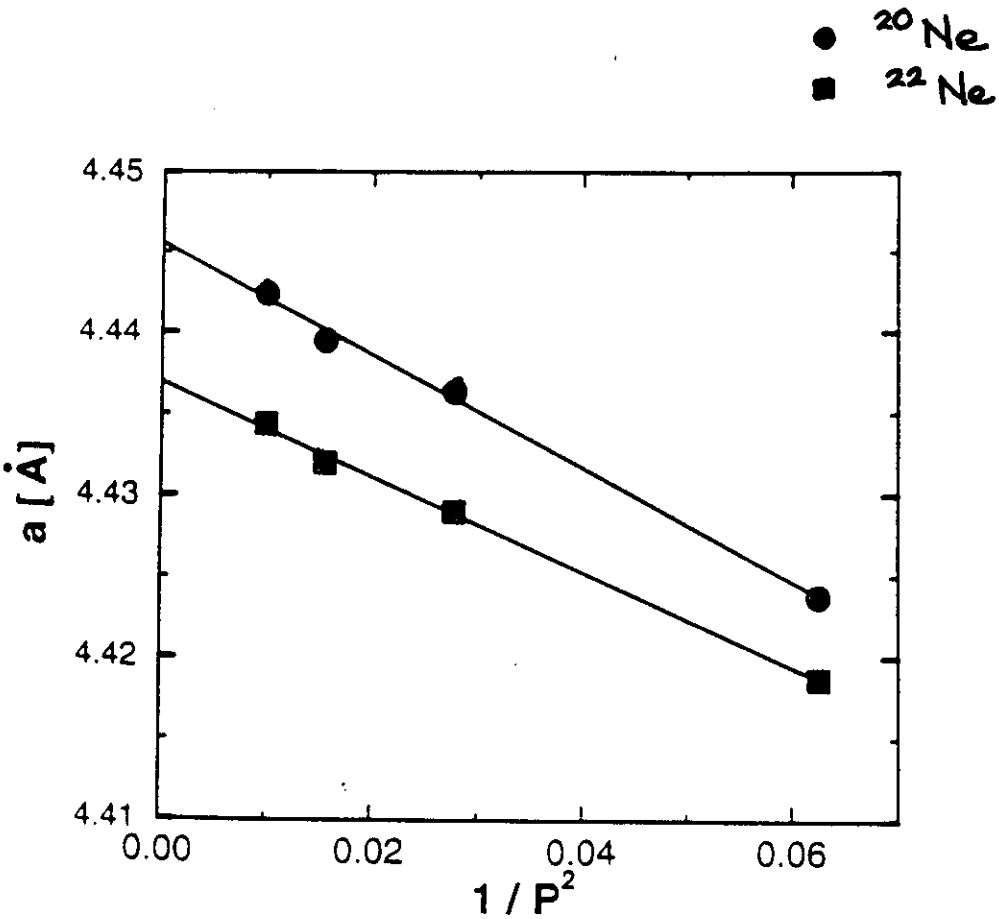


FIG. 6. Trotter scaling plot for the lattice constant a of solid neon. The upper curve corresponds to ^{20}Ne, the lower curve to ^{22}Ne at $T = 16$ K. Symbols: PIMC results, error bars are smaller than symbol sizes.

Muser et al.
Phys. Rev. B , '93

PAIR-PRODUCT ACTION

Feynman-Kac formula

$$\langle \mathbf{x}| \exp\{-\beta \hat{H}\} |\mathbf{x}'\rangle = \int \mathcal{D}(\mathbf{x}(u)) \exp\{-S(\mathbf{x}(u))\}$$

Contribution to the action from inter-particle interactions

$$\exp\{-U(\mathbf{x}, \mathbf{x}'; \beta)\} = \frac{\langle \mathbf{x}| \exp\{-\beta \hat{H}\} |\mathbf{x}'\rangle}{\langle \mathbf{x}| \exp\{-\beta \hat{K}\} |\mathbf{x}'\rangle}$$

Path integral representation

$$\exp\{-U(\mathbf{x}, \mathbf{x}'; \beta\} = \frac{\int \mathcal{D}(\mathbf{x}(u)) \exp\{-\int_0^{\beta\hbar} (K(x(u)) + V(x(u))) \, du\}}{\int \mathcal{D}(\mathbf{x}(u)) \exp\{-\int_0^{\beta\hbar} K(x(u)) \, du\}}$$

Average over random walks of the free particles:

$$\exp\{-U(\mathbf{x}, \mathbf{x}'; \beta\} = \left\langle \exp\{-\int_0^{\beta\hbar} V(x(u)) \, du\} \right\rangle_{RW}$$

For a **pair of atoms** i and j

$$\exp\{-u_2(\mathbf{x}_{ij}, \mathbf{x}'_{ij}; \beta)\} = \langle \exp\{-\int_0^{\beta\hbar} v_2(\mathbf{x}_i - \mathbf{x}_j) \, du\}$$

can be evaluated very accurately using a number of different techniques, such as matrix squaring, eigenfunction expansion and Monte Carlo.

Action along a path $\mathbf{x}(u)$ is a sum of the exact action of the possible pairs of particles.

$$U(\mathbf{x}, \mathbf{x}'; \beta) \approx \sum_{i>j} u_2(\mathbf{x}_{ij}, \mathbf{x}'_{ij}; \beta)$$

- Very efficient for pair potentials with a steeply varying repulsive wall.
- Ignores three-body and higher-order correlations
- Requires the exact action to be stored as a three-dimensional look-up table at a given temperature.

D.M. Ceperley,
Rev. Mod. Phys., '95

NORMAL MODES OF THE QUANTUM POLYMER

- For a single degree of freedom, the harmonic intrapolymer potential is given by

$$V_p = (mM/2\beta\hbar^2) \sum_{l=1}^{M} (x_l - x_{l+1})^2$$

- Normal coordinates, $\{Q_k\}$, $k = 1$ to M,

$$Q_k = (1/\sqrt{M}) \sum_{l=1}^{M} x_l \exp(2\pi i k l/M)$$

- The kinetic energy contribution to the path action

$$\int_0^{\beta\hbar} \frac{m}{2} \left(\frac{d\,x(u)}{dt}\right)^2 du = \frac{2mM}{\beta\hbar^2} \sum_{k=1}^{M} |Q_k|^2 \sin^2(\pi k/M)$$

- The zero-frequency mode, $k = 0 = M$, centre-of-mass motion.

