13. Molecular dynamics simulations what types of information do we expect to retrieve from MC & MD simulations?

MOLECULAR DYNAMICS SIMULATIONS

Equations of motion in Cartesian coordinates:

$$m_i \frac{d^2 \vec{r_i}}{dt^2} = \vec{f_i} \qquad i = 1, N \text{ equations for } N \text{ particles}$$

where

force $\vec{f_i} = -\vec{\nabla}_{r_i} U(r^N)$

$$= -\left[\frac{d}{x_i} U(r^N) \hat{i} + \frac{\partial}{\partial y_i} U(r^N) \hat{j} + \frac{\partial}{\partial z_i} U(r^N) \hat{k} \right]$$

velocity $\frac{d\vec{r_i}}{dt} = \vec{P_i}/m_i$; $\frac{d\vec{P_i}}{dt} = \vec{f_i}$

It is essential that the particle positions vary smoothly with time

[When the potential varies sharply, hard sphere or square well models, then impulsive "collisions" between particles occur at which the velocities typically change discontinuously. In such models, the particle dynamics at the moment of each collision must be treated explicitly and separately from the smooth inter-collisional motion.]

Solving ordinary differential equations:
   use a standard method

FINITE DIFFERENCE APPROACH

FINITE DIFFERENCE METHOD:
General characteristics

- Given r_i, v_i, and other dynamic information at time t, attempt to obtain positions, velocities, etc at a later time $t + \delta t$
- δt $<<$ typical time taken for a molecule to travel its own length
- several possible algorithms

desirable characteristics of algorithm:
- fast and require little memory
- → should permit the use of a long time step δt
- should duplicate the classical trajectory as closely as possible
- and still acceptable energy conservation should satisfy the known conservation laws for energy and momentum and be time-reversible
- should be simple in form and easy to program

As time step is increased, energy conservation is degraded. Trade-off between accuracy and economy.

Need shorter time steps at
- high temperatures
- light molecules
- rapidly varying potential functions

Best coefficients $c_0, c_1, c_2, c_3 \ldots$ [Gear 1966]
are the set that leads to optimum stability
and accuracy of the trajectories.

The corrector step can be iterated (once or twice)
new correct accelerations are calculated
from the corrected positions $\vec{r}^c(t + \delta t)$
and compared with $\vec{a}^c$ to further
refine the positions, velocities, etc.

1. Current values of positions, velocities, accel.

2. Predict positions, velocities, accelerations
   at time $(t + \delta t)$

3. Evaluate forces, accelerations
   $$a_i = f_i / m_i$$
   from the new positions

4. Correct the predicted positions, velocities,
   accelerations, using the new
   accelerations

5. Calculate properties of interest
   (energy, etc.) that will be
   accumulated to get time-average
   values

6.

Predictor - corrector algorithm :

(1) Prediction step :

Predict the values at $t + \delta t$ by using a Taylor expansion about time t

$$\vec{r}^P(t + \delta t) = \vec{r}(t) + (\delta t)\vec{v}(t) + \frac{1}{2}(\delta t)^2 \vec{a}(t)$$
$$+ \frac{1}{6}(\delta t)^3 \vec{b}(t) + \cdots$$

$$\vec{v}^P(t + \delta t) = \vec{v}(t) + (\delta t)\vec{a}(t) + \frac{1}{2}(\delta t)^2 \vec{b}(t) + \cdots$$

$$\vec{a}^P(t + \delta t) = \vec{a}(t) + (\delta t)\vec{b}(t) + \cdots$$

$$\vec{b}^P(t + \delta t) = \vec{b}(t) + \cdots$$

(1) could store four vectors $\{ \vec{r} \ \vec{v} \ \vec{a} \ \vec{b} \}_{at \ t}$

(2) other possibilities include using old velocities and $\vec{v}(t - \delta t)$, $\vec{v}(t - 2\delta t)$ ...

Correct the above values by using the equations of motion

calculate from $\vec{r}^P(t + \delta t)$ forces $(t + \delta t)$

$$\downarrow$$
$$\vec{a}^C(t + \delta t)$$

correction to the acceleration
$$\Delta a(t + \delta t) = \vec{a}^C(t + \delta t) - \vec{a}^P(t + \delta t)$$

(2) Correction step :

$$r^C(t + \delta t) = r^P(t + \delta t) + c_0 \, \Delta a(t + \delta t)$$
$$v^C(t + \delta t) = v^P(t + \delta t) + c_1 \, \Delta a(t + \delta t)$$
$$a^C(t + \delta t) = a^P(t + \delta t) + c_2 \, \Delta a(t + \delta t)$$
$$b^C(t + \delta t) = b^P(t + \delta t) + c_3 \, \Delta a(t + \delta t)$$

Verlet algorithm [1967]

Use positions $\vec{r}(t)$
+ accelerations $a(t)$.
+ positions from previous step $\vec{r}(t-\delta t)$

Advance the positions:

$$r(t+\delta t) = 2\vec{r}(t) - \vec{r}(t-\delta t) + (\delta t)^2 \vec{a}(t)$$

(velocities do not appear at all since

$$r(t+\delta t) = r(t) + (\delta t)v(t) + \frac{1}{2}(\delta t)^2\vec{a}(t) + \ldots$$

$$+ \quad r(t-\delta t) = r(t) - (\delta t)v(t) + \frac{1}{2}(\delta t)^2\vec{a}\,t - \ldots$$

