INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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College on Computational Physics

15 May - 9 June 1995

Stochastic Simulation Methods II

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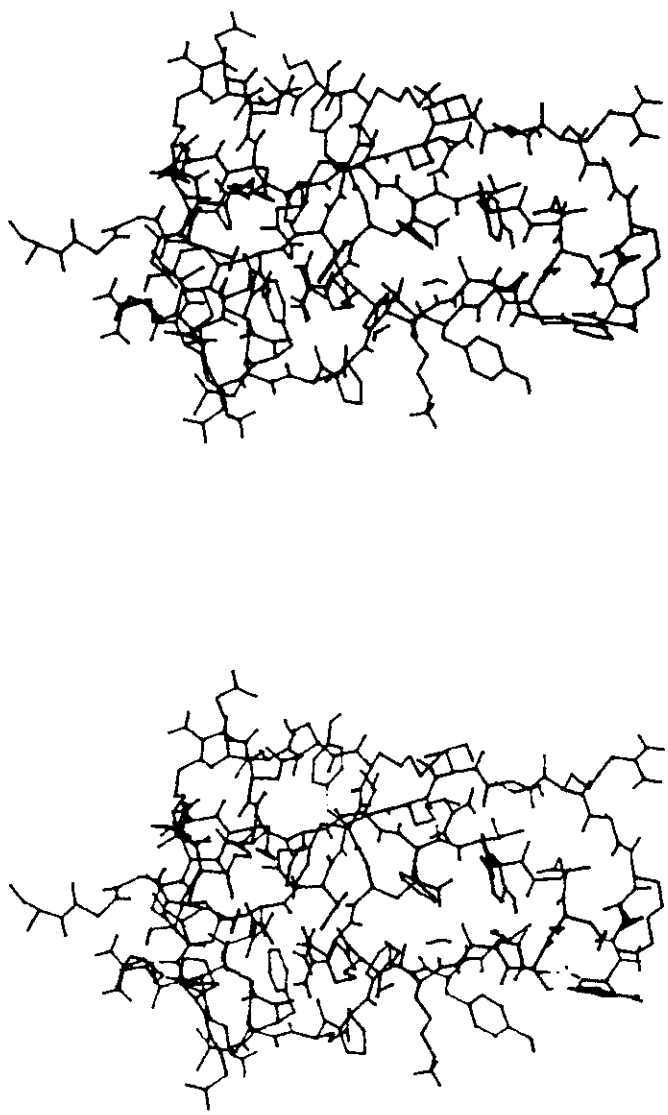
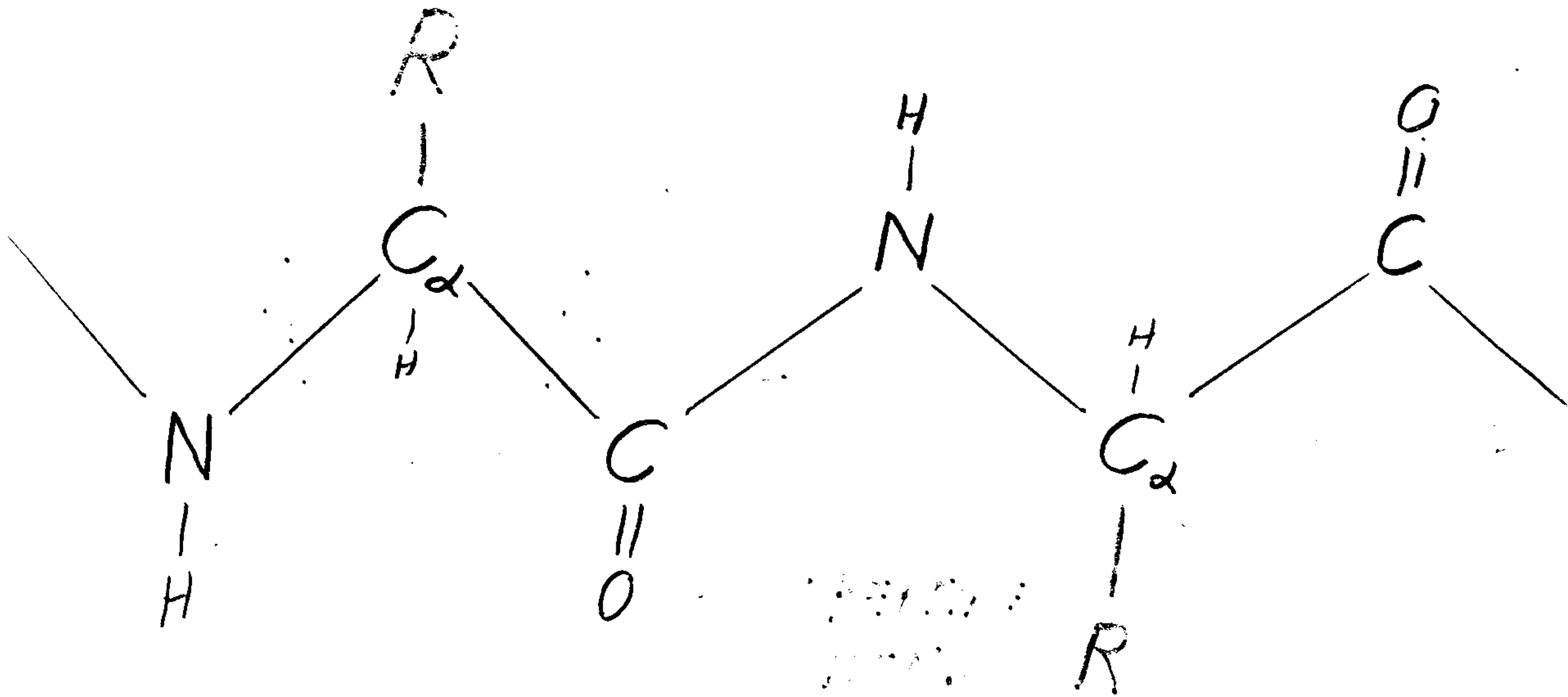
Computer Simulation of Biological Molecules

Robert H. Swendse



BPTI



Empirical potential energy function

- Bond Stretching:

$$\frac{1}{2}\sum_{bonds} K_b(b - b_{eq})^2$$

- Angle Bending:

$$\frac{1}{2}\sum_{angles} K_\theta(\theta - \theta_{eq})^2$$

- Torsion:

$$\frac{1}{2}\sum_{dihedrals} V_\varphi[1 + \cos(n\varphi - \delta)]$$

- Lennard-Jones, and electric:

$$\sum_{non-bonds}[\frac{A}{r^{12}} - \frac{B}{r^6} + \frac{q_i q_j}{\varepsilon r}]$$

Molecular Dynamics

MD is a *deterministic* method:

$$m_i \frac{d^2 r_i}{dt^2} = -\nabla U(r_1, r_2, \cdots, r_N) \qquad i = 1, N$$

- Initial configuration (*eg. X-ray*)
- Initial Maxwellian velocities.
- Equilibration.
- Adjustment. (Scaling velocities)

$$\sum_{i=1}^{N} m_i v_i^2 = 3 N k_B T(t)$$

- $< A >_{(t)} = < A >_{ens.}$?

Classical Paper:

Rahman et. al., Phys. Rev. A136, 404 (1964)

Monte Carlo

MC is a *stochastic* method:

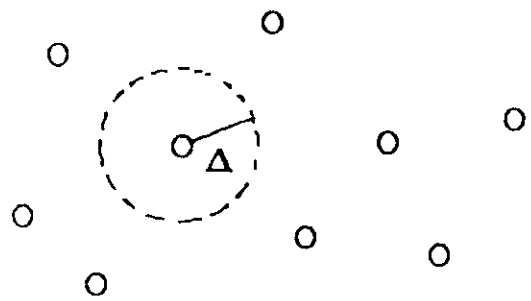
- Generate a sequence of system configurations which is distributed according to the Boltzmann distribution.
- Equilibrium properties are found by computing appropriate averages over the resulting set of configurations.
- **Metropolis Algorithm:**
  - Pick an atom, make random move.
  - Compute ΔE.
  - If $\Delta E < 0$, the move is accepted.
  - If $\Delta E > 0$, the move is accepted with probability $\exp(-\beta \Delta E)$.
- Ideal acceptance ratio is about 50%.

Classical Paper:

Metropolis et. al., Jour. Chem. Phys., Vol. 21 (6), 1087 (1953)

Simulation of liquids

How does one simulate a liquid?



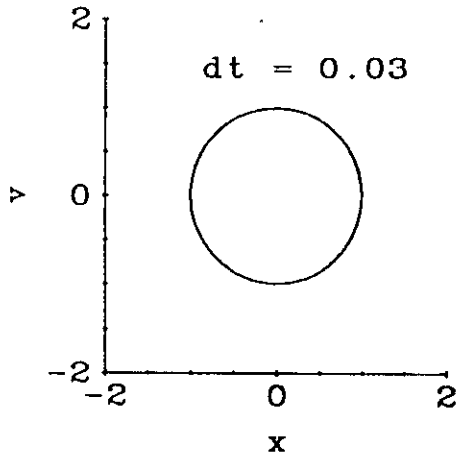
Atoms are moved randomly inside spheres of equal radii.