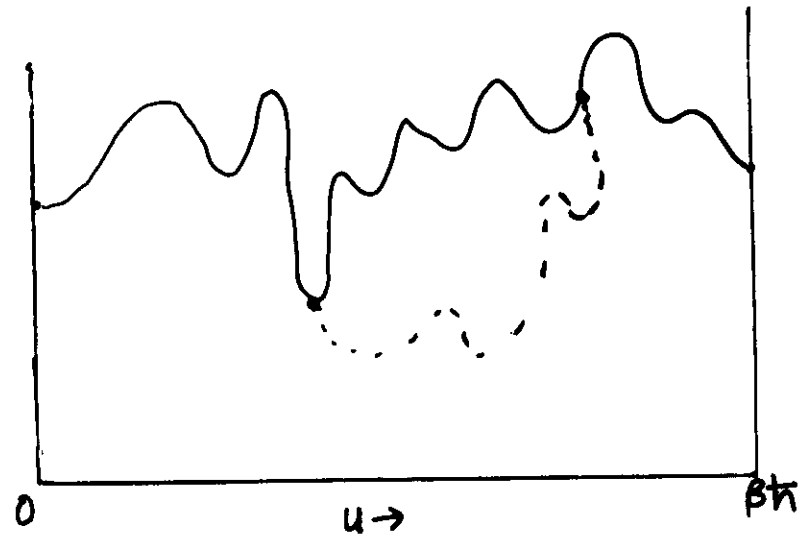
- All other normal modes mode, are Gaussian distributed for a free particle with variance

$$\sigma_k^2 = \beta\hbar^2/4mM \sin^2(\pi k/M)$$

- The potential energy term will couple these normal modes and cause distortions from the free-particle distribution.

Runge & Chester
Phys. Rev. B, '85

BISECTION ALGORITHM



- Trial paths are most likely to be rejected due to changes in the midpoint of the path.
- Grow a new segment of the path of length m in stages or levels.
- No. of levels, l, such that $m = 2^l$.
- Product rule property

$$\rho(\mathbf{x}, \mathbf{x}'; \beta) = \int d\mathbf{x}_m \rho(\mathbf{x}, \mathbf{x}_m; \beta/2)\rho(\mathbf{x}_m, \mathbf{x}'; \beta/2)$$

- Conditional probability

$$\Pi_1(\mathbf{x}_m; \mathbf{x}, \mathbf{x}') = \frac{\rho(\mathbf{x}, \mathbf{x}_m; \beta/2)\rho(\mathbf{x}_m, \mathbf{x}'; \beta/2)}{\rho(\mathbf{x}, \mathbf{x}'; \beta)}$$

Density matrix element

$$\rho(\mathbf{x}, \mathbf{x}'; \beta)$$
$$= \int d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_M \rho(\mathbf{x}, \mathbf{x}_1; \beta/M)\rho(\mathbf{x}_1, \mathbf{x}_2; \beta/M) \ldots \rho(\mathbf{x}_{M-1}, \mathbf{x}'; \beta/M)$$

can be rewritten using conditional probabilities

$$\rho(\mathbf{x}, \mathbf{x}'; \beta)$$
$$= \Pi_1(\mathbf{x}_{M/2}; \mathbf{x}, \mathbf{x}')\Pi_2(\mathbf{x}_{M/4}; \mathbf{x}, \mathbf{x}_{M/2})\Pi_2(\mathbf{x}_{3M/4}; \mathbf{x}_{M/2}, \mathbf{x}') \ldots$$

Approximation for conditional probability distributions

$$\rho(\mathbf{x}_i, \mathbf{x}_f; u) \approx \pi(\mathbf{x}_i, \mathbf{x}_f; u) = \rho_{fp}(\mathbf{x}_i, \mathbf{x}_f; u) \exp(-0.5u(V(\mathbf{x}_i) + V(\mathbf{x}_f))$$

where ρ_{fp} is the free particle density matrix. This choice of π ensures that the weights associated with a given configuration in Z_{NM} unchanged.

Algorithm

1. The end-points of the path are $\mathbf{x}_i$ at $u = n\beta/2^{l-1}$ and $\mathbf{x}_f$ at $u = (n+1)\beta/2^{l-1}$. The old value of the midpoint of this segment of the path is denoted by $\mathbf{x}_m$.

2. The trial value of the midpoint $\mathbf{x}_t$ is sampled with probability

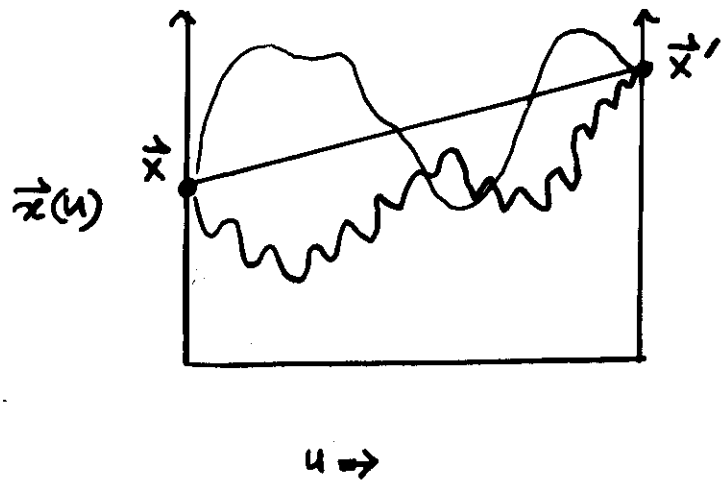
$$T_l(\mathbf{x}_t) = \frac{\rho_{fp}(\mathbf{x}_i, \mathbf{x}_t; \beta/2^l)\rho_{fp}(\mathbf{x}_t, \mathbf{x}_f; \beta/2^l)}{\rho_{fp}(\mathbf{x}_i, \mathbf{x}_f; \beta/2^{l-1})}$$

3. Acceptance probability: $min\{1, \exp(-\frac{\beta}{2^{l-1}}(V(\mathbf{x}_t) - V(\mathbf{x}_m))\}$

Fourier Path Integral Representation

$$\langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \langle \vec{x} | e^{-it\hat{H}/\hbar} | \vec{x}' \rangle, \quad t = -i\beta\hbar$$

≡ Propagator in imaginary time, $u = it$, going from $\vec{x}$ at $u = 0$ to $\vec{x}'$ at $u = \beta\hbar$



Classical free particle path: $x_c(u) = \vec{x} + (\vec{x}' - \vec{x}) \dfrac{u}{\beta\hbar}$

Classical path in a potential: least action path

Quantum paths can be described as <u>fluctuations about reference path</u>:

$$\vec{x}(u) = \vec{x}_c(u) + \sum_{k=1}^{k_{max}} \vec{a}_k \sin\left(\frac{k\pi u}{\beta\hbar}\right)$$

$\vec{x}(0) = \vec{x}(\beta\hbar) = \vec{x}$ for acyclic path

$\vec{x}(0) = \vec{x}$, $\vec{x}(\beta\hbar) = \vec{x}'$ for off-diagonal density matrix

Path: $\vec{x}(u) = \vec{x} + (\vec{x}' - \vec{x})\frac{u}{\beta\hbar} + \sum_{k=1}^{k_{max}} \vec{a}_k \sin\left(\frac{k\pi u}{\beta\hbar}\right)$

Action: $S(\vec{x}(u)) = \frac{-1}{\hbar}\int_0^{\beta\hbar}\left[\frac{m}{2}\left(\frac{dx}{du}\right)^2 + V(x(u))\right]du$

Density matrix element:

$$\rho(\vec{x}, \vec{x}'; \beta) = \rho_{fp}(\vec{x}, \vec{x}'; \beta)\frac{\int d\vec{x}\, d\vec{a}\, \exp\left[-\sum_k \frac{a_k^2}{2\sigma_k^2} - \beta V_{eff}(\vec{x}, \vec{a})\right]}{\int d\vec{a}\, \exp\left[-\sum_k \frac{a_k^2}{2\sigma_k^2}\right]}$$