Assume that we have available the current and old positions. The current accelerations are evaluated in the force loop as usual. Then, the coordinates are advanced in the following way.

```
SUMVSQ = 0.0
SUMVX  = 0.0
SUMVY  = 0.0
SUMVZ  = 0.0

DO 100 I = 1, N

   RXNEWI    = 2.0 * RX(I) - RXOLD(I) + DTSQ * AX(I)
   RYNEWI    = 2.0 * RY(I) - RYOLD(I) + DTSQ * AY(I)
   RZNEWI    = 2.0 * RZ(I) - RZOLD(I) + DTSQ * AZ(I)
   VXI       = ( RXNEWI - RXOLD(I) ) / DT2
   VYI       = ( RYNEWI - RYOLD(I) ) / DT2
   VZI       = ( RZNEWI - RZOLD(I) ) / DT2
   SUMVSQ    = SUMVSQ + VXI ** 2 + VYI ** 2 + VZI ** 2
   SUMVX     = SUMVX + VXI
   SUMVY     = SUMVY + VYI
   SUMVZ     = SUMVZ + VZI
   RXOLD(I) = RX(I)
   RYOLD(I) = RY(I)
   RZOLD(I) = RZ(I)
   RX(I)     = RXNEWI
   RY(I)     = RYNEWI
   RZ(I)     = RZNEWI

100    CONTINUE
```
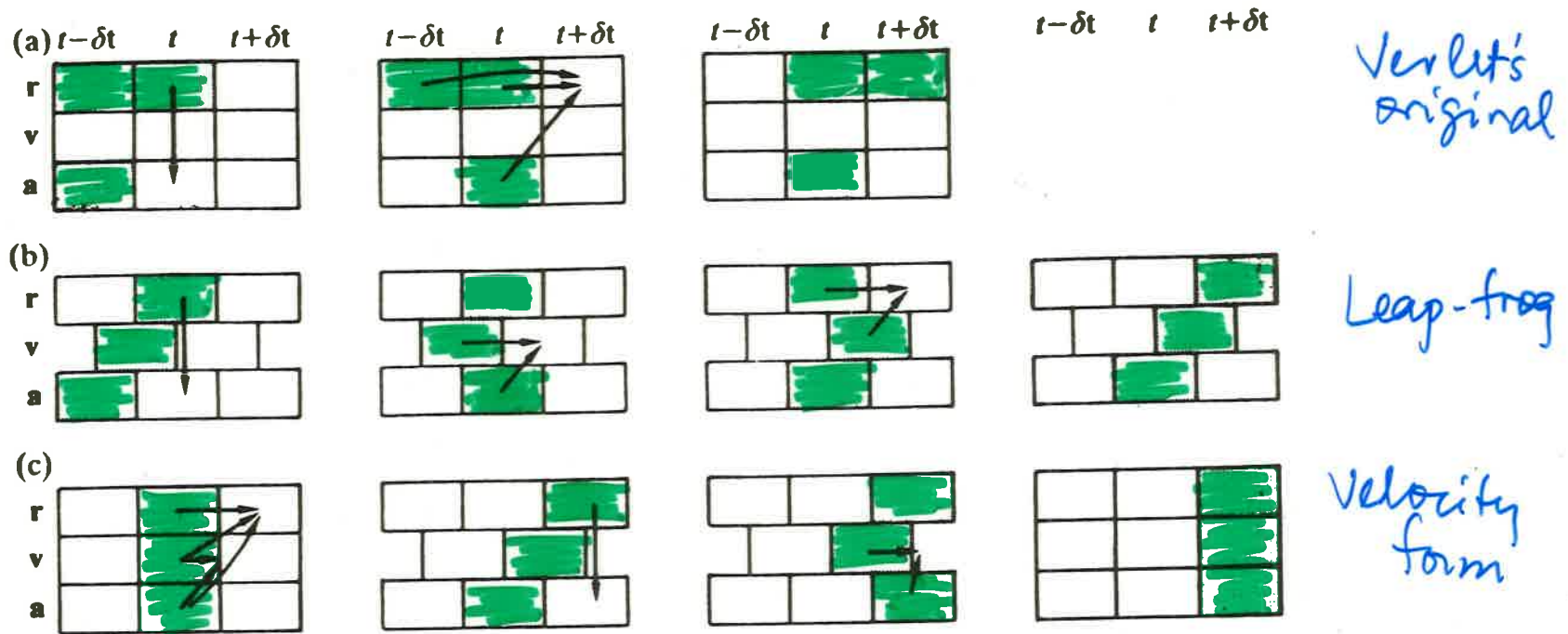
The variables DTSQ and DT2 store, respectively, δt^2 and $2\delta t$. Note the use of temporary variables RXNEWI, RYNEWI and RZNEWI to store the new positions within the loop. This is necessary because the current values must be transferred over to the 'old' position variables before being overwritten with the new values. This shuffling operation takes place in the last six statements within the loop. Note also that the calculation of kinetic energy (from SUMVSQ) and total linear momentum (from SUMVX, SUMVY and SUMVZ), is included in the loop, since this is the only moment at which both $r(t + \delta t)$ and $r(t - \delta t)$ are available to compute velocities. Following the particle move, we are ready to evaluate the forces for the next step. The overall

```fortran
      SUMVSQ = 0.0
      SUMVX  = 0.0
      SUMVY  = 0.0
      SUMVZ  = 0.0

      DO 100 I = 1, N

         RXNEWI    = 2.0 * RX(I) - RXOLD(I) + DTSQ * AX(I)
         RYNEWI    = 2.0 * RY(I) - RYOLD(I) + DTSQ * AY(I)
         RZNEWI    = 2.0 * RZ(I) - RZOLD(I) + DTSQ * AZ(I)
         VXI       = ( RXNEWI - RXOLD(I) ) / DT2
         VYI       = ( RYNEWI - RYOLD(I) ) / DT2
         VZI       = ( RZNEWI - RZOLD(I) ) / DT2
         SUMVSQ    = SUMVSQ + VXI ** 2 + VYI ** 2 + VZI ** 2
         SUMVX     = SUMVX + VXI
         SUMVY     = SUMVY + VYI
         SUMVZ     = SUMVZ + VZI
         RXOLD(I) = RX(I)
         RYOLD(I) = RY(I)
         RZOLD(I) = RZ(I)
         RX(I)     = RXNEWI
         RY(I)     = RYNEWI
         RZ(I)     = RZNEWI

  100 CONTINUE
```

MOLECULAR DYNAMICS

Fig. 3.2 Various forms of the Verlet algorithm.   (a) Verlet's original method.   (b) The leap-frog form.   (c) The velocity form. We show successive steps in the implementation of each algorithm. In each case, the stored variables are in grey boxes.

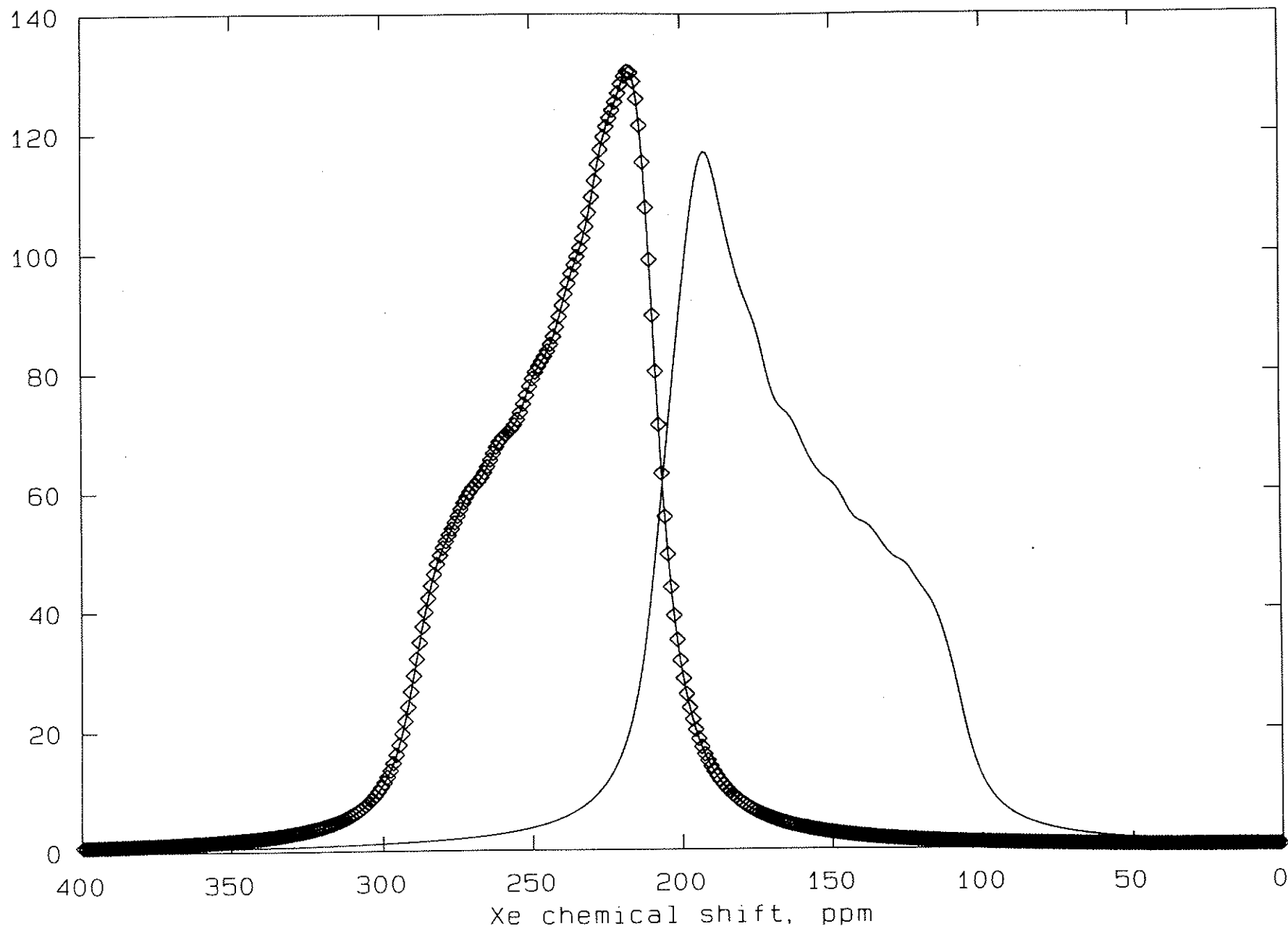What types of information do we expect to retrieve from MC/MD simulations?