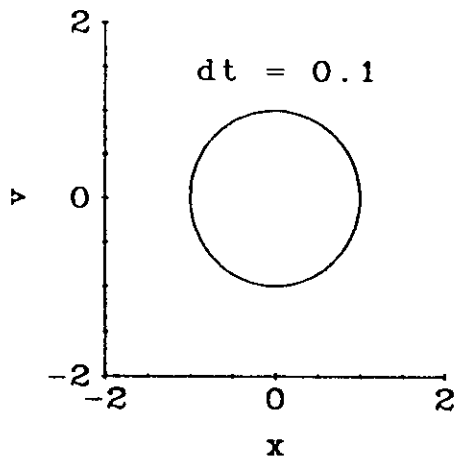
System is:

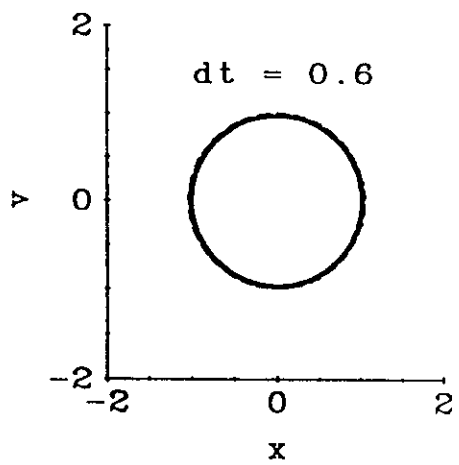
- homogeneous.
- isotropic.

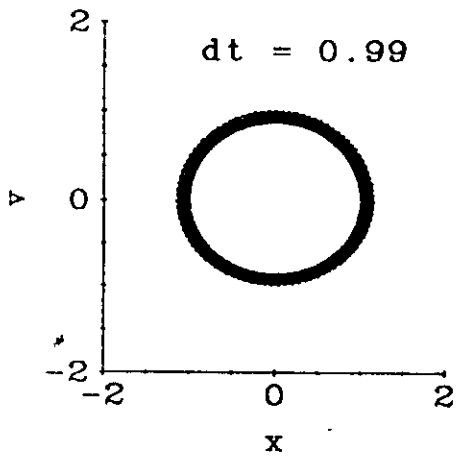
Differences in simulating liquids and molecules

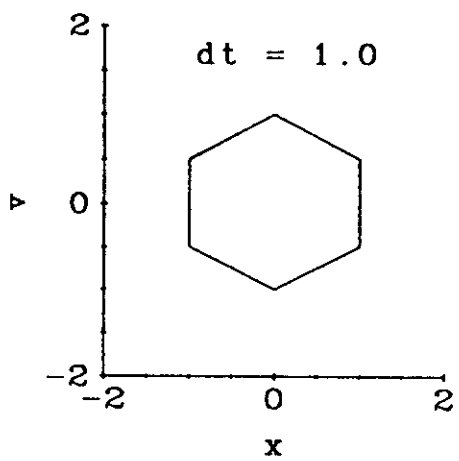
- **Inhomogeneity**
  - Each atom of the molecule sees a different environment.
  - Wide range of variation in the atomic fluctuations.
- **Anisotropy**
  - Highly anisotropic potentials.
  - Local effective potentials change during simulation.