Free particle density matrix:

$$\rho_{fp}(\vec{x}, \vec{x}'; \beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} e^{-\frac{m}{2\beta\hbar^2}(\vec{x} - \vec{x}')^2}$$

Length scale associated with a Fourier coefficient of order k:

$$\sigma_k = \sqrt{\frac{2\beta\hbar^2}{m\pi^2 k^2}}$$

Path averaged Potential

$$V_{eff} = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} V(\vec{x}(u))\, du$$

Partition Function:

$$Z = J \int d\vec{x}\, d\vec{a}\, \exp\left\{ - \sum_k \frac{a_k^2}{2\sigma_k^2} - \beta V_{eff}(\vec{x}, \vec{a}) \right\}$$

- Quantum-classical isomorphism

- Metropolis Monte Carlo:

  Variables: 3N spatial coordinates
  $3Nk_{max}$ Fourier coefficients

  Weights: $W(\vec{x}, \vec{a}) = \exp\left(- \sum_k \frac{a_k^2}{2\sigma_k^2} - \beta V_{eff} \right)$

- Kinetic energy term decoupled into contributions from $3Nk_{max}$ independent degrees of freedom.

- Fourier coefficients obey a Gaussian distribution in the absence of a potential.

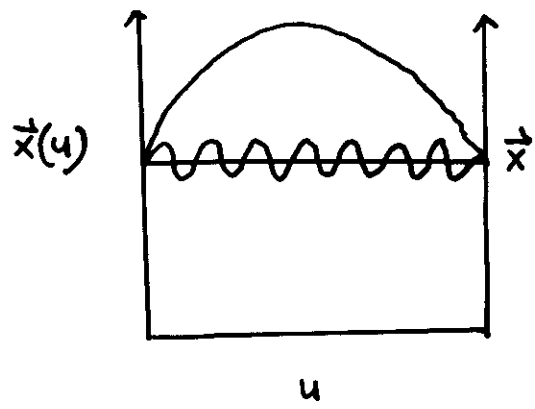
- Length scales decrease quite rapidly with the order of the fluctuation variable.

PARTIAL AVERAGING

$$k \to \infty \quad , \quad \sigma_k^2 = \frac{2\beta\hbar^2}{m k^2 \pi^2} \to 0$$

Higher order Fourier coefficients represent very small length scale fluctuations

$\Leftrightarrow$ changing a_k when k is large will make more difference to the kinetic than the potential energy



$\Leftrightarrow$ if k is large, assume Fourier coefficient to be a purely Gaussian variable.

$$Z = J\int d\vec{x}\, d\vec{a}\; e^{-\sum_{k}^{k_{max}} \frac{a_k^2}{2\sigma_k^2}}\; e^{-\sum_{k>k_{max}} \frac{a_k^2}{2\sigma_k^2}}\; e^{-\beta V_{eff}(\vec{x},\vec{a})}$$

$$= J\int d\vec{x}\, d\vec{a}\; e^{-\sum_{k}^{k_{max}} \frac{a_k^2}{2\sigma_k^2}} \left\langle e^{-\beta V_{eff}(\vec{x},\vec{a})} \right\rangle_G$$

$$\vec{x}(u) = \vec{x}_c(u) + \sum_{k=1}^{k_{max}} \vec{a}_k \sin\left(\frac{k\pi u}{\beta\hbar}\right) + \sum_{k>k_{max}} \vec{a}_k \sin\left(\frac{k\pi u}{\beta\hbar}\right)$$

$$\sum_{k>k_{max}} a_k \sin\left(\frac{k\pi u}{\beta\hbar}\right) = \sum_{\ell} b_\ell \lambda_\ell = p$$

$\equiv$ linear combination of Gaussian variables results in single Gaussian variable p of variance $\sigma^2(u) = \sum_i \lambda_i^2 \sigma_i^2$

$$\left\langle e^{-\beta V_{eff}} \right\rangle_G = \int dp\, e^{-\frac{p^2}{2\sigma^2(u)}} e^{-\beta V_{eff}(x(u)+p)}$$

$$\sigma^2(u) = \frac{\beta\hbar^2}{m}\left[u(1-u) - \frac{2}{\pi^2}\sum_{k=1}^{k_{max}} \frac{\sin^2\left(\frac{k\pi u}{\beta\hbar}\right)}{k^2}\right]$$

$$\left\langle \exp\left(-\beta V_{eff}\right)\right\rangle_G \geq \exp\left(-\beta \langle V_{eff}\rangle_G\right)$$

High-order fourier coefficients, $k > k_{max}$, result in a Gaussian averaging over $\langle V_{eff}\rangle_G$.

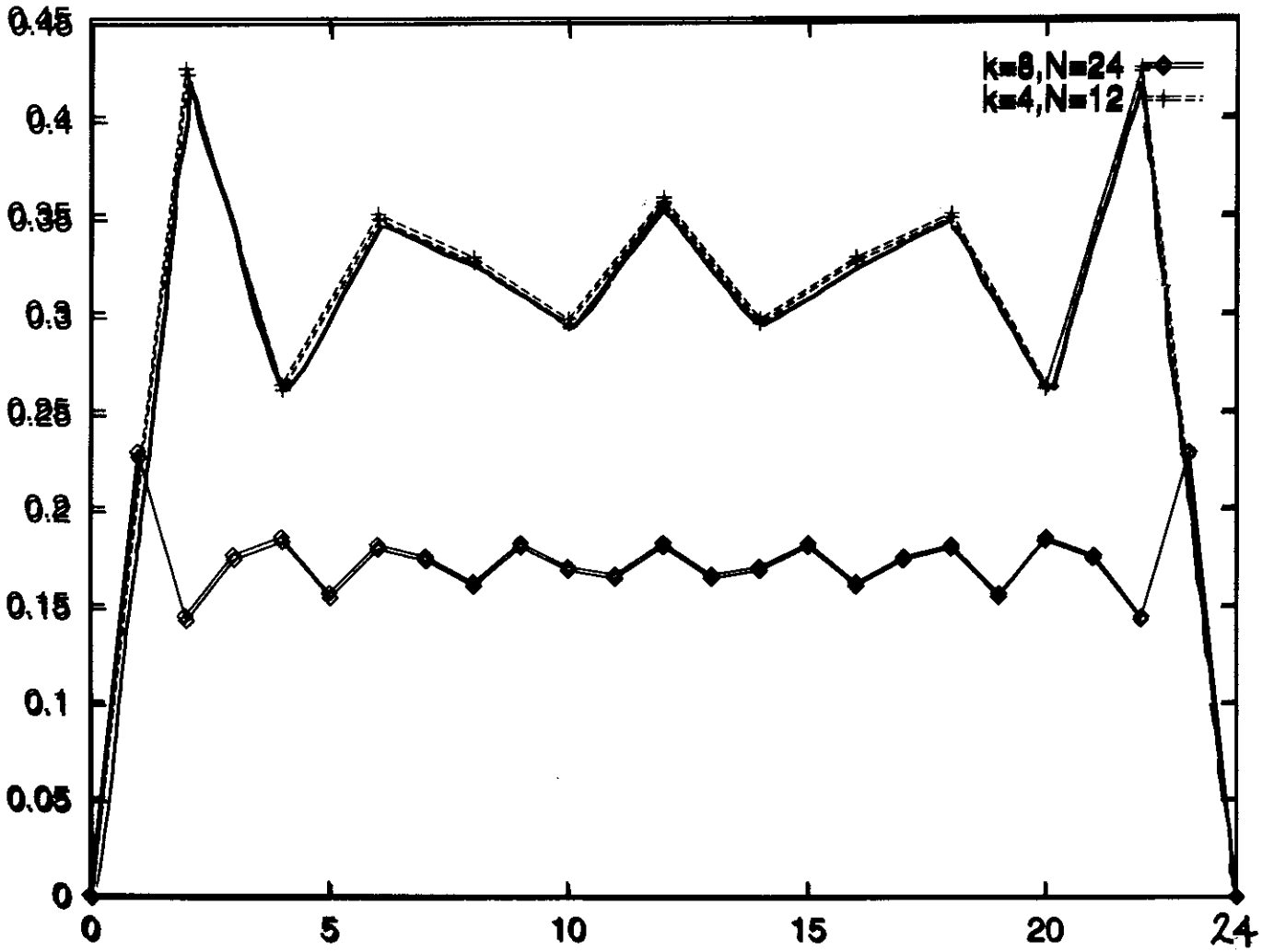
$$V_{eff} = \int dp\, e^{-p^2/2\sigma^2(u)} \int_0^{\beta\hbar} du\, V(x(u)+p)$$