I. Average values of <u>any</u> equilibrium property. Requires only that we know how to express the property in terms of the configuration of the system, then we can get this ensemble or time average out of an MC or MD simulation.
For example $\sigma(r^N)$

                      ↑

      electronic property

Can even do it for a <u>tensor</u> quantity.
For example can simulate the spectrum as a function of orientation of the single crystal with respect to a field.

broadened Xe NMR spectrum with complete averaging

example of
simulation of
a tensor property

intensity

Xe chemical shift, ppm

II Distributions, structural quantities

(a) One-body distribution of the particles of the system, that is, a density distribution, cluster formation, or between two phases in a grand-canonical scheme (adsorption isotherm, partition coefficients)

(b) Distributions of an equilibrium property — i.e. where are the contributions coming from? If we know this, maybe we will have a better idea of what is the measured (expt'l) value of the property telling us about the physical system.

(c) Pair distribution functions $g(r_{1,2})$

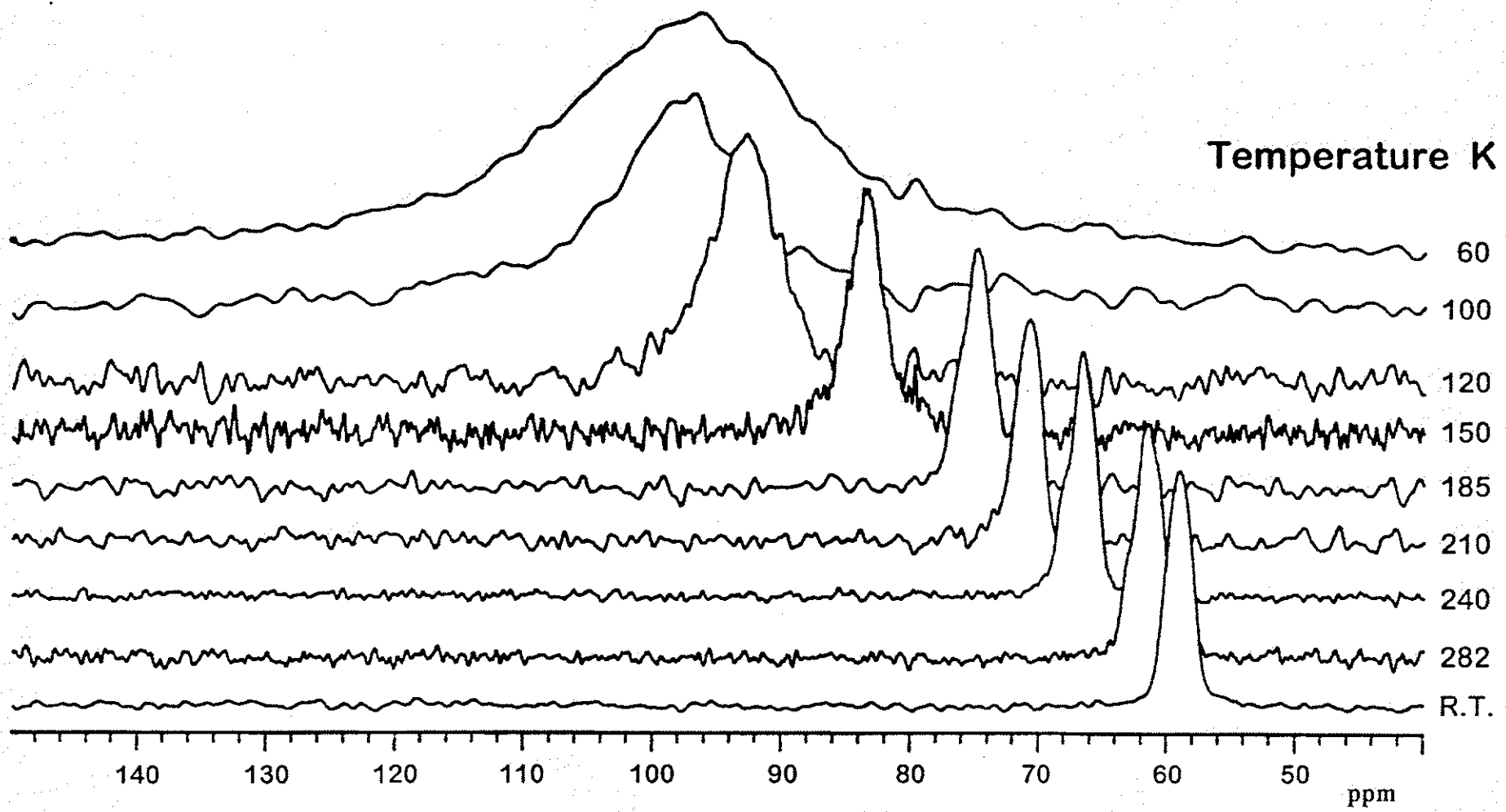1 and 2 can be any two atoms or centers, e.g. 1 on the membrane 2 on the molecule.