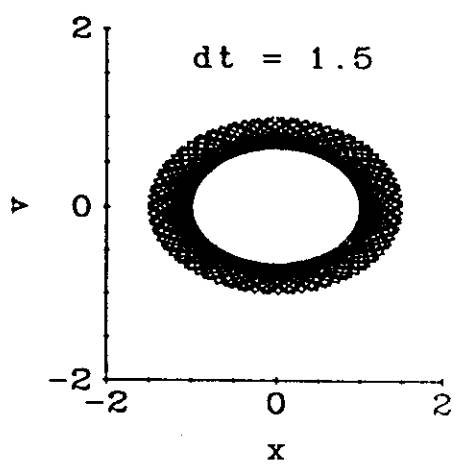

dt = 0.03
2
0
-2
v
-2
0
2
x

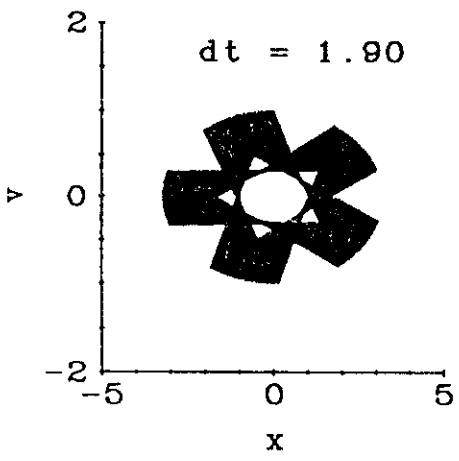

dt = 0.1
2
0
-2
v
-2
0
2
x

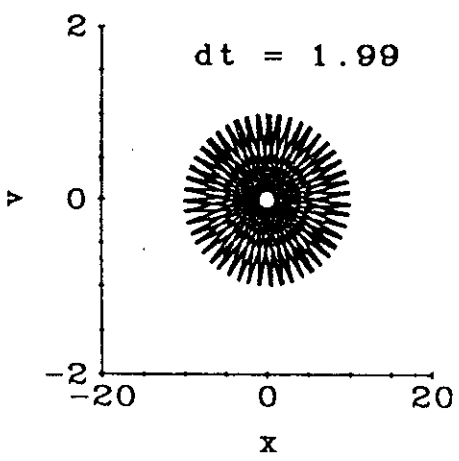

dt = 0.6
2
0
-2
v
-2
0
2
x

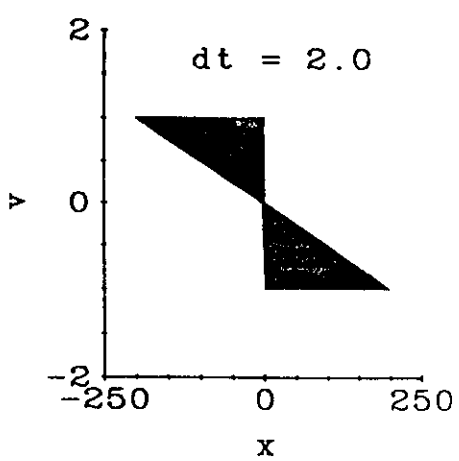

dt = 0.99
2
0
-2
v
-2
0
2
x


dt = 1.0
2
0
-2
v
-2
0
2
x


dt = 1.5
2
0
-2
v
-2
0
2
x


dt = 1.90
2
0
-2
v
-5
0
5
x


dt = 1.99
2
0
-2
v
-20
0
20
x


dt = 2.0
2
0
-2
v
-250
0
250
x

$d = 1$ SHO

$$E = \frac{1}{2} k x^2$$

Monte Carlo move Δx

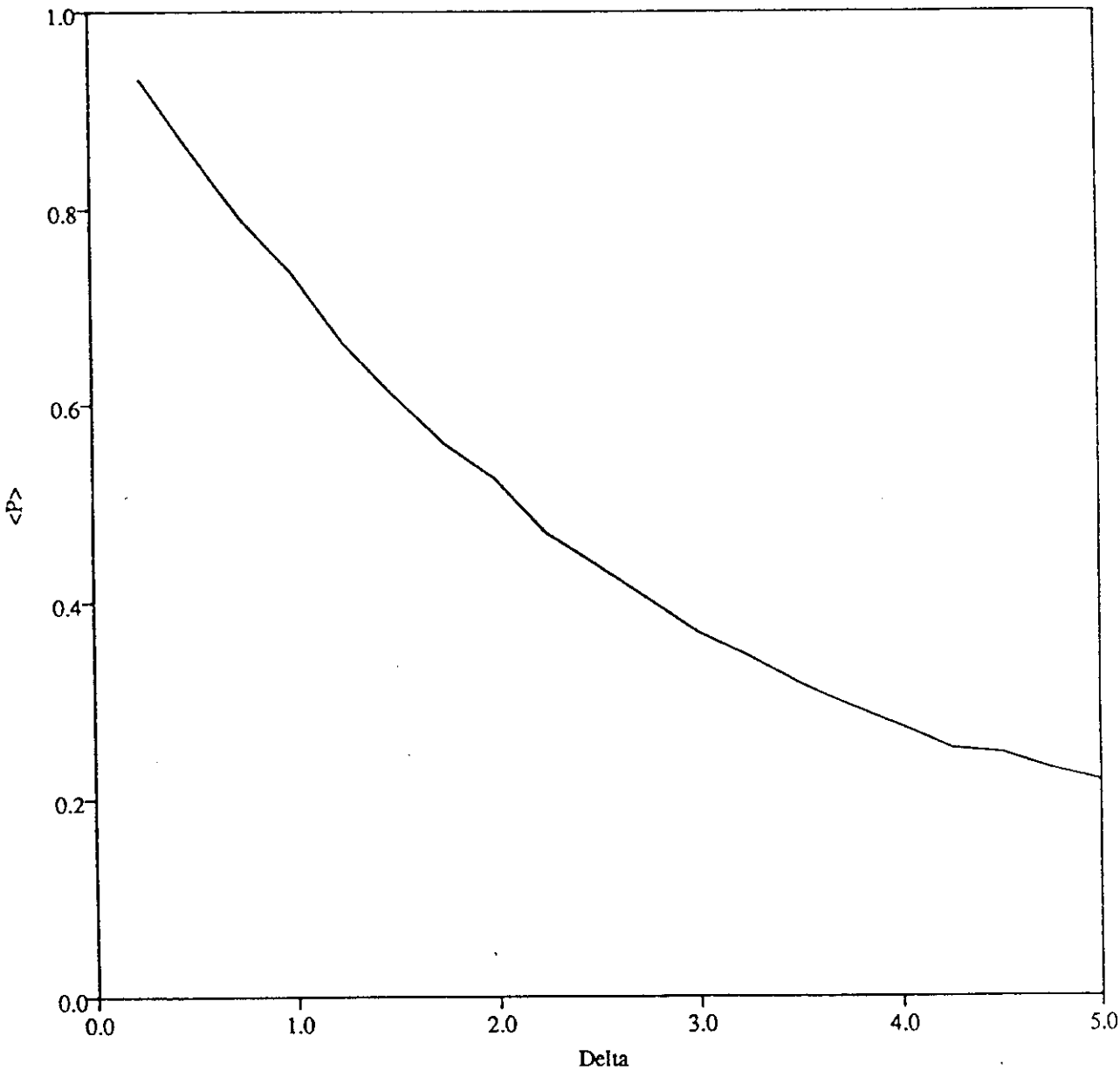
$$\delta \geq \Delta x \geq -\delta$$

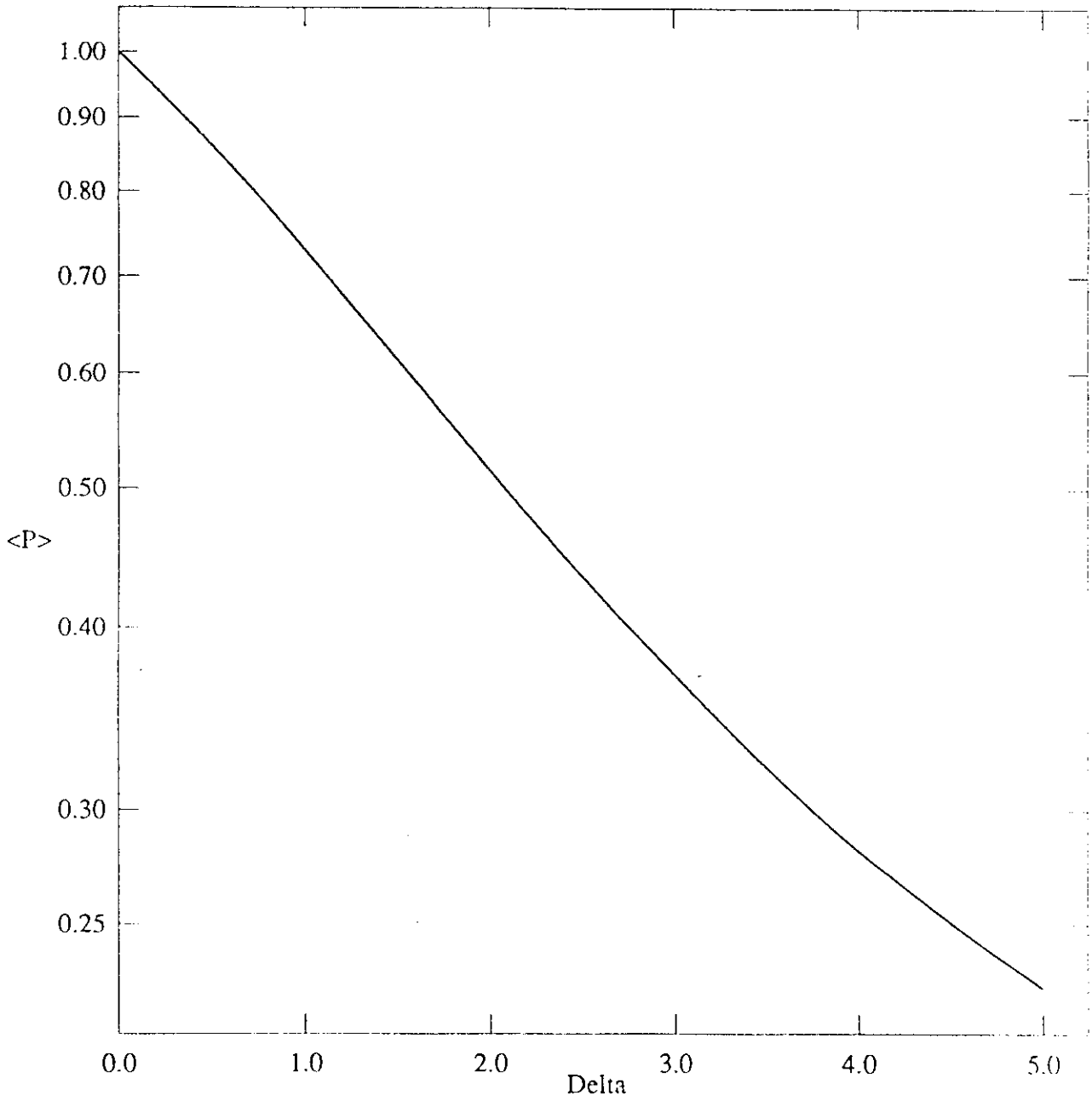
δ = optimal step size

Scaling relation:

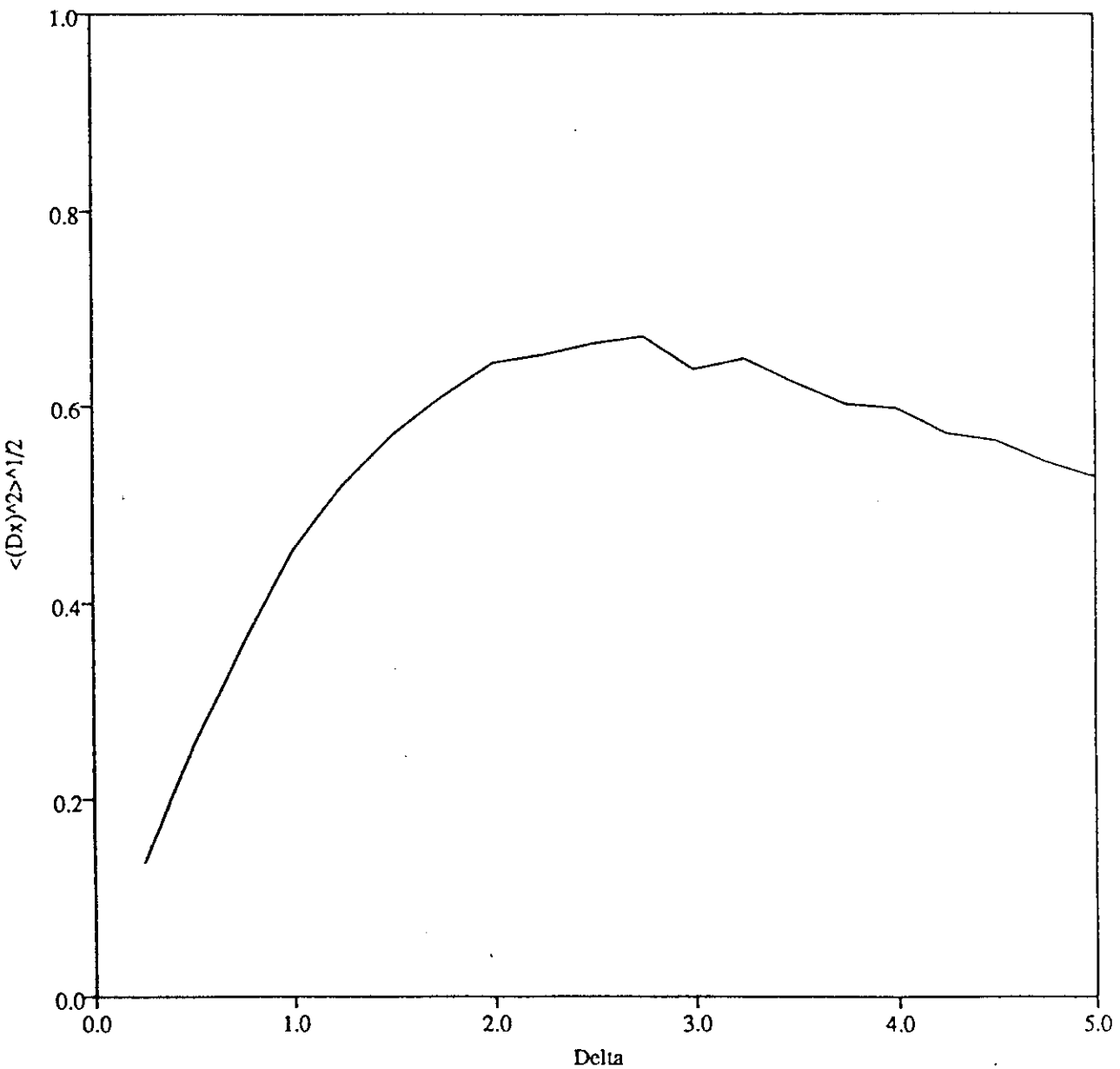
$$\frac{1}{2} \beta k \delta^2 = F^2$$

$V(x) = x^2$ $T = 1.0$ MC

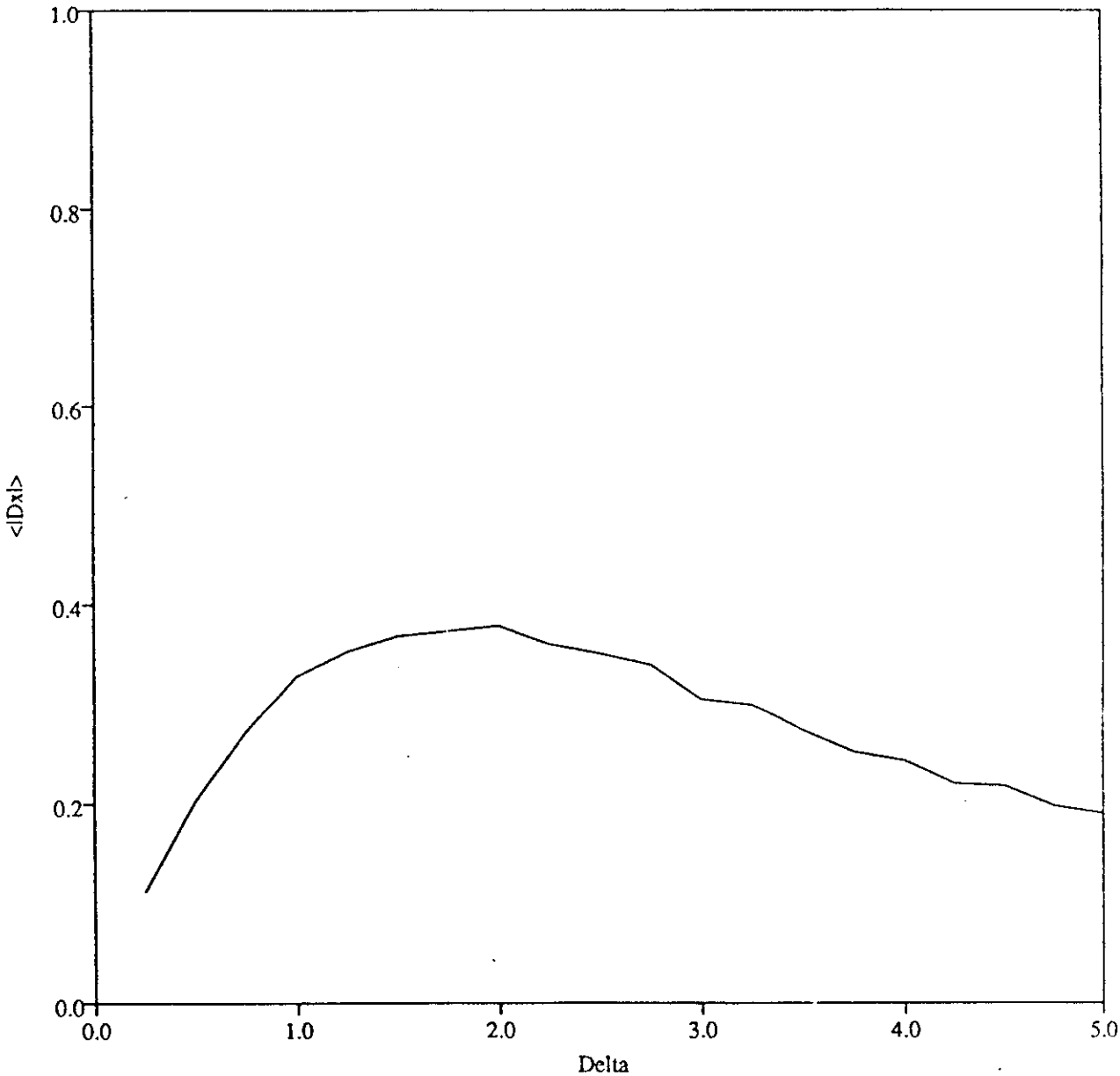


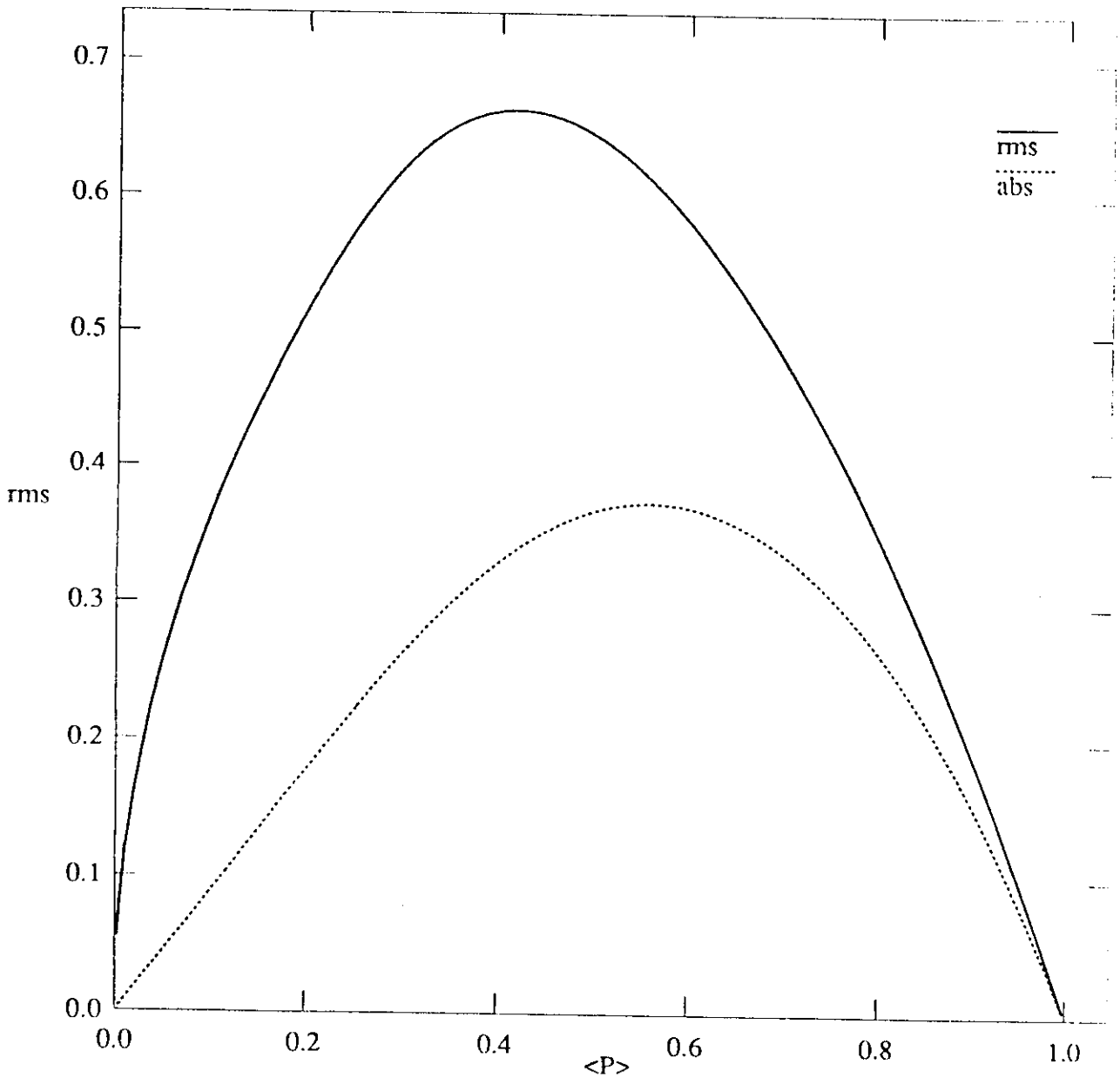

1.00
0.90
0.80
0.70
0.60
0.50
<P>
0.40
0.30
0.25
0.0
1.0
2.0
3.0
4.0
5.0
Delta

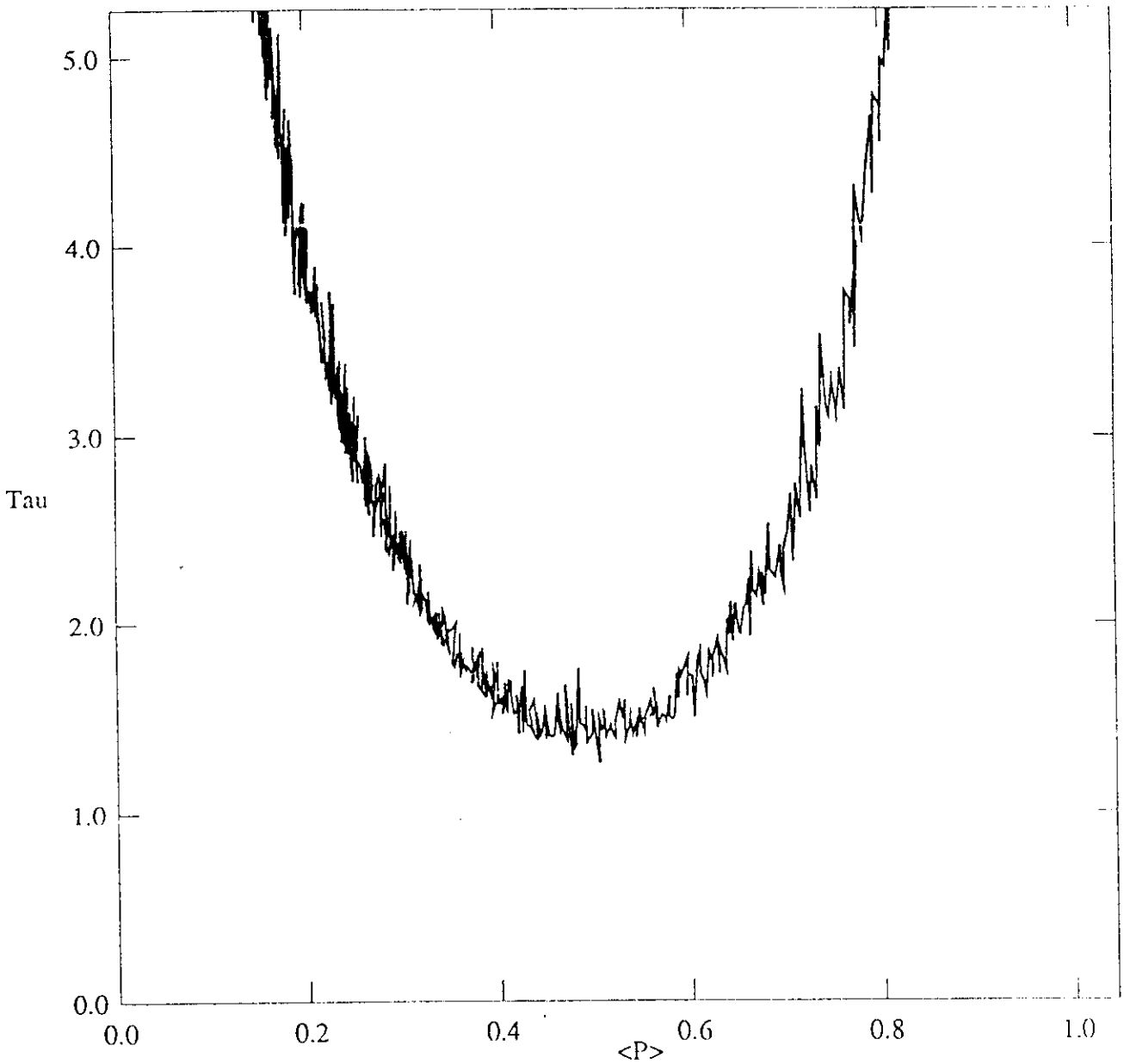
$V(x) = x^2$ $T = 1.0$ MC



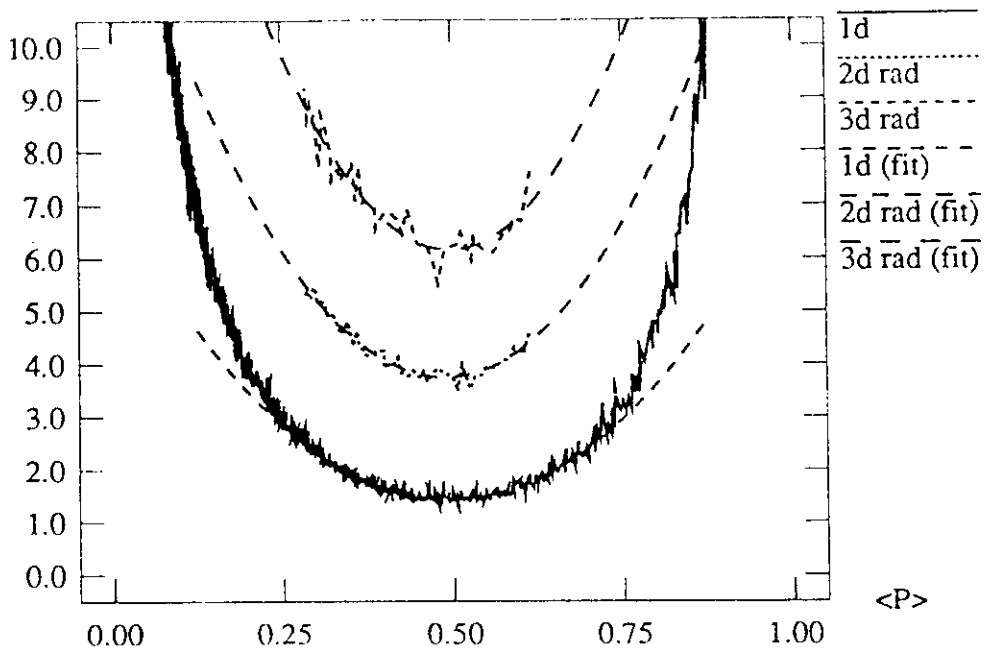
$V(x) = x^2$ $T = 1.0$ MC



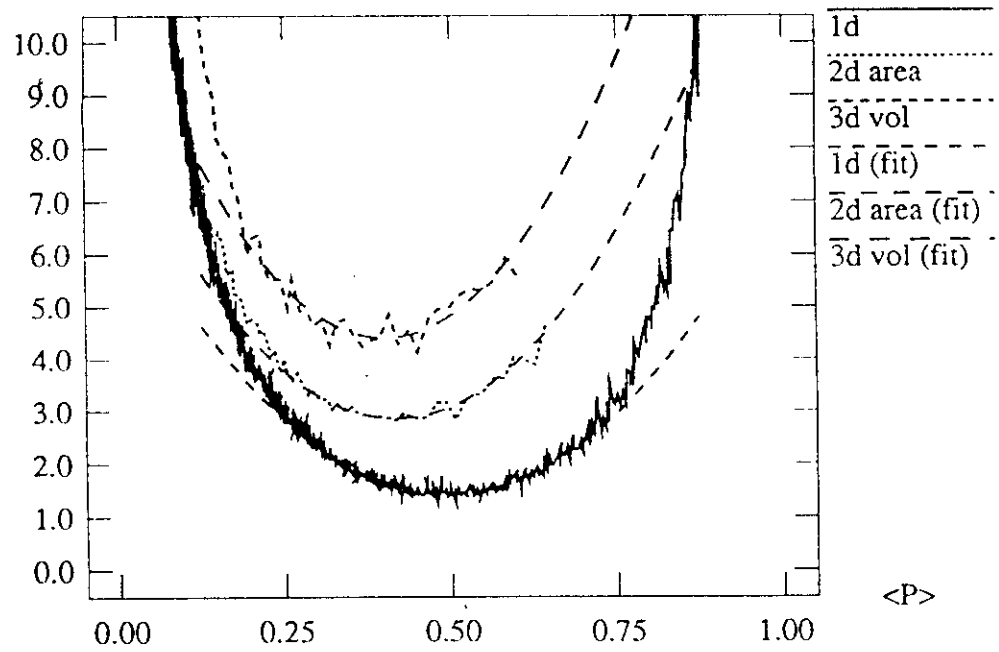

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