$$= \int dp\, e^{-p^2/2\sigma^2(u)} \sum_{i=0}^{N_q} \Delta u\, V(x(u_i)+p)$$

$$= \sum_i \Delta u \int dp\, e^{-p^2/2\sigma^2(u_i)} V(x(u_i)+p)$$

$$= \sum_{i=1}^{N_q} \Delta u \left[V(x(u_i)) + \sum_{j=1}^{3N} \frac{1}{2}\sigma^2(u_i) V_{jj}(x(u_i))\right]$$

Quantum Correction to Potential.



$\sigma^2(u)$

T = 6K

m = 2. a.m.u.

Identical Particle Exchange

Indistinguishable particles: $\rho_I(\vec{x}, \vec{x}'; \beta)$

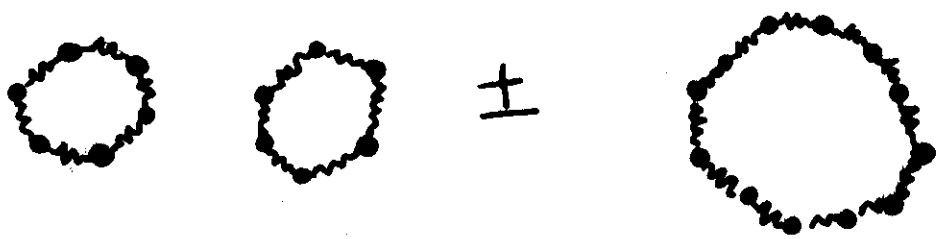
Distinguishable particles: $\rho_D(\vec{x}, \vec{x}'; \beta)$

$$\rho_I(\vec{x}, \vec{x}'; \beta) = \frac{1}{N!} \sum_P \xi^P \rho_D(\vec{x}, P\vec{x}'; \beta)$$

Bosons: $\xi^P = +1$
Fermions: $\xi^P = +1$ even permutations
-1 odd permutations

$$\rho_D(\vec{x}, P\vec{x}; \beta) = \int d\vec{x}\, \rho_{fp,D}(\vec{x}, P\vec{x}; \beta) \int d\vec{\alpha}\, e^{-\sum_k \frac{a_k^2}{2\sigma_k^2} - \beta V_{eff}(\vec{x}, \vec{\alpha}, P)}$$

- Paths contributing to $\rho_I(\vec{x}, \vec{x}'; \beta)$ can end at any permutational variant of $\vec{x}'$.
- Identity ± Pair exchange



Weight of non-identity permutations

$$\rho_{free}(\vec{x}, P\vec{x}; \beta) = \prod_{i=1}^{3N} \sqrt{\frac{m}{2\pi\beta\hbar^2}} \exp\left[-\frac{m}{2\beta\hbar^2} (x_i - Px_i)^2 \right]$$

$\beta \to 0$, $T \to \infty$: Only the identity permutation survives

$\beta \to \infty$, $T \to 0$: All permutations equally probable

$0 < \beta < \infty$: Pair exchanges
Cyclic permutations of three particles
" " " four " etc.

Partition Functions:

$$Z = \sum_P \xi^P \int d\vec{x}\, d\vec{a}\; e^{-S(\vec{x}, \vec{a}, P)}$$

Bosons: must sample over discrete space of permutations

Fermions: 'sign' problem

Bosonic Systems

- Necessary to make joint path and permutation moves.
- Use bisection but add a zeroth level for sampling permutations.
- Build up a table of probabilities of free particle permutational exchanges.
- Probable permutations are those involving atoms which are within a thermal wavelength of the exchanging partner.

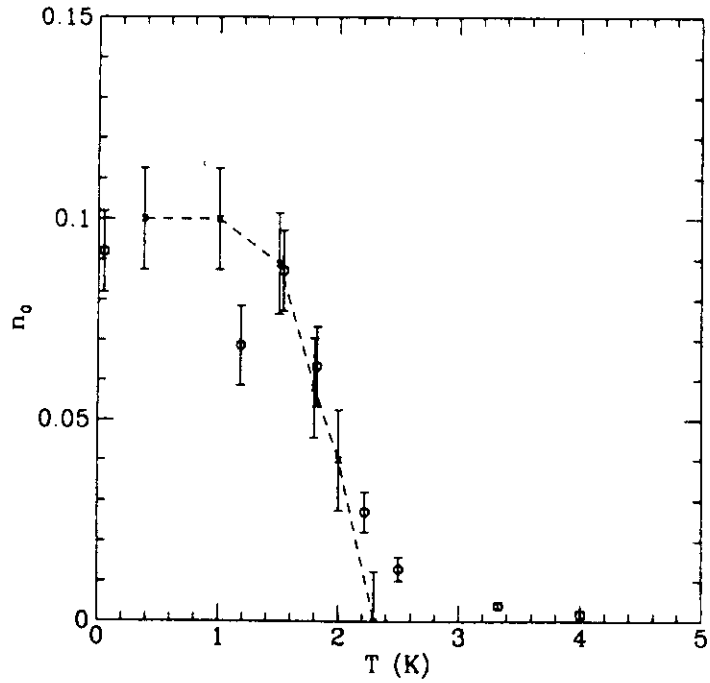


FIG. 23. The condensate fraction in ^{4}He as estimated from PIMC at SVP as a function of temperature.