lead to structure factors measured experimentally in diffraction experiments

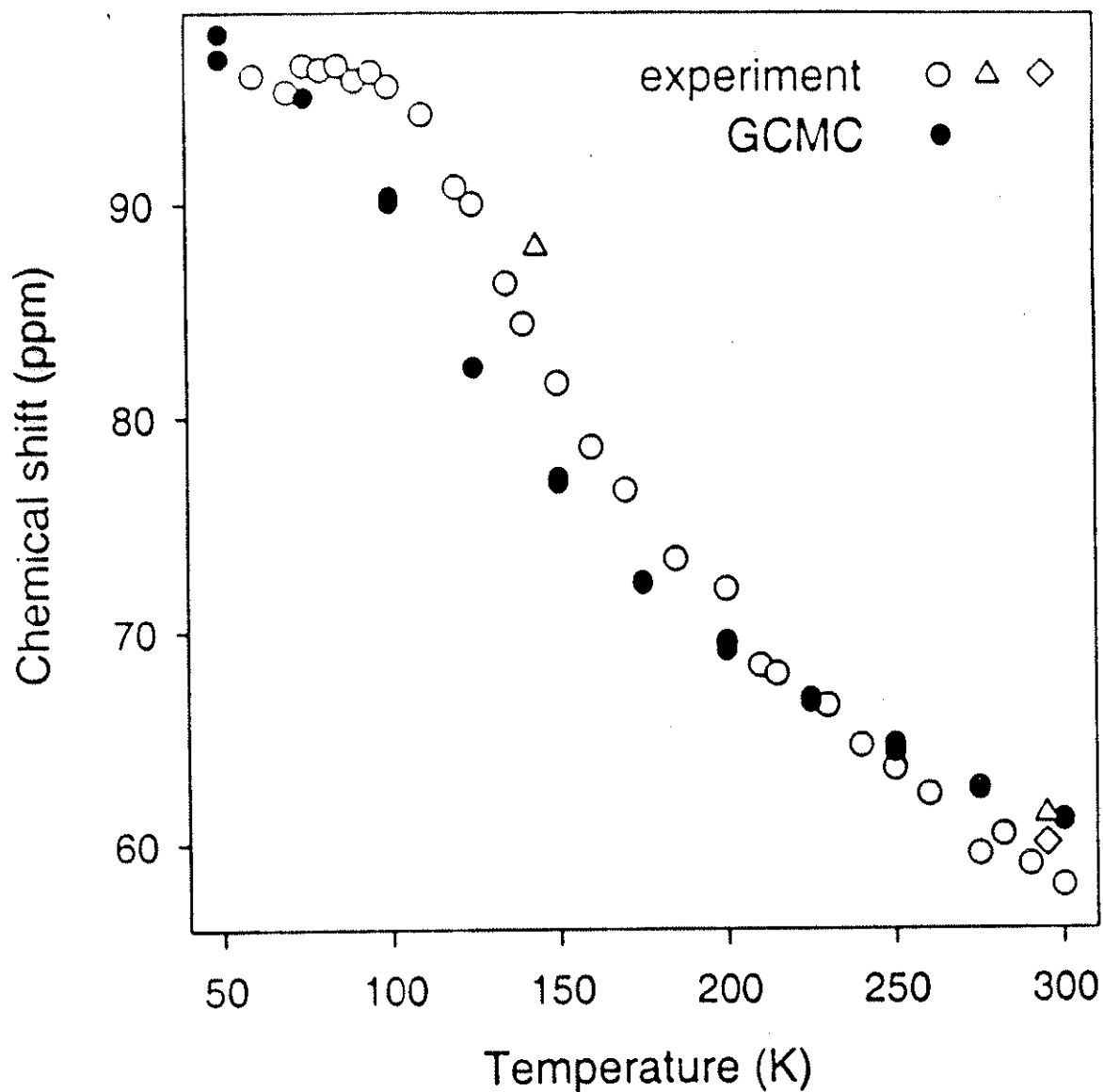(d) orientation distributions, order parameters, e.g. in liquid crystals.

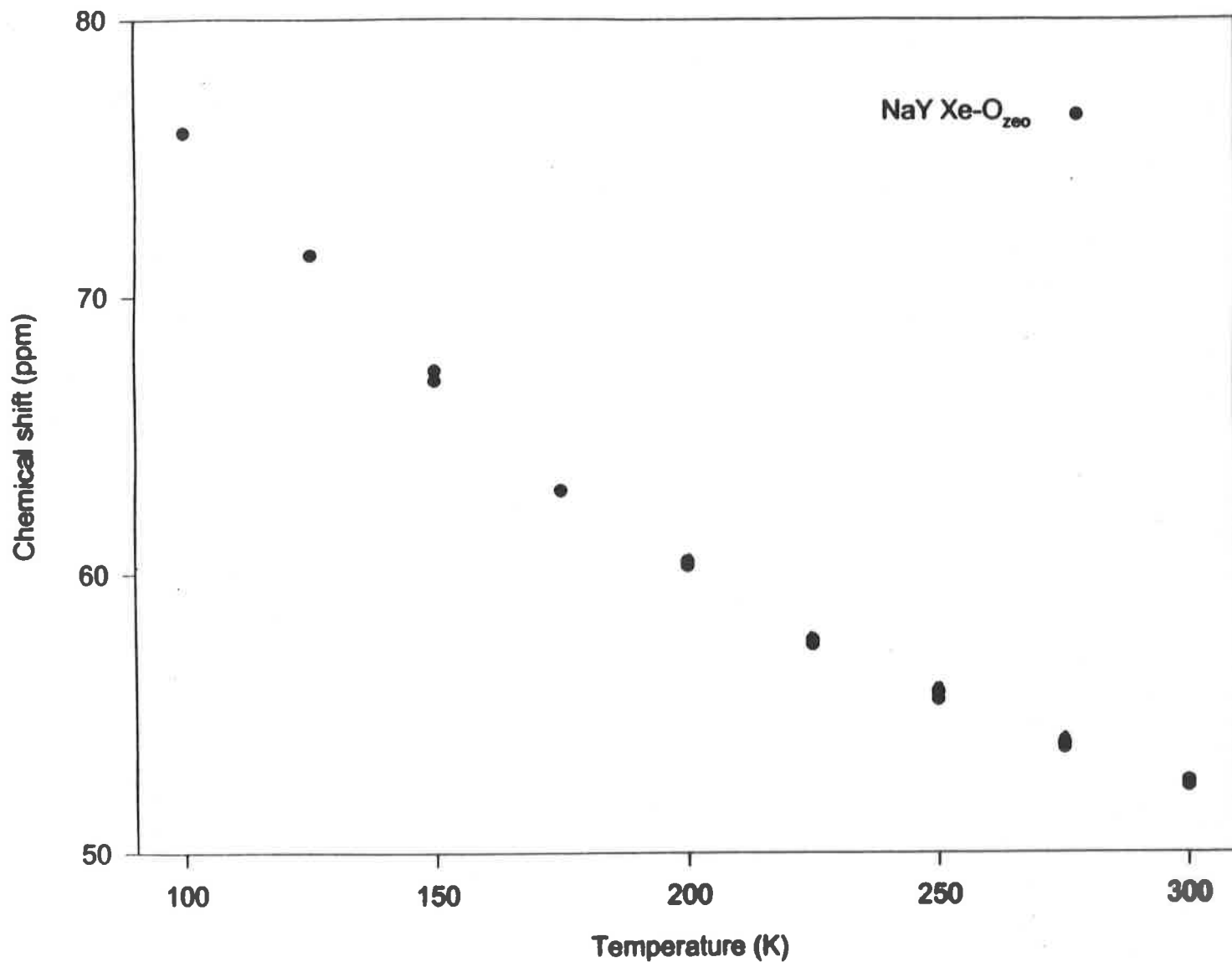Temperature K

60

100

120

150

185

210

240

282

R.T.