rms
0.0
0.2
0.4
0.6
0.8
1.0
<P>
rms
abs

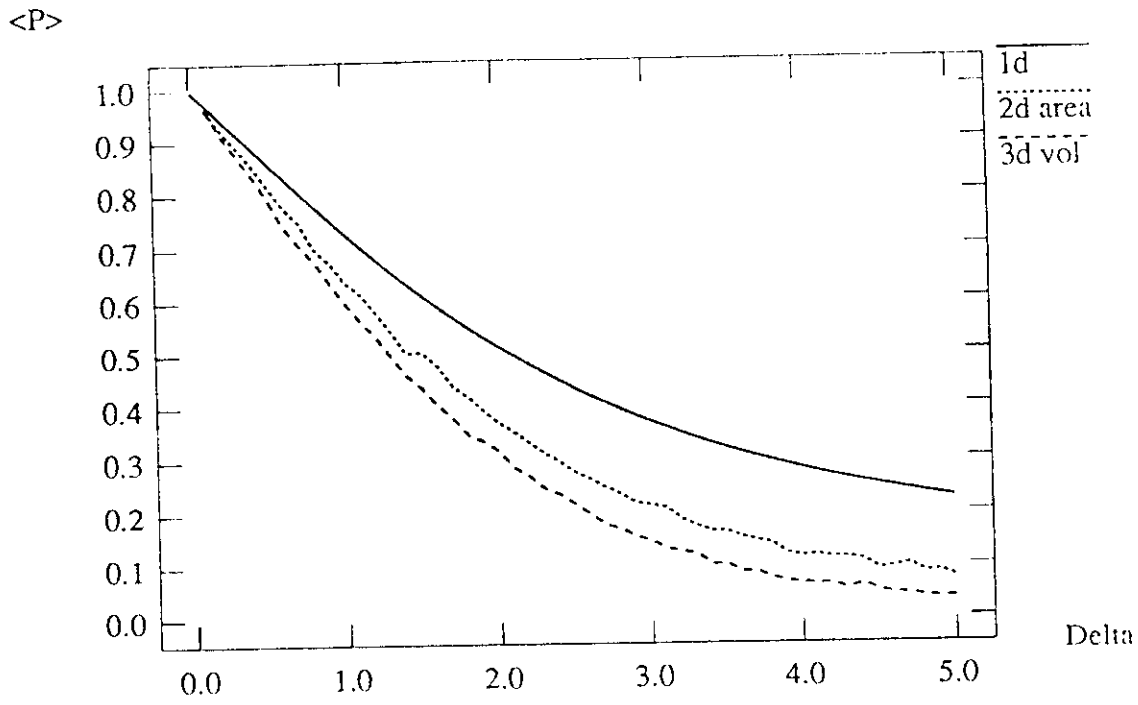

5.0
4.0
3.0
2.0
1.0
0.0
Tau
0.0
0.2
0.4
0.6
0.8
1.0
<P>

Tau

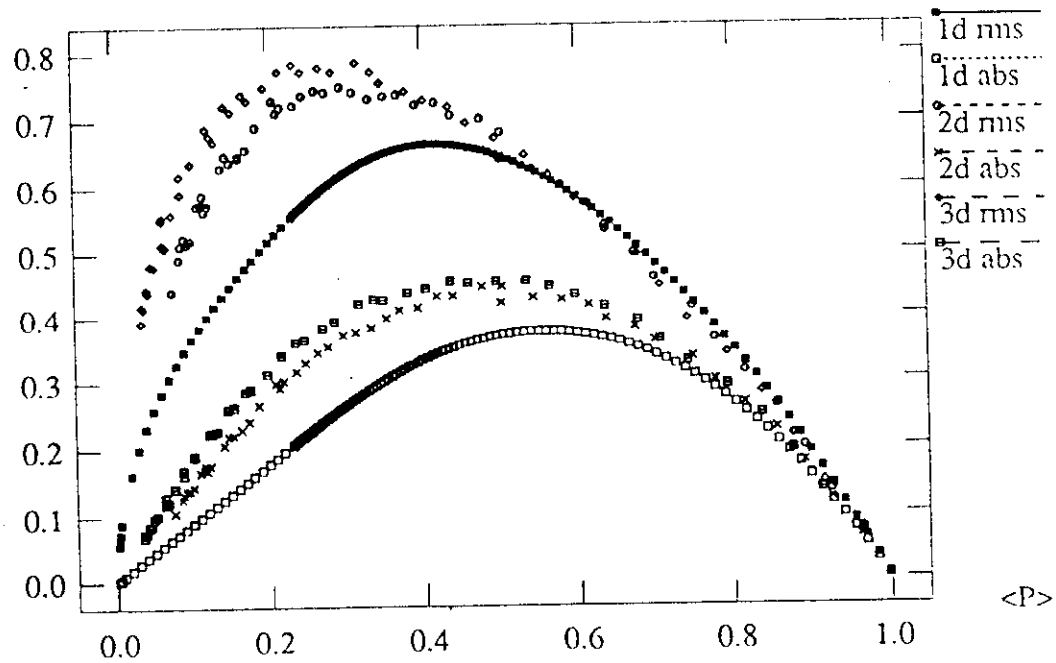

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.00
0.25
0.50
0.75
1.00
<P>
1d
2d rad
3d rad
1d (fit)
2d rad (fit)
3d rad (fit)

Tau


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.00
0.25
0.50
0.75
1.00
<P>
1d
2d area
3d vol
1d (fit)
2d area (fit)
3d vol (fit)



