# 8. Fluctuations

density fluctuations in the grand ensemble

the random walk

diffusion and random walk

# FLUCTUATIONS

A basic assumption in the theory developed in previous lectures is that if we make a large number of measurements of the value of some physical quantity (ENERGY, DENSITY, COMPOSITION, PRESSURE, MAGNETIC MOMENT, etc) on a macroscopic system, the AVERAGE of these measurements can be identified with the ensemble average for this property FOR AN APPROPRIATELY CONSTRUCTED ENSEMBLE (microcanonical, canonical or grand canonical).

Next question: What is the probability of observing a value for a given physical quantity which is DIFFERENT FROM THE AVERAGE VALUE?

In other words, what can we say about fluctuations at equilibrium?

## How sharp is a physical quantity?

Measure of the sharpness is MEAN SQUARE DEVIATION or root mean square deviation.

$$\langle F \rangle \text{ or } \bar{F} = \sum_j P_j F_j$$

$P_j$ = probability of finding a system in the state $j$

$F_j$ = value of the physical quantity when the system is in state $j$

Of course, $\sum_j P_j = 1$ (probability is normalized)

$$\langle (F-\bar{F})^2 \rangle = \sum_j P_j (F_j - \bar{F})^2$$

$$= \underbrace{\sum_j P_j F_j^2}_{\langle F^2 \rangle} - 2\bar{F} \underbrace{\sum_j P_j F_j}_{\langle F \rangle \text{ or } \bar{F}} + (\bar{F})^2 \underbrace{\sum_j P_j}_{1}$$

$$= \langle F^2 \rangle - \langle F \rangle^2$$ is the mean square deviation of the physical quantity $F$

Example:

Fluctuation in Energy in a Canonical Ensemble:

Recall that $P_j = \frac{e^{-\beta E_j}}{Q}$ for a Canonical Ensemble

$$\langle (E-\bar{E})^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad \text{(from above)}$$

Recall $\langle E \rangle = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V$

$$\langle E^2 \rangle = \sum_j P_j E_j^2 = \frac{\sum_j E_j^2 e^{-\beta E_j}}{Q} = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2}$$

$$= \frac{1}{Q}\frac{\partial}{\partial \beta}\left(\frac{\partial Q}{\partial \beta}\right) = \frac{1}{Q}\frac{\partial}{\partial \beta}(-\langle E \rangle Q)$$

$$= -\frac{\langle E \rangle}{Q}\left(\frac{\partial Q}{\partial \beta}\right) - \frac{\partial \langle E \rangle}{\partial \beta} = \langle E \rangle^2 - \frac{\partial \langle E \rangle}{\partial \beta}$$

$$kT^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V \text{ or } kT^2 C_V$$

$\therefore$ $\langle (E-\bar{E})^2 \rangle = kT^2 C_V$

If a perfect monatomic gas, $\langle E \rangle = \frac{3}{2} NkT$

$C_V = \frac{3}{2} Nk$

$$\langle (E-\bar{E})^2 \rangle = \frac{3}{2} N k^2 T^2$$

$rms = \sqrt{\frac{3}{2}N}\, kT$ ← Note! $rms \propto \sqrt{N}$

so that $\frac{\text{rms}}{\langle E \rangle}$ the fractional fluctuation in energy is $\frac{2}{3\sqrt{N}}$

## Density Fluctuations in the Grand Ensemble

Express this in terms of $\langle (N-\bar{N})^2 \rangle$ or in terms of $\frac{\langle (N-\bar{N})^2 \rangle^{1/2}}{\bar{N}}$

Recall $P_N = \frac{e^{\beta N\mu} Q_N(T,V)}{\mathcal{Z}}$ where $\mathcal{Z} = \sum_N e^{\beta N\mu} Q_N(T,V)$

$$\langle N \rangle \text{ or } \bar{N} = \sum_N N P_N = \frac{1}{\beta \mathcal{Z}} \left( \frac{\partial \mathcal{Z}}{\partial \mu} \right)_{T,V} \quad *$$

$$\langle N^2 \rangle = \sum_N N^2 P_N = \frac{\sum_N N^2 e^{\beta N\mu} Q_N(T,V)}{\mathcal{Z}} = \frac{1}{\beta^2 \mathcal{Z}} \left( \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right)_{T,V}$$

$$= \frac{1}{\beta^2 \mathcal{Z}} \frac{\partial}{\partial \mu} \left( \frac{\partial \mathcal{Z}}{\partial \mu} \right)_{T,V} = \frac{1}{\beta^2 \mathcal{Z}} \left[ \frac{\partial (\beta \mathcal{Z} \bar{N})}{\partial \mu} \right]_{T,V}$$

$$= \frac{\bar{N}}{\beta \mathcal{Z}} \left( \frac{\partial \mathcal{Z}}{\partial \mu} \right)_{T,V} + \frac{1}{\beta} \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{T,V}$$

$$= (\bar{N})^2 + kT \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{T,V}$$

$$\langle (N-\bar{N})^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = kT \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V}$$