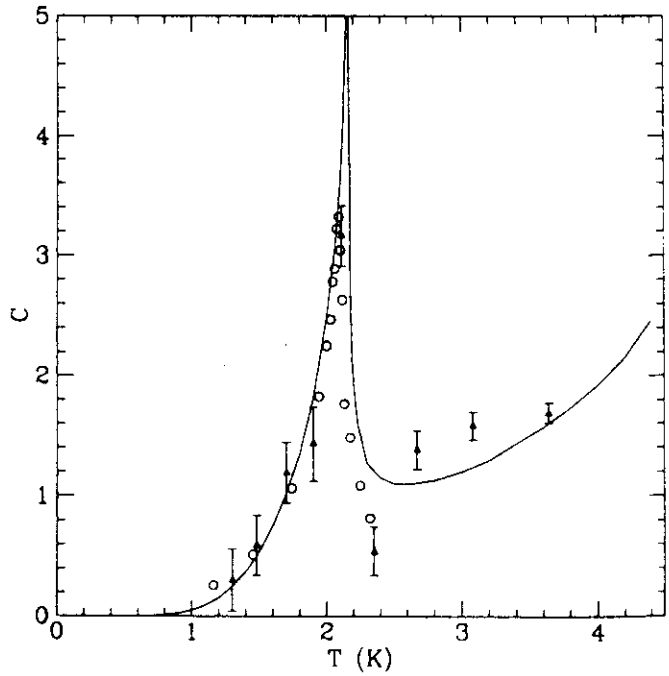


FIG. 11. The specific heat of ^{4}He: solid line, experiment at saturated vapor pressure (Wilks, 1967); triangles with error bars, PIMC calculations (Ceperley and Pollock, 1986); open circles, Feynman-Kikuchi model with 20^3 sites (Elser, 1984). In Elser's calculation, only the fluctuation term in the specific heat has been included, and the temperature has been scaled to match the experimental transition temperature.

MOLECULAR DYNAMICS

Partition function of N interacting, distinguishable quantum particles with Trotter index M

$$Z_{NM} = \left(\frac{m}{2\pi\epsilon\hbar}\right)^{3NM/2} \int \left(\prod_{i=0}^{M-1} d\mathbf{x}_i\right) \exp\left[\frac{-m}{2\epsilon\hbar^2} \sum_{i=0}^{M-1} (\mathbf{x}_i - \mathbf{x}_{i+1})^2 - \epsilon \sum_{i=0}^{M-1} V(\mathbf{x}_i)\right]$$

Introducing NM classical particles, each of fictitious mass m'_j and momentum p'_j one can write a Lagrangian

$$\mathcal{L} = \sum_{j=1}^{3NM} \frac{p'^2_j}{2m'_j} - \frac{m}{2\epsilon\hbar^2} \sum_{i=0}^{M-1} (\mathbf{x}_i - \mathbf{x}_{i+1})^2 - \frac{1}{M} \sum_{i=0}^{M-1} V(\mathbf{x}_i)$$

- Configurational averages will be exactly the same as those obtained from an MC scheme
- Dynamics will be entirely fictitious and unrelated to the true quantum dynamics.
- Quantum statistics cannot be incorporated
- Ergodicity is problematic specially for high Trotter numbers; multiple time-step methods, Nose-Hoover chains etc.
- Higher-order propagators harder to use because gradient of the action is required.
- Can be very efficiently coupled with Car-Parinello codes for obtaining the ground electronic states.

AB INITIO PATH INTEGRAL METHODS

The Hamiltonian for a molecular system

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

The electronic Hamiltonian,

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

The nuclear Hamiltonian,

$$\hat{H}_n = \hat{T}_n + \hat{V}_{nn}$$

The Born-Oppenheimer electronic wavefunctions $\phi_e(\mathbf{r};\mathbf{R})$

$$\hat{H}_e\phi_e = V_e(\mathbf{R})\phi_e$$

$V_e(\mathbf{R})$: electronic potential energy surface on which the nuclei move .
Complete coordinate basis: $|\mathbf{r}\rangle|\mathbf{R}\rangle$
Mixed basis: $|\phi\rangle|\mathbf{R}\rangle$

Partition function evaluated in the mixed basis:

$$Z = \int d\mathbf{R} \sum_{\alpha} \langle \mathbf{R} | \langle \phi_\alpha | \exp\{-\beta(\hat{H}_e + \hat{H}_n)\} | \phi_\alpha \rangle | \mathbf{R} \rangle$$

Trotter approximation

$$Z = \int d\mathbf{R} \sum_{\alpha} \langle \mathbf{R} | \langle \phi_\alpha | [\exp\{-(\beta/M)(\hat{H}_e + \hat{H}_n)\}]^M | \phi_\alpha \rangle | \mathbf{R} \rangle$$

Inserting M-1 complete sets of states $|\mathbf{X}_j\rangle = |\mathbf{R}_j\rangle|\phi_{\alpha(j)}\rangle$

$$\int (\prod_j d\mathbf{R}_j) \sum_{\alpha(1)} \sum_{\alpha(2)} \cdots \sum_{\alpha(M)} \rho(\mathbf{X}, \mathbf{X}_1; \epsilon)\rho(\mathbf{X}_1, \mathbf{X}_2; \epsilon) \ldots \rho(\mathbf{X}_{M-1}, \mathbf{X}; \epsilon)$$

High temperature density matrix element

$$\rho(\mathbf{X}_i, \mathbf{X}_j; \epsilon) = \int d\mathbf{R}_j \sum_{\alpha(j)} \langle \mathbf{R}_j | \langle \phi_{\alpha(j)} | \exp\{-\epsilon(\hat{H}_n + \hat{H}_e)\} | \phi_{\alpha(j)} \rangle | \mathbf{R}_j \rangle$$

$$= \int d\mathbf{R}_j \sum_{\alpha(j)} \langle \mathbf{R}_j | \langle \phi_{\alpha(j)} | \exp(-\epsilon \hat{T}_n) | \phi_{\alpha(i)} \rangle | \mathbf{R}_i \rangle \exp(-\epsilon(V_{\alpha(i)}(\mathbf{R}_i) + V_{nn}(\mathbf{R}_i))$$

Coupling of BO states:

$$\langle \phi_{\alpha(j)} | \exp(-\epsilon \hat{T}_n) | \phi_{\alpha(i)} \rangle = \langle \phi_{\alpha(j)} | 1 - \epsilon \hat{T}_n + 0.5\epsilon^2 \hat{T}_n^2 + \ldots | \phi_{\alpha(i)} \rangle.$$

Born-Oppenheimer Partition function in the primitive approximation

$$Z = \sum_{\alpha} \int (\prod_j d\mathbf{R}_j) \exp\{-\frac{m_n}{2\epsilon\hbar^2}(\mathbf{R}_i - \mathbf{R}_j)^2 - \epsilon V_\alpha(\mathbf{R}_i) - \epsilon V_{nn}(\mathbf{R}_i)\}$$