Displacements



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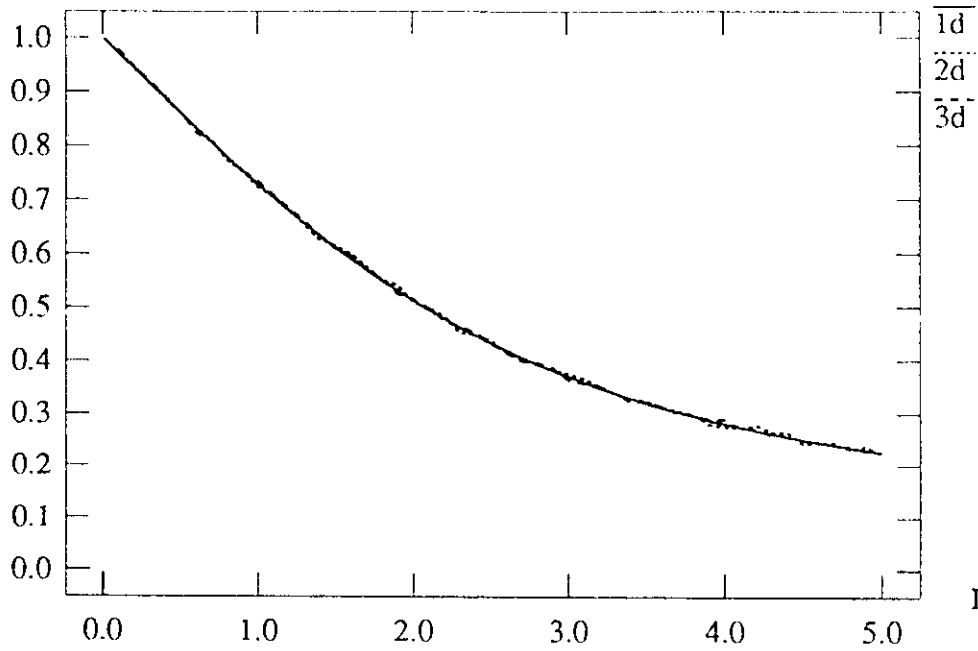
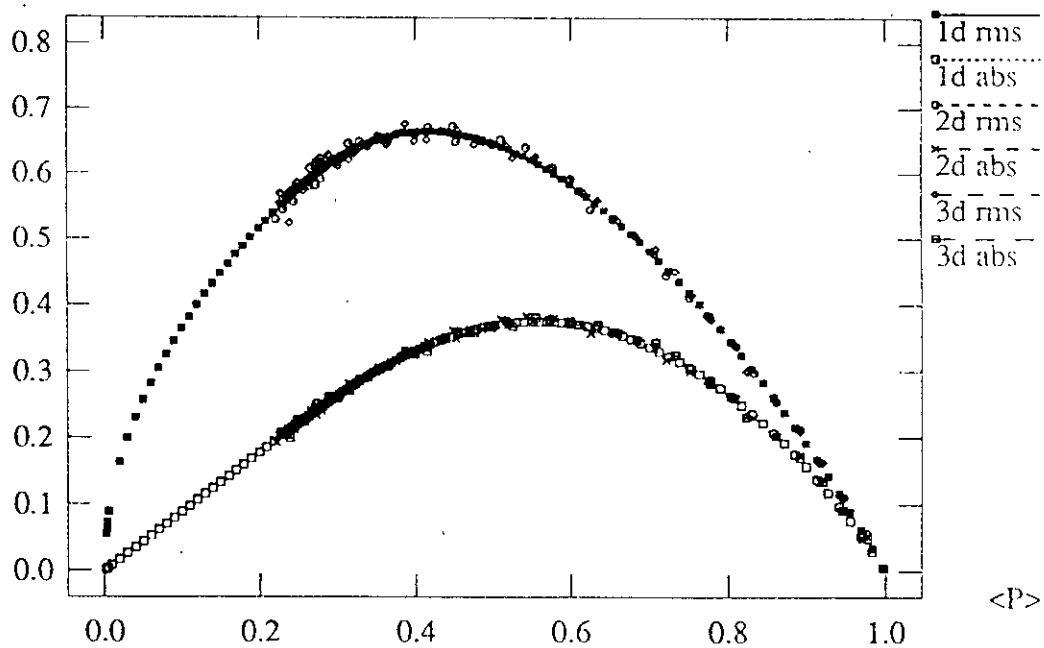


Displacements



Acceptance Ratio Method

$$P \approx \exp[-\Delta/\Delta_0]$$

Ideal ratio $\leftrightarrow$ ideal step size

$$P_i = \exp[-\Delta_i/\Delta_0]$$

$$\Rightarrow \Delta_{new} = \Delta_{old} \ln P_i / \ln P$$

Actually use:

$$\Delta_{new} = \Delta_{old} \frac{\ln(a P_i + b)}{\ln(a P + b)}$$

Dynamically Optimized Monte Carlo

DOMC

$$E = \frac{1}{2} k x^2$$

$$\Delta E = \frac{1}{2} k (x + \Delta x)^2 - \frac{1}{2} k x^2$$

$$\Delta E = k x \Delta x + \frac{1}{2} k (\Delta x)^2$$

$[\ldots]$ = average over all attempted moves

$$[\Delta x] = 0$$

$$[\Delta E] = \frac{1}{2} k [(\Delta x)^2]$$

$$\frac{1}{2} \beta k \delta^2 = F^2$$

$$\delta = F \left(\frac{[(\Delta x)^2]}{\beta [\Delta E]} \right)^{\frac{1}{2}}$$

DOMC for $d > 1$

$$E = \frac{1}{2} \sum_{i,j} k_{ij} x_i x_j$$

MC moves $\{\eta_i\}$ in an ellipsoid

$$\eta_i = \sum_{j=1} D_{ij} \xi_j$$

$\{\xi_i\}$ is a random vector from the unit sphere.

Scaling relation:

$$F^2 = \frac{1}{2} \beta \, \bar{\bar{D}}^t \cdot \bar{\bar{k}} \cdot \bar{\bar{D}}$$

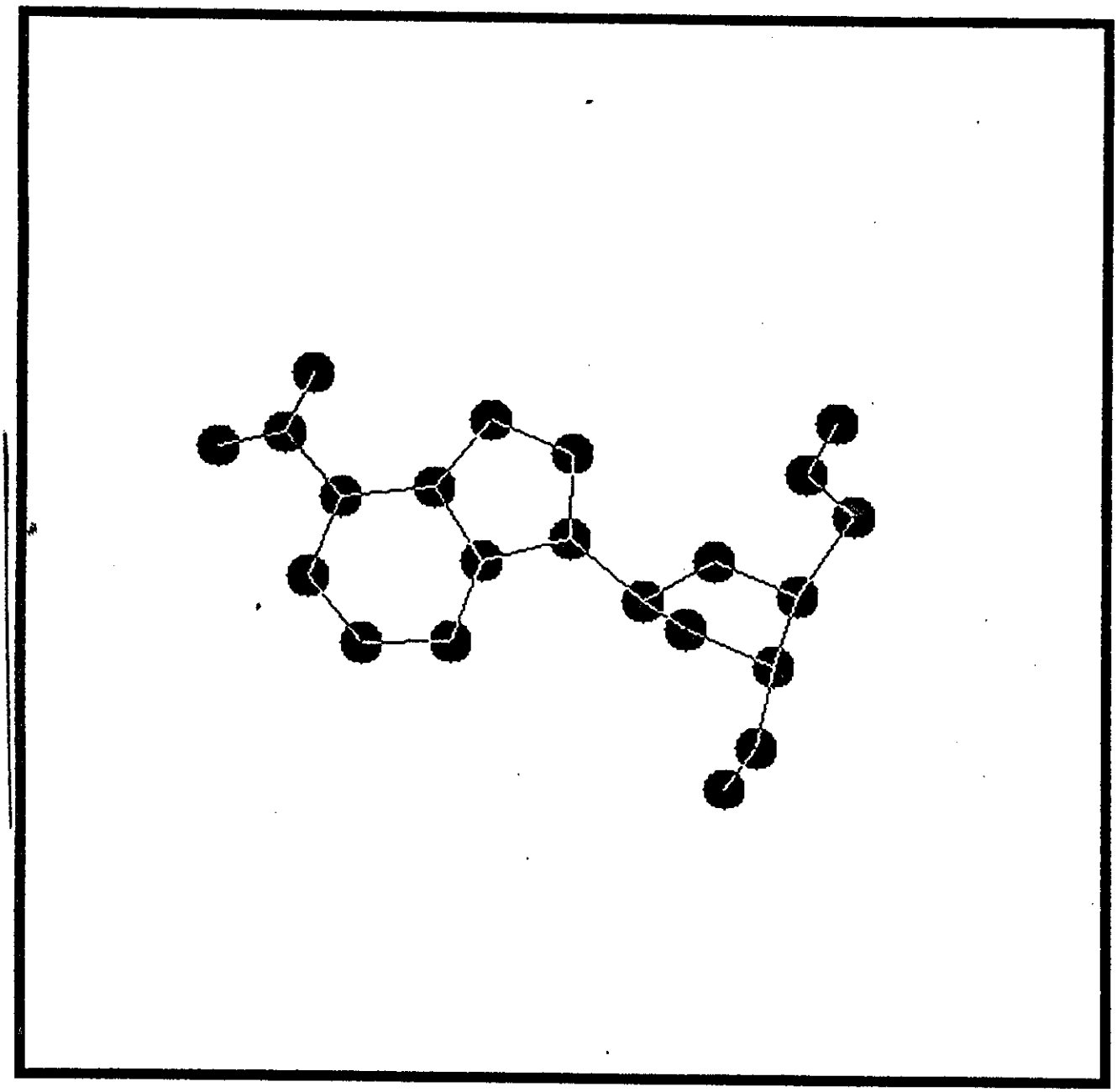
$$[\Delta E \, \eta_l \eta_m] = \frac{1}{2} \sum_{i,j} k_{ij} [\eta_i \eta_j \eta_l \eta_m]$$