140   130   120   110   100   90   80   70   60   50

ppm

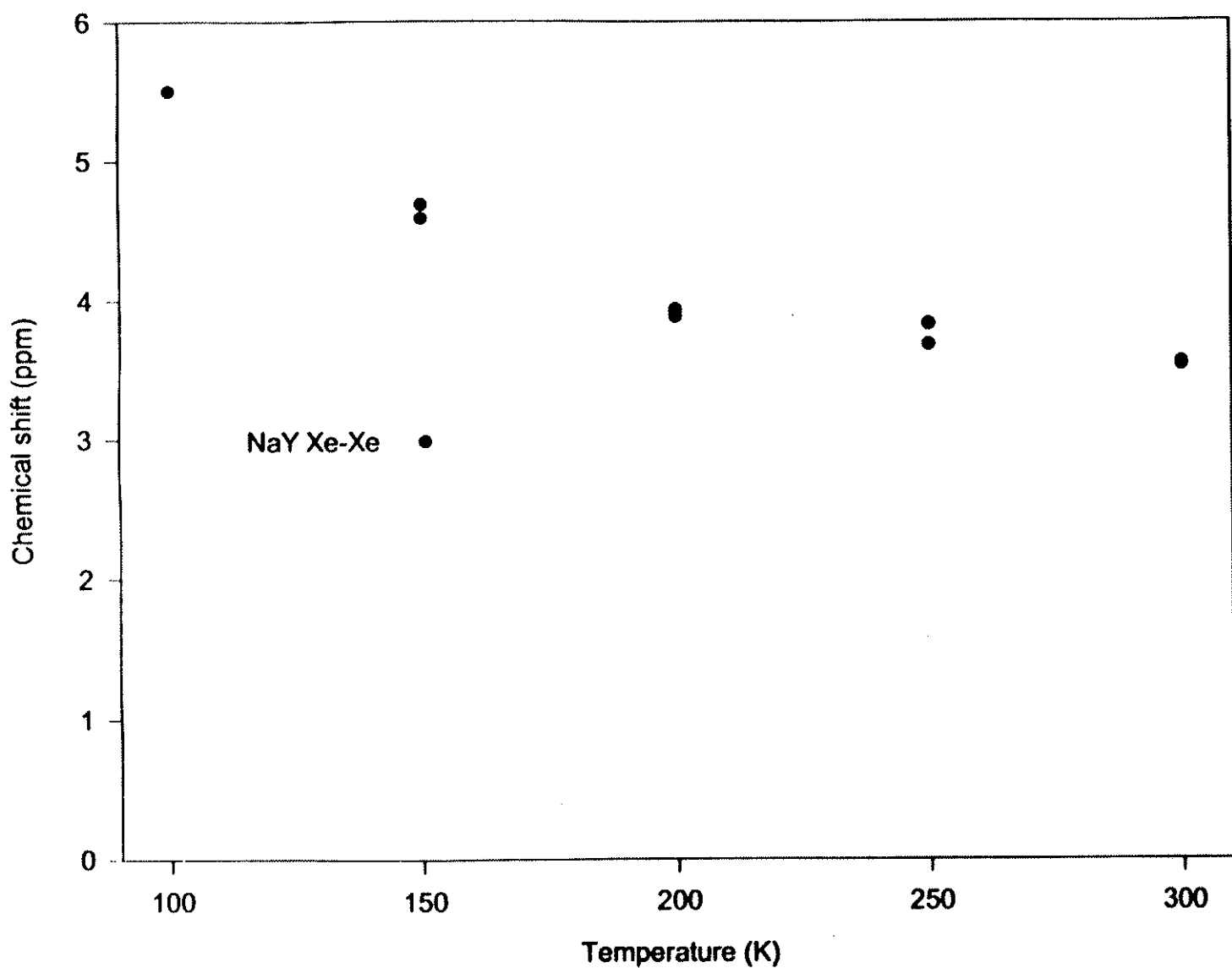# Temperature dependence of ^{129}Xe chemical shift at near-zero loading in zeolite NaY

○ Expt., Pietraß et al. 1999 $\langle n \rangle_{Xe} = 0.25$ atoms/cage

△ Expt., Cheung, 1988 $\langle n \rangle_{Xe} = 0.2$ atoms/cage

◇ Expt., S. B. Liu, 1994 $\langle n \rangle_{Xe} = 0.2$ atoms/cage

● GCMC calculations $\langle n \rangle_{Xe} = 0.250(5)$ atoms/cage

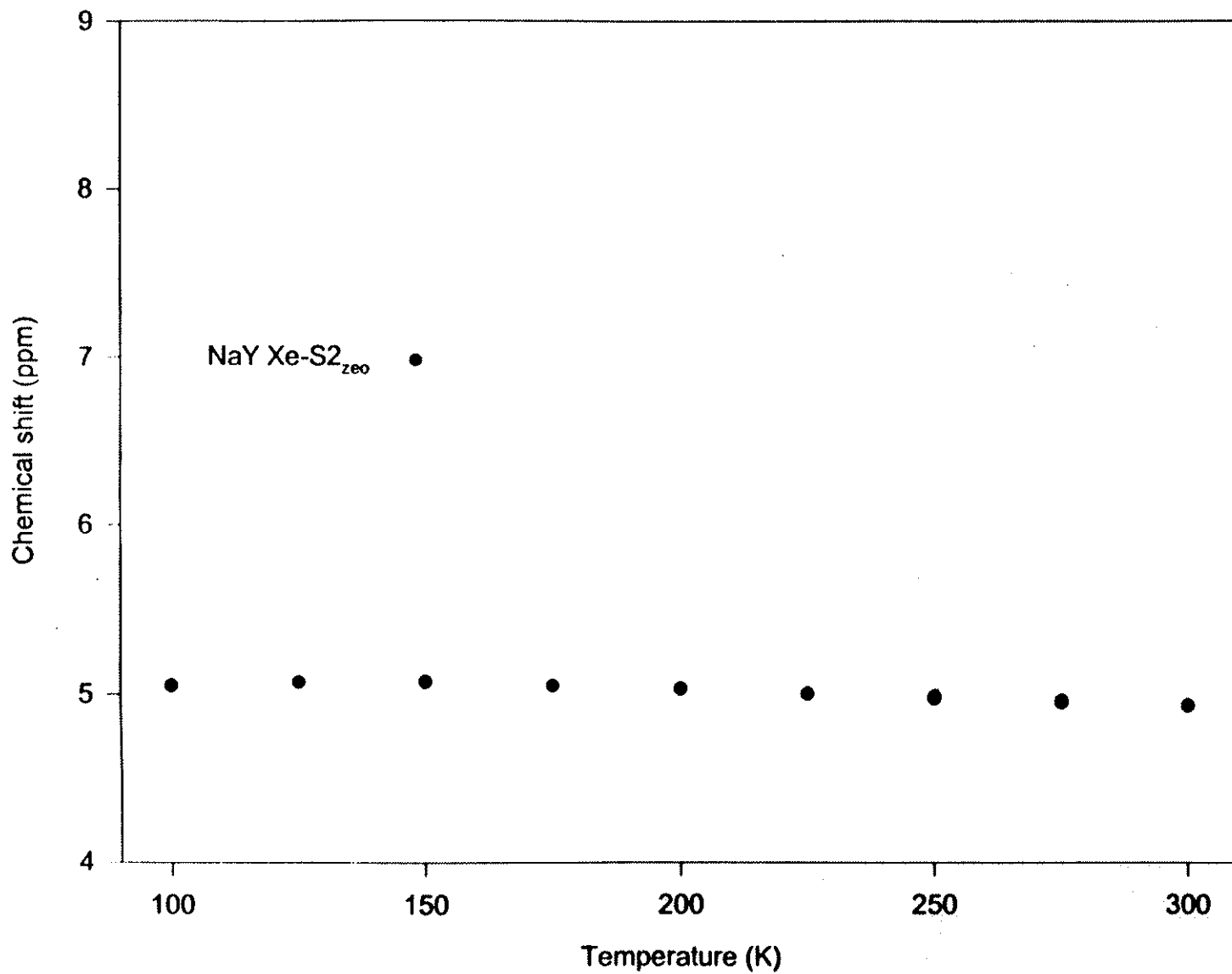^{129}Xe chemical shift in NaY zeolites - GCMC results
$(<n>_{Xe} = 0.250(5), nloop = 1'000'000)$

Chemical shift (ppm) vs Temperature (K)