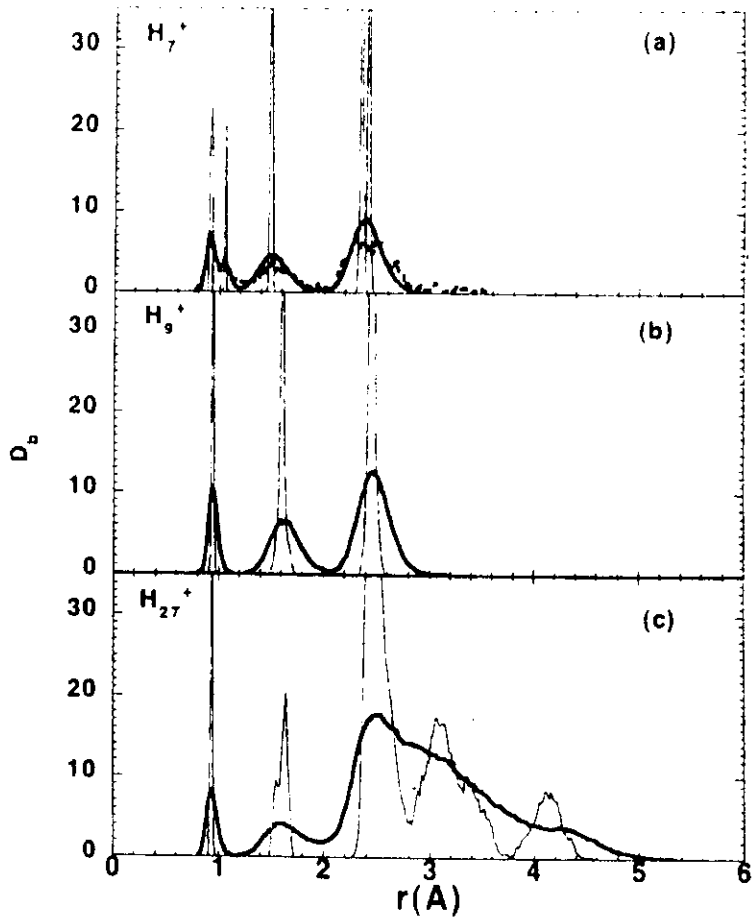
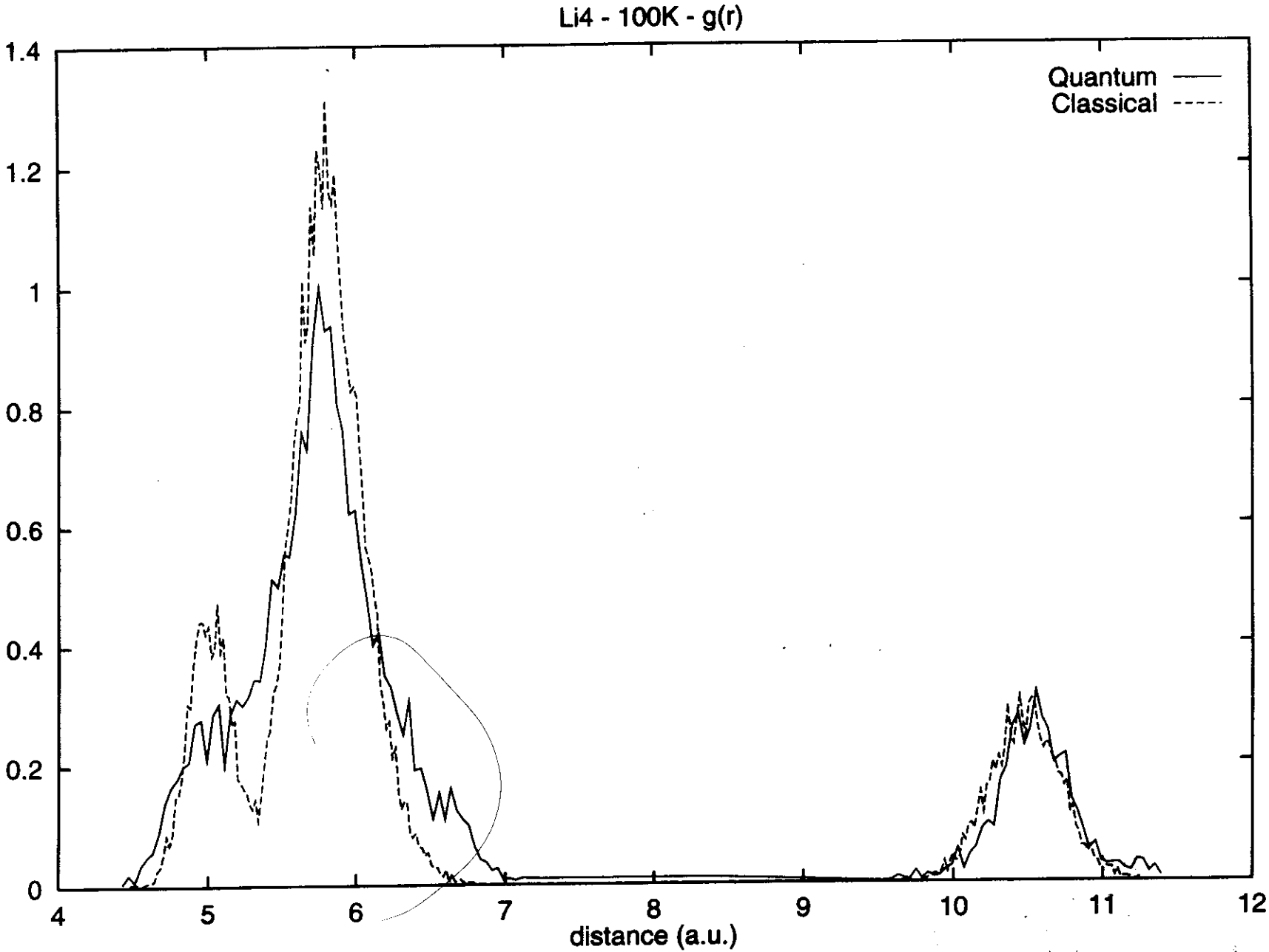


FIG. 2. Normalized partial distribution functions $[\int D_h(r)\,dr = n - 1]$ of bond distances involving at least one proton from the H_3^+ core. (a) H_7^+, (b) H_9^+, and (c) H_{27}^+. Bold solid lines: quantum simulation at 5 K; light solid lines: classical simulation at 5 K; dashed line in (a): classical simulation of H_7^+ at 500 K (this particular trajectory contains only about 800 configurations because the cluster dissociated into H_5^+ and H_2).

Stich, Marx, Parrinello & Terakura
PRL, May '97



Kohanoff, Weht, Batcho & Chakrabarty

NPT Ensemble

$$Q_{NPT} = \int dV\, e^{-\beta P_{ext} V}\, Q(V)$$

$$= \int dV\, e^{-\beta P_{ext} V} \int d\vec{x}\, d\vec{a}\, e^{-S(\vec{x},\vec{a})}$$

$$= \int dV\, e^{-\beta P_{ext} V}\, V^{N(k_{max}+1)} \int d\vec{s}\, d\vec{b}\, e^{-S(\vec{s},\vec{b};L)}$$

$$L = V^{1/3}$$
$$\vec{s} = \vec{x}/L$$
$$\vec{b} = \vec{a}/L$$

$$S(\vec{s},\vec{b};L) = \frac{1}{\hbar}\int_0^{\beta\hbar}\left[\frac{1}{2}m\left(\frac{dx}{du}\right)^2 + V(x(u))\right] du$$

$$= L^2 \sum_k \frac{b_k^2}{2\sigma_k^2} + \frac{1}{\hbar}\int_0^{\beta\hbar} V(\vec{s}(u);L)\, du$$