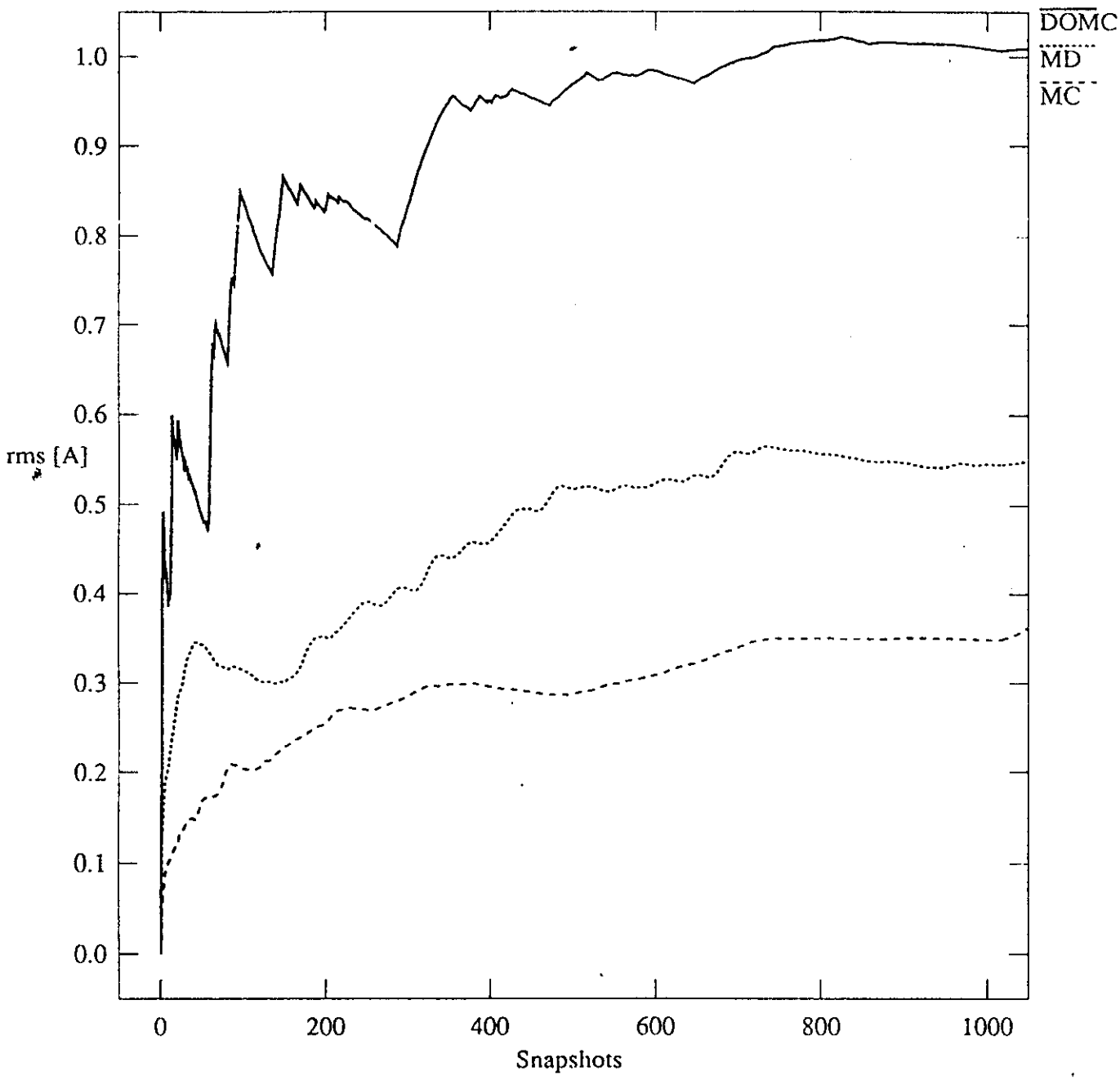
Solve for $\{k_{ij}\}$

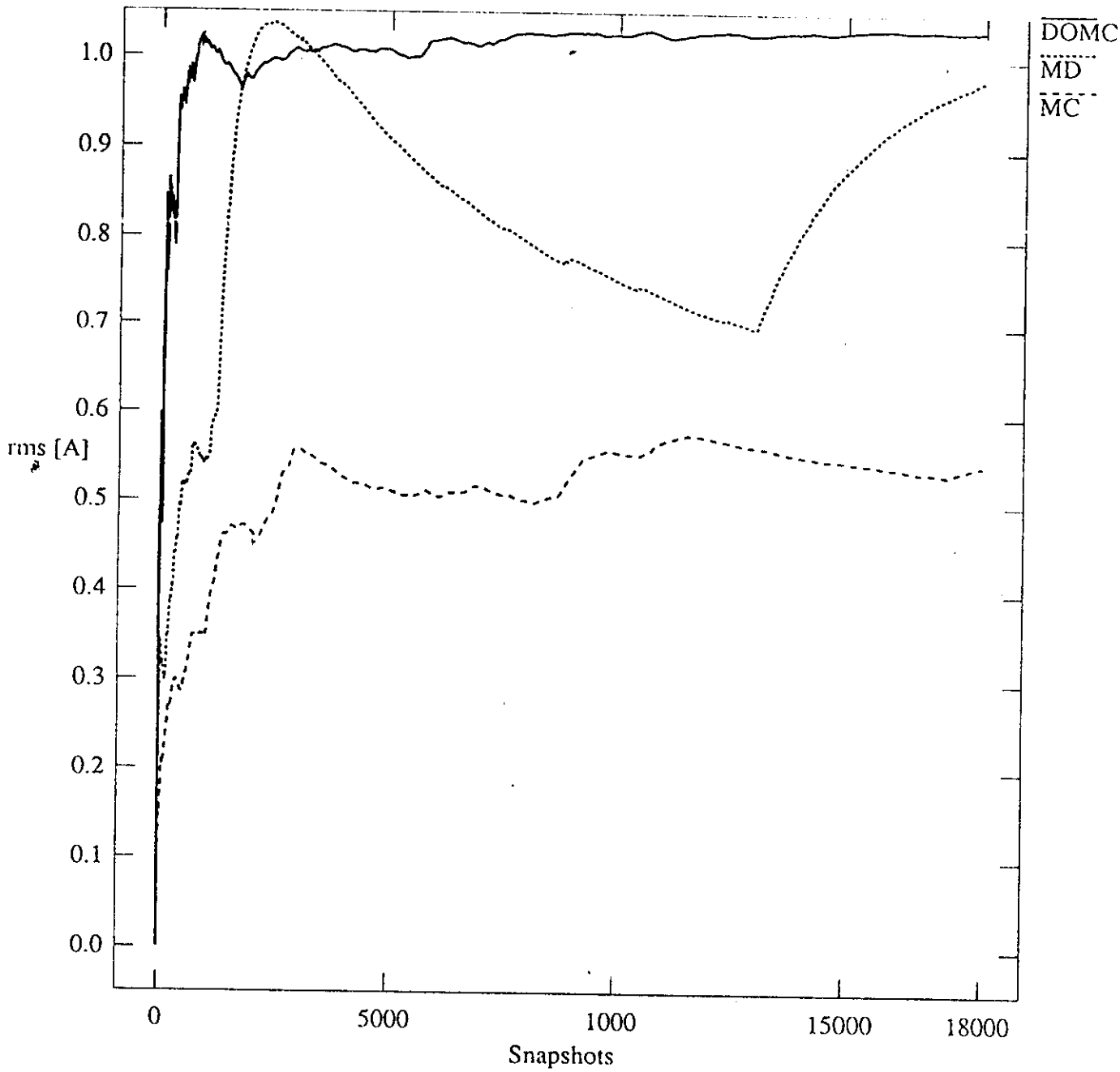
λ_l = eigenvalue of $\{k_{ij}\}$

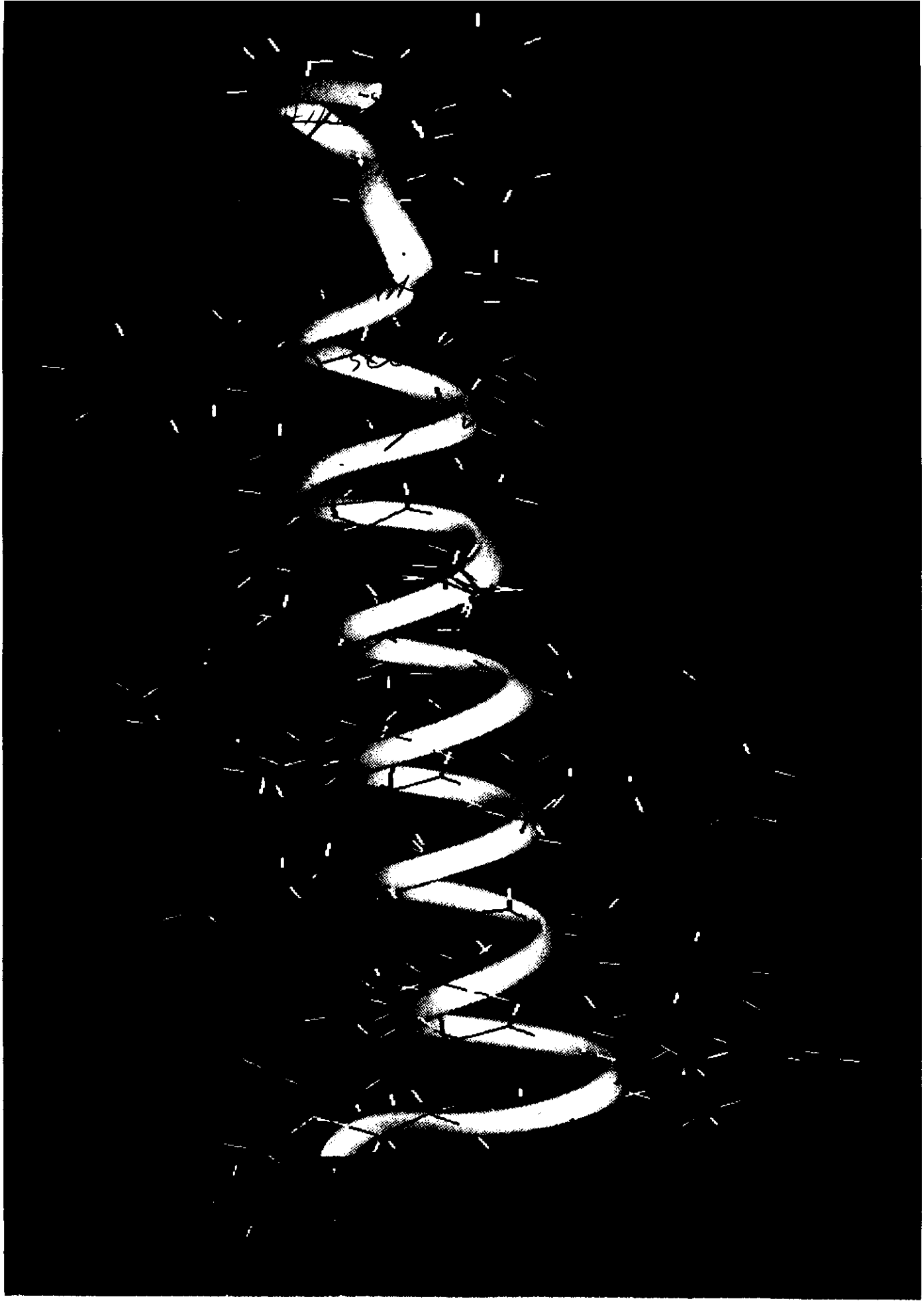
V_{il} = eigenvector of "