NaY Xe-O_{zeo}

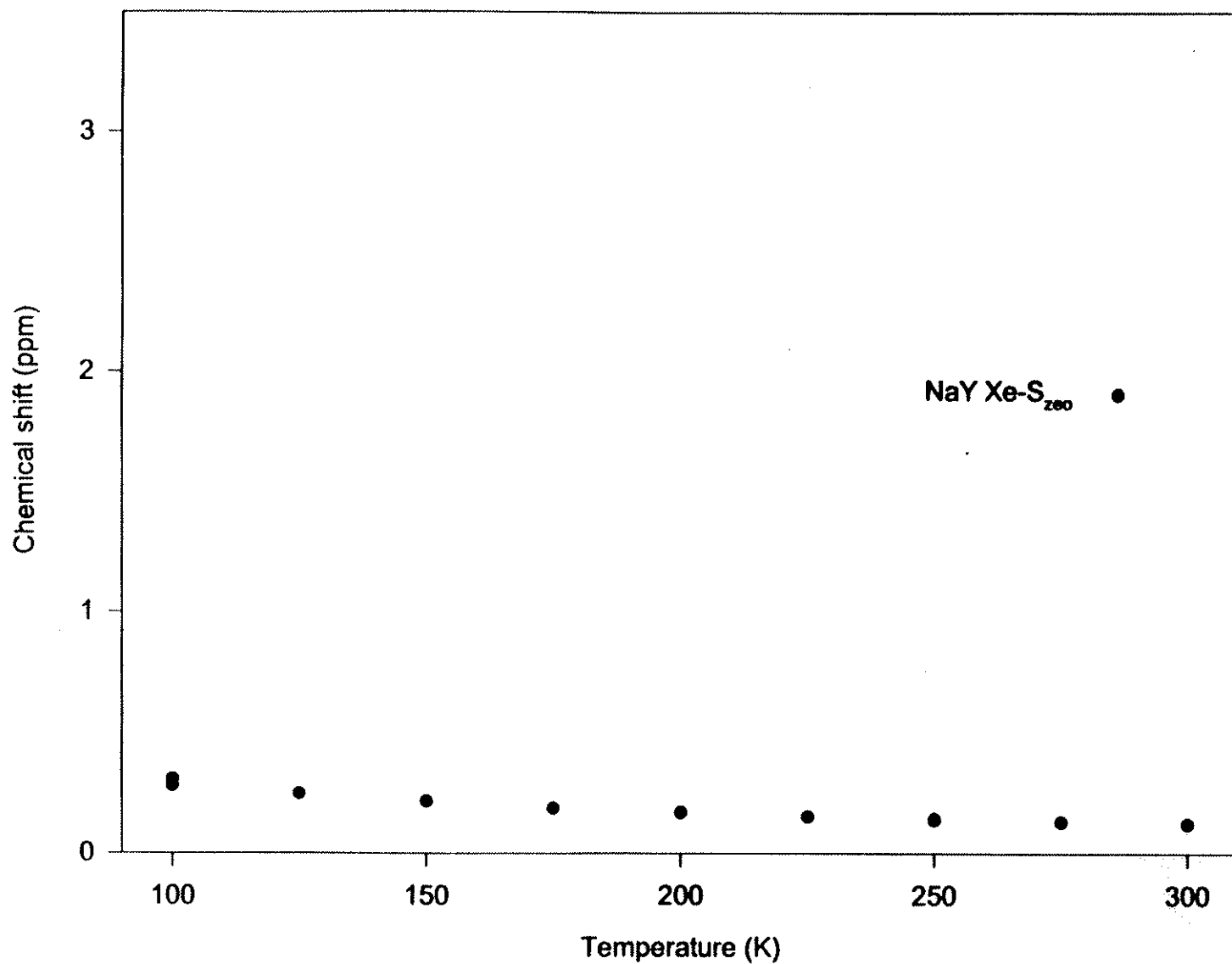^{129}Xe chemical shift in NaY zeolites - GCMC results
$(<n>_{Xe} = 0.250(5)$, nloop = 1'000'000)

^{129}Xe chemical shift in *NaY* zeolites - GCMC results
($<n>_{Xe} = 0.250(5)$, *nloop = 1'000'000*)

^{129}Xe chemical shift in NaY zeolites - GCMC results
($<n>_{Xe} = 0.250(5)$, nloop = 1'000'000)

NaY Xe-S_{zeo}

(c) Other quantities that can be
derived from the calculated
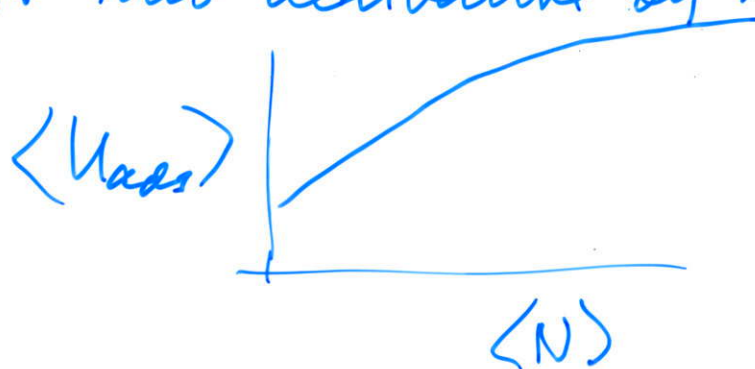ensemble or time averages
For example,
"isosteric heat of adsorption"
the ΔH that appears in the Clapeyron
equation for adsorption, analogous
to ΔH_{vap} or other!

$$\Delta H = \frac{1}{Z} \left\{ U_{gas} + PV_{gas} - \right.$$

$$\left. \langle U_{ads} \rangle_{\mu VT} - \langle N \rangle \left(\frac{\partial U_{ads}}{\partial \langle N \rangle} \right)_T \right\}$$

get this derivative by:

$\langle U_{ads} \rangle$ vs $\langle N \rangle$

III Information from RMS fluctuations

RMS deviation of $A = \langle A^2 \rangle_{ensemble} - \langle A \rangle^2_{ensemble}$

For example, can get

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \text{ from }$$

$$k_B T^2 C_V = \langle E^2 \rangle_{ens.} - \langle E \rangle^2_{ens.}$$

Can find various such quantities by thermodynamic manipulations

In a GC ensemble, energy, pressure and number fluctuations occur.

- Number fluctuations yield isothermal compressibility:

$$\langle N^2 \rangle_{\mu V T} - \langle N \rangle^2_{\mu V T} = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{VT}$$
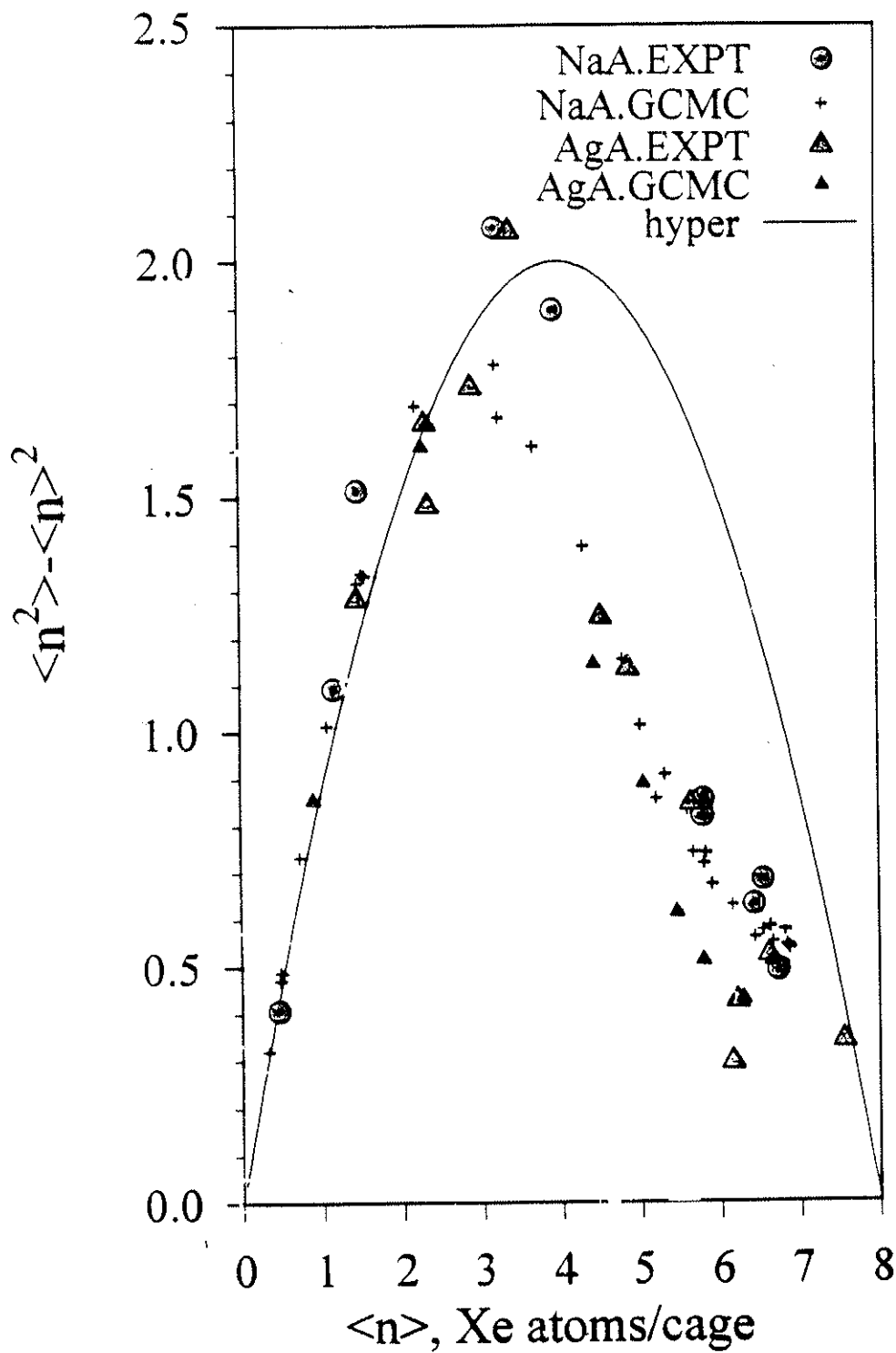
$$= \frac{N^2}{V} k_B T \beta_T$$

isothermal compressibility

$$\beta_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

- Number fluctuations may yield information about the rate processes that lead to the equilibrium distributions, since there is a relationship between the equilibrium constant and the rate constants for forward and back processes.
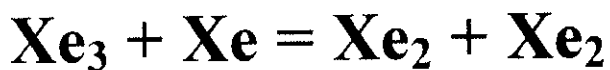
Dispersion of distribution

STRICTLY STATISTICAL?

Distribution of particles into N boxes each having 8 sites (hypergeometric distribution) gives ratios of rate constants, $k_{row,col} / k_{col,row}$:

	1	2	3	4	5	6	7
2	7/8						
3	6/8	6/7					
4	5/8	5/7	5/6				
5	4/8	4/7	4/6	4/5			
6	3/8	3/7	3/6	3/5	3/4		
7	2/8	2/7	2/6	2/5	2/4	2/3	
8	1/8	1/7	1/6	1/5	1/4	1/3	1/2

If the resulting equilibrium distribution is hypergeometric, what does this imply about the relative rates of the forward versus reverse process? The rate constants are in the ratio
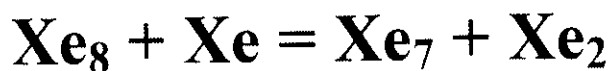
forward/backward =

$Xe_3 + Xe = Xe_2 + Xe_2$	7/6	0.90
$Xe_7 + Xe_3 = Xe_6 + Xe_4$	5/2	8.3
$Xe_8 + Xe = Xe_7 + Xe_2$	7/1	21.7

EXPT.

IV From MD alone:
Time correlation functions

(a) Time integrals of correlation functions may often be related directly to macroscopic transport coefficients

(b) Fourier transforms of correlation functions may often be related directly to experimental spectra

V From MD alone:
Rates of processes, mechanisms of processes.

An auto-correlation function is defined as

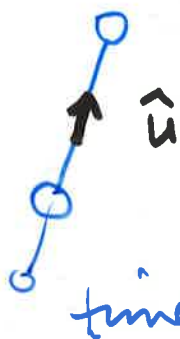$$C(t) = \langle a(0) \cdot a(t) \rangle$$

for a dynamical quantity $a(t)$.
Often, the dynamical quantities are defined in a way that the ensemble average of a is zero, so that as the time becomes large; as $t \rightarrow \infty$ $C(t) \rightarrow 0$

The shape of vibration-rotation bands in ir absorption and Raman scattering experiments on linear molecules depend on the auto-correlation functions

$$\langle \hat{u}(0) \cdot \hat{u}(t) \rangle \quad \text{and} \quad \langle P_2 [\hat{u}(0) \cdot \hat{u}(t)] \rangle$$

where
$\hat{u}$ is a unit vector pointing along the molecular axis and $P_2[\cdot]$ is the Legendre polynomial of index 2

time zero   time t $\hat{u}(0) \cdot \hat{u}(t)$
                                   gives $\cos\theta$

$$P_2[\hat{u}(0) \cdot \hat{u}(t)] = (3\cos^2\theta - 1)/2$$

These correlation functions measure the rate of reorientational motion of the molecules in the system, a liquid, for example.

In conventional Schrödinger picture, focus attention on the energy levels of the system rather than their time development.

In Heisenberg picture focus attention on time development of the system rather than on its quantum states. In this way can relate nature of rotational and translational motion from the broadened content of a pure rotational or ro-vibnl band.

Heisenberg picture:

spectrum is considered the Fourier transform of an appropriate time correlation function

Inversion of this relationship gives the correlation function (an experimental measure of it) as a Fourier integral over a complete experimental frequency spectrum.

See review by R. T. Bailey QC 454 M6 M64
p. 173   molecular spectry

Infrared absorption in an isotropic
system (gas, liquid, glass)

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ \exp^{-i\omega t} \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle$$

↗ spectral density
or spectral distribution

an equilibrium average over the initial states

In the Heisenberg picture the spectral
distribution is given by the Fourier
transform of a correlation function of
the dipole moment operator μ of the
absorbing molecules.

inversion:

$$\langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle = \int_{band} d\omega \ \exp^{i\omega t} \ I(\omega)$$

if we normalize the observed spectrum

$$I_{norm}(\omega) = \frac{I(\omega)}{\int_{band} I(\omega) d\omega}$$

then $\hat{u}(0) \cdot \hat{u}(t)$

↑ unit vector along
direction of
transition dipole

$$= \int_{band} d\omega \ \exp^{i\omega t} \ I_{norm}(\omega)$$

Raman scattering example

For the totally symmetric vibration in a linear molecule or a symmetric top the anisotropic part of the transition polarizability has the form

$$B_{ij} \propto \left(\underbrace{\mu_i^c \; \mu_j^c}_{} - \frac{1}{3} \underbrace{\delta_{ij}}_{} \right)$$

i$^{\underline{th}}$ component of a unit vector fixed along the symmetric axis c of the molecule

← Kronecker delta

$$\text{Trace of } \beta(0) \cdot \beta(t) \propto \sum_{i,j=1}^{3} \left\{ \mu_i^c(0) \mu_j^c(0) \mu_i^c(t) \mu_j^c(t) - \frac{1}{3} \right\}$$

Correlation function that gives rise to the Raman band intensity is

$$C(t) = \frac{1}{2} \left\langle P_2 \left[\mu^c(0) \cdot \mu^c(t) \right] \right\rangle$$

similarly for a degenerate vibration of a tetrahedral molecule, except here the unit vector along any of the two-fold axes is involved.