Quantum Lennard-Jones Systems

Parameters : m, ε, σ

m: mass

ε: Well-depth of pair potential

σ: size

Thermal de Broglie wavelength :

$$\lambda_T = \hbar / \sigma\sqrt{m\varepsilon T^*} \quad , \quad T^* = k_B T/\varepsilon$$

de Boer parameter

$$\Lambda = \hbar / \sigma\sqrt{m\varepsilon}$$

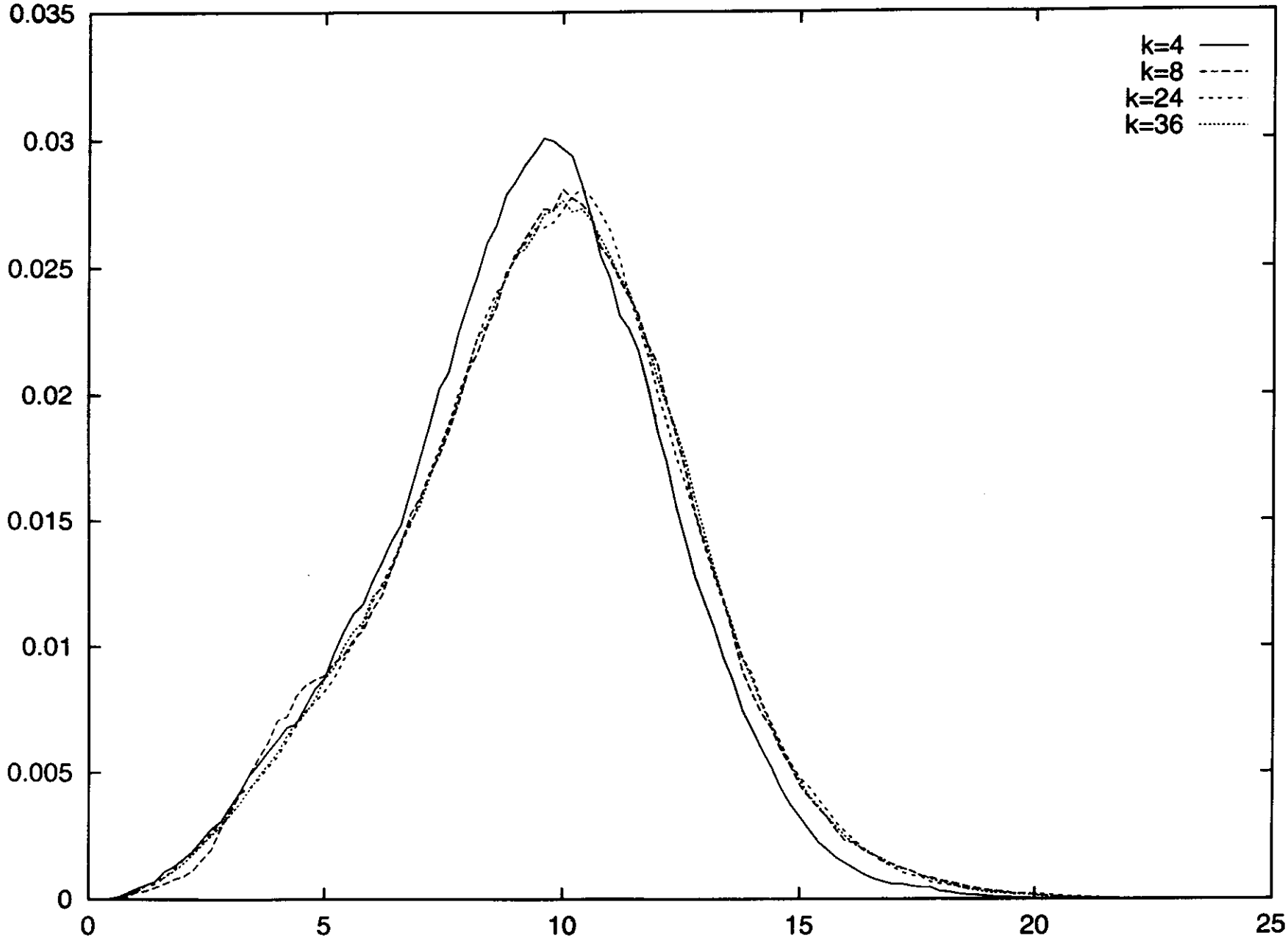
	Λ	m/amu	ε/K	σ/A°
Neon	0.095	20	35.6	2.75
ortho-D_2	0.201	4	34.2	2.96
para-H_2	0.284	2	34.2	2.96
^4He	0.427	4	10.2	2.55

Metropolis Monte Carlo

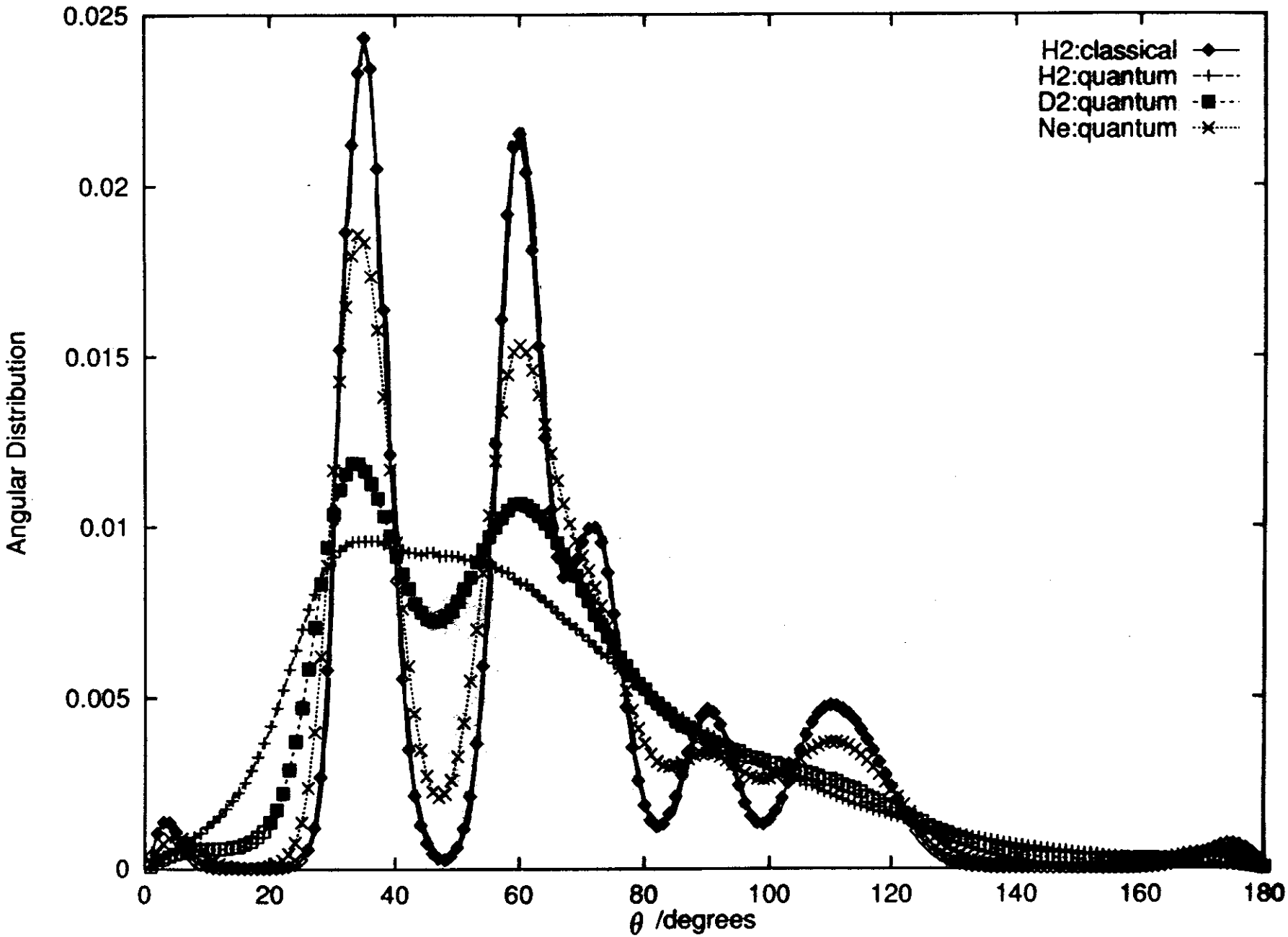
Convergence Parameters:

Number of Fourier coefficients.

Number of Quadrature points used to evaluate V_{eff}


0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
5
10
15
20
25
k=4
k=8
k=24
k=36

C. Chakravarty, Mol. Phys., 54, 845 (1985).



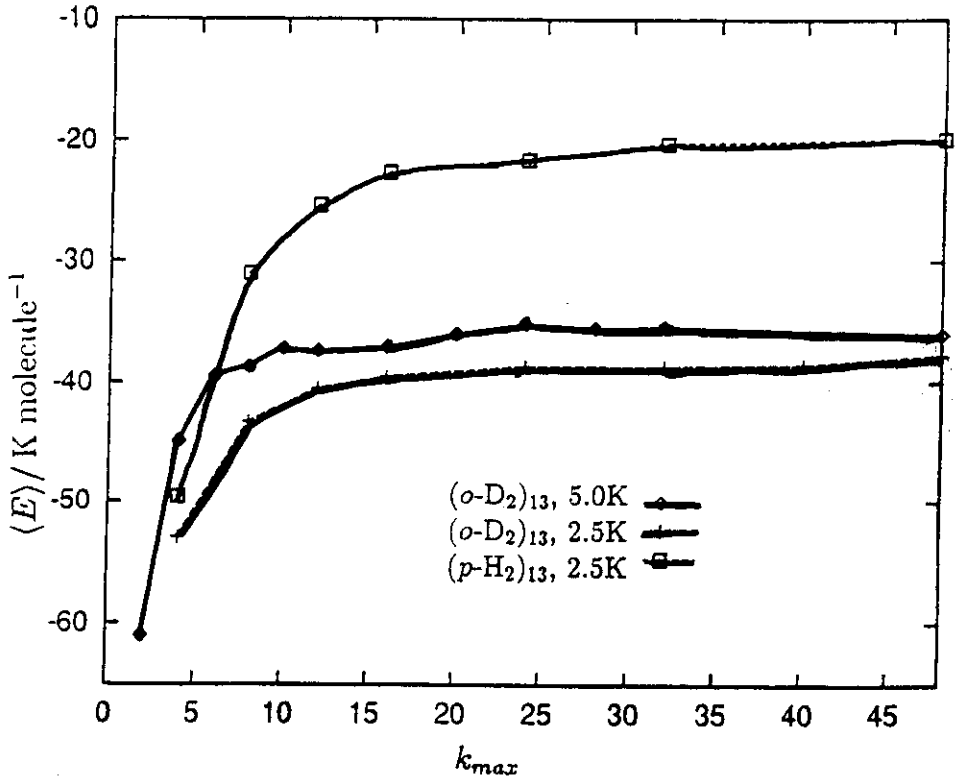


Figure 2. Convergence of $\langle E \rangle$ as a function of k_{max} for $(o\text{-}D_2)_{13}$ at 2·5 K and 5 K and for $(p\text{-}H_2)_{13}$ at 2·5 K. The units of $\langle E \rangle$ are kelvin per molecule and the maximum error bar is ±1·0. The straight lines joining the simulation data points are given as visual guides.

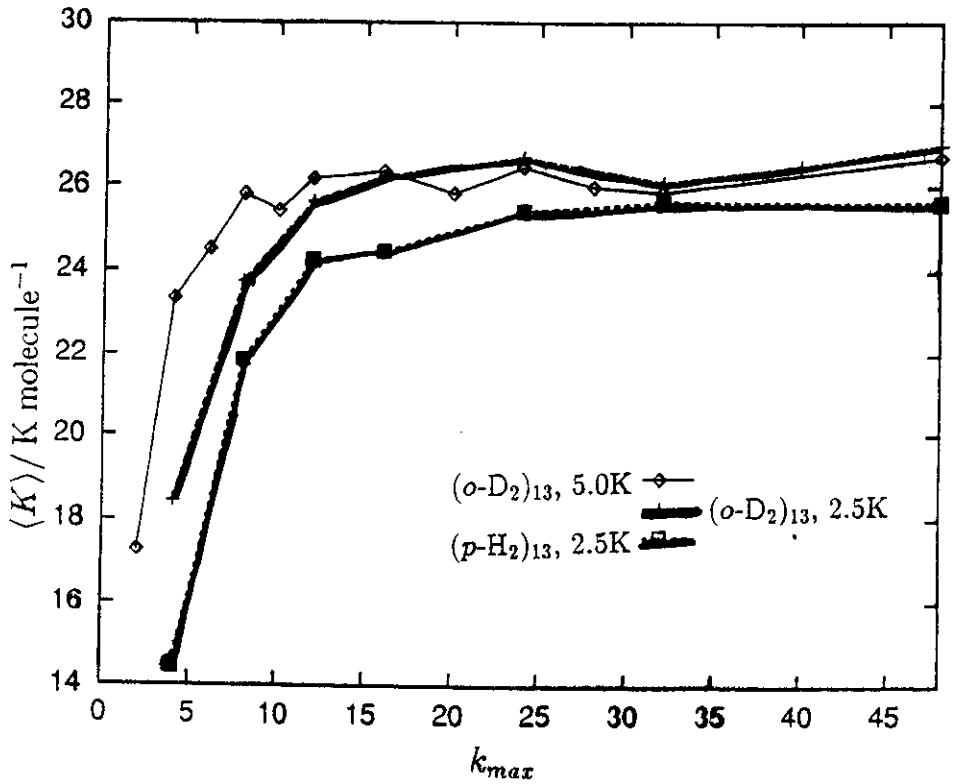


Figure 3. Convergence of $\langle K \rangle$ as a function of k_{max} for $(o\text{-}D_2)_{13}$ at 2·5 K and 5 K and for $(p\text{-}H_2)_{13}$ at 2·5 K. The units of $\langle K \rangle$ are kelvin per molecule and the maximum error bar is ±1·5. The straight lines joining the simulation data points are given as visual guides.