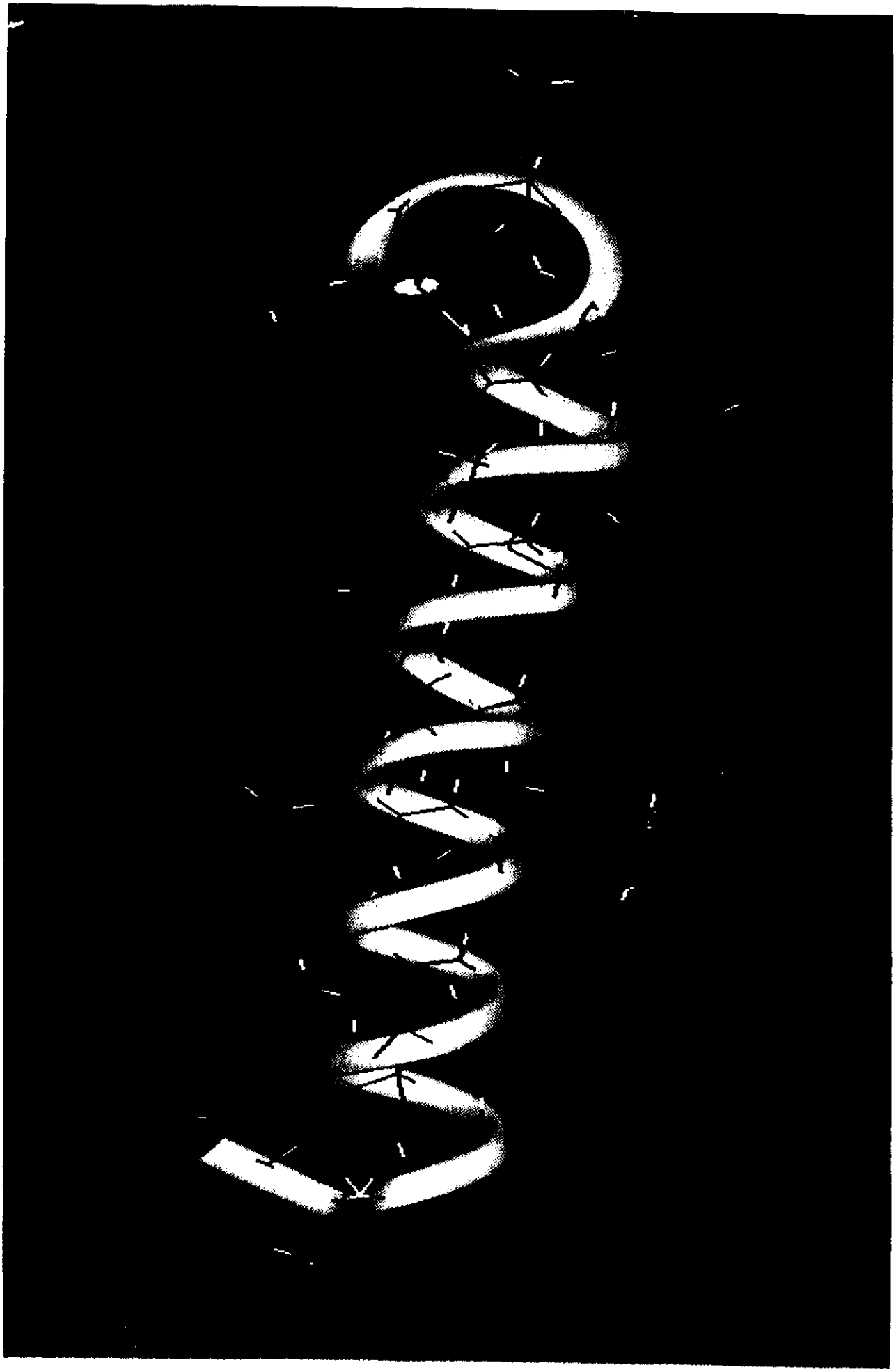
$$D_{il} = F \left(\frac{2}{\beta \lambda_l} \right)^{\frac{1}{2}} V_{il}$$

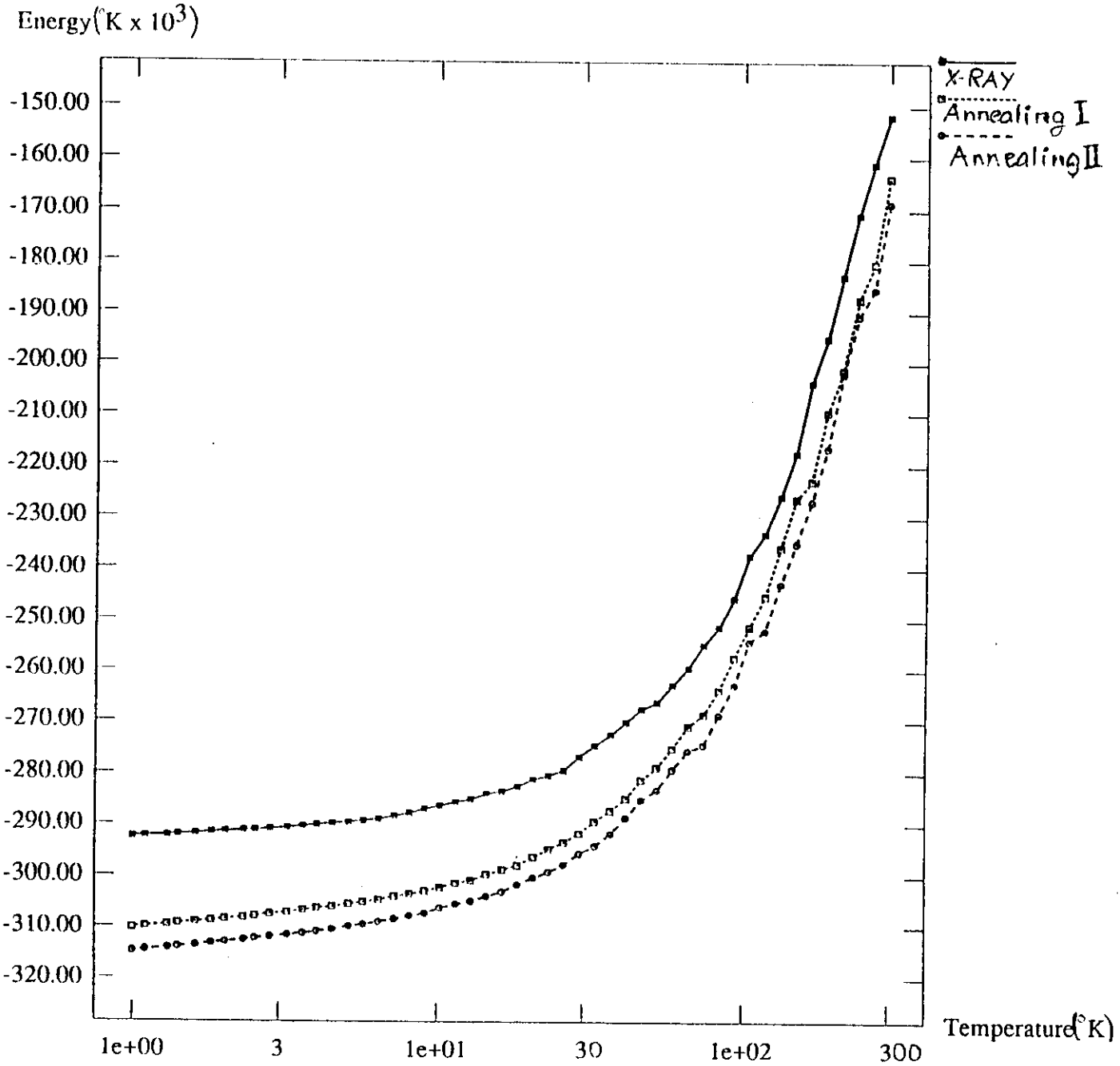



DOMC
MD
MC
rms [A]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
Snapshots


DOMC
MD
MC
rms [A]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5000
1000
15000
18000
Snapshots






Energy(°K x 10^3)
-150.00
-160.00
-170.00
-180.00
-190.00
-200.00
-210.00
-220.00
-230.00
-240.00
-250.00
-260.00
-270.00
-280.00
-290.00
-300.00
-310.00
-320.00
1e+00
3
1e+01
30
1e+02
300
Temperature(°K)
X-RAY
Annealing I
Annealing II