$$\left\langle \text{Trace of } \beta(0) \cdot \beta(t) \right\rangle = \frac{\int_{-\infty}^{+\infty} I_\perp(\omega) \exp^{-i\omega t} d\omega}{\int_{-\infty}^{+\infty} I_{vib}(\omega) \exp^{-i\omega t} d\omega}$$

for perpendicular-scattered Raman intensity $I_\perp(\omega)$

Spin relaxation of a quadrupolar nucleus

$$\frac{1}{T_1} = \frac{3(2I+3)}{80\,I^2(2I-1)} \left(\frac{eqQ}{\hbar}\right)^2 \int_{-\infty}^{+\infty} \langle P_2[\hat{u}(0)\cdot\hat{u}(t)\rangle\,dt$$
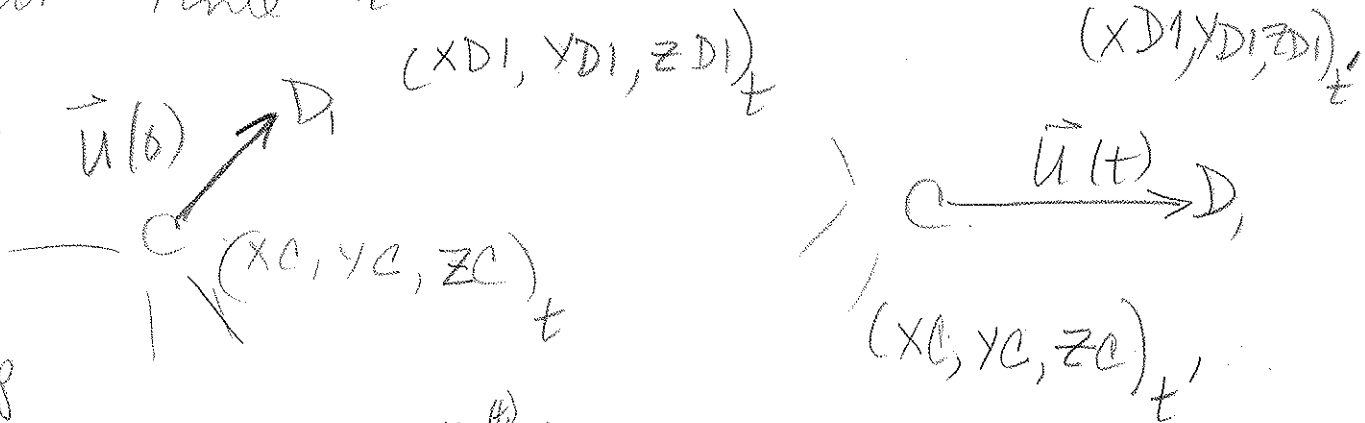
Correlation functions &
Calculation of relaxation time from
MD simulations

$$\frac{1}{T_1} = \frac{3(2I+3)}{40 I^2(2I-1)}\underbrace{\left(\frac{e q Q}{\hbar}\right)^2}_{} \int_{t=0}^{\infty} \langle P_2[\vec{u}(0)\cdot\vec{u}(t)]\rangle \, dt$$

measures strength of the interaction ...

$\vec{u}(0)$ = unit vector along CD, bond
at time zero

$\vec{u}(t)$ = unit vector along CD, bond
at time t

$(XD1, YD1, ZD1)_t$ $(XD1, YD1, ZD1)_{t'}$

$(XC, YC, ZC)_t$ $(XC, YC, ZC)_{t'}$

where
$x = i + i + \ldots$
$uu(i,i')$

old $\vec{u}(t)$ $XCD(t) = \frac{XD1 - XC}{RCD}$ new $\vec{u}(t)$ $XCD(t) =$
$YCD(t) =$ $YCD(t) =$
$ZCD(t) =$ $ZCD(t) =$

$uu(i,i') = \vec{u}(t)\cdot\vec{u}(t') = \dfrac{XCD(t)XCD(t') + YCD(t)YCD(t') + ZCD(t)ZCD(t')}{RCD**2}$

$\vec{u}(0)\cdot\vec{u}(0) = \dfrac{XCD**2 + YCD**2 + ZCD**2}{RCD**2} = 1$

$P_2[\vec{u}(t)\cdot\vec{u}(t')] = \frac{1}{2}(3\,uu - 1.0) \equiv P_2(n)$ for $t'-t = n$
$P_2[\vec{u}(t)\cdot\vec{u}(t')] = 1$

replace the integral by a sum

$$\sum_{N=0}^{N=NGTEPS} P2AV(n) * \underbrace{TSTEP}_{dt}$$

To get $P2AV(n) =$ for

$$\left\langle P_2\left[\vec{u}(t) \circ u(t')\right]\right\rangle \quad \text{for } t'-t = n * TSTEP$$

$$P2AV(n) = \frac{1}{nmax}\sum_{i=1}^{nmax} P_2(n)$$

t old point $= 5i$ $\Big\}$ separated by

t' new point $= 5i+n$ $\quad$ n steps

Example have collected NPTS config

n = 1

$P_2(1)$

sampling every step

old point is i

new point is $i+1$

difference is 1

or

old point is $2i$

new point is $2i+1$
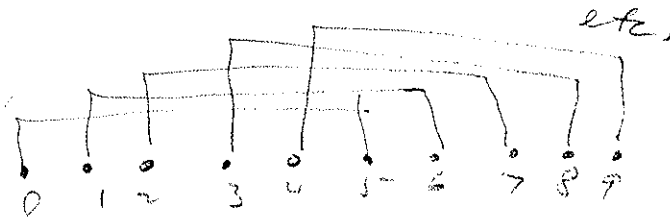
difference is also 1

or

old point is $5i$

new point is $5i+1$
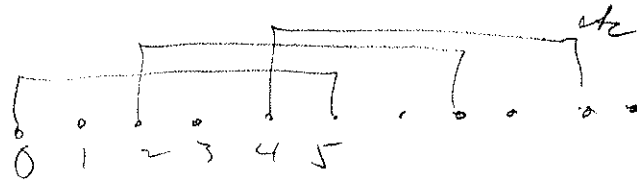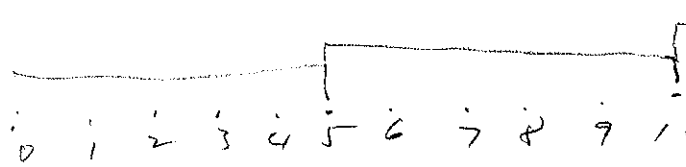
Example
n = 5

sampling every step
old point is i
new point is i+5
difference is 5

n

old point is 5i
new point is 5i+5

DO 100 n = 0 to NSTEPS

To get P2AV(n) we calculate for a given choice of sampling frequency (every 5)

$P2AV(n) = 0$

$nmax = 0$

DO 10 i = 0, NPTS while $(5i + n) \leq$ NSTEPS

$nmax = nmax + 1$

$$P2AV(n) = P2AV(n) + \left\{ \frac{3* UU(i, i+n)**2 - 1.0}{3* UU(i, i)**2 - 1.0} \right\}$$

10 continue

$P2AV(n) = 0.5D0 * P2AV(n) / nmax$

↑

This is $\langle P_2 [\vec{u}(t) \cdot \vec{u}(t')] \rangle$ for $t' - t = n * tstep$

100 continue

To get the integral $\int_{t=0}^{\infty} \langle P_2[\vec{u}(0) \cdot \vec{u}(t)] \rangle dt$

TSTEP

$$= \sum_{n=0}^{NSTEPS} P2AV(n) * TSTEP$$