Fluctuations:

heat capacities

$C_V$ $\left(\partial E/\partial T\right)_V$

$C_P$ $\left(\partial H/\partial T\right)_P$

thermal expansion coeff $\alpha_P$ $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

isothermal compressibility $\beta_T$ $\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

thermal pressure coeff $\gamma_V$ $\left(\frac{\partial P}{\partial T}\right)_V$

Example: $kT^2 C_V$ = mean square deviation or fluctuation in $E$

$\langle E^2\rangle - \langle E\rangle^2$

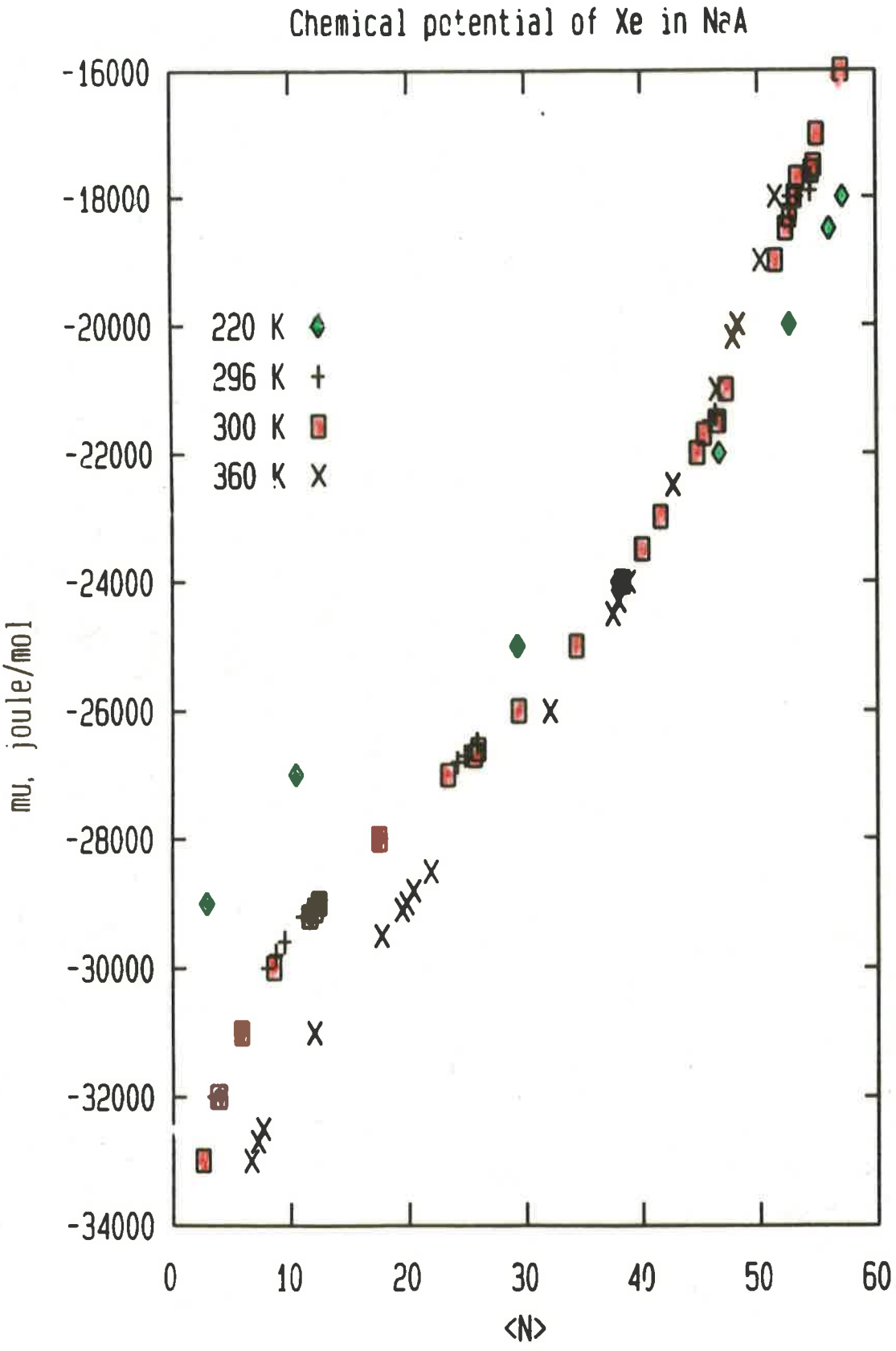
Can derive

$$\langle \delta P\, \delta T\rangle_{NVE} = \langle \delta P\, \delta E\rangle_{NVE} = \frac{Nk^2T^2}{V}\left(1 - \frac{3V\gamma_V}{2C_V}\right)$$

($P$: pressure; $T$: K.E.; $E$: P.E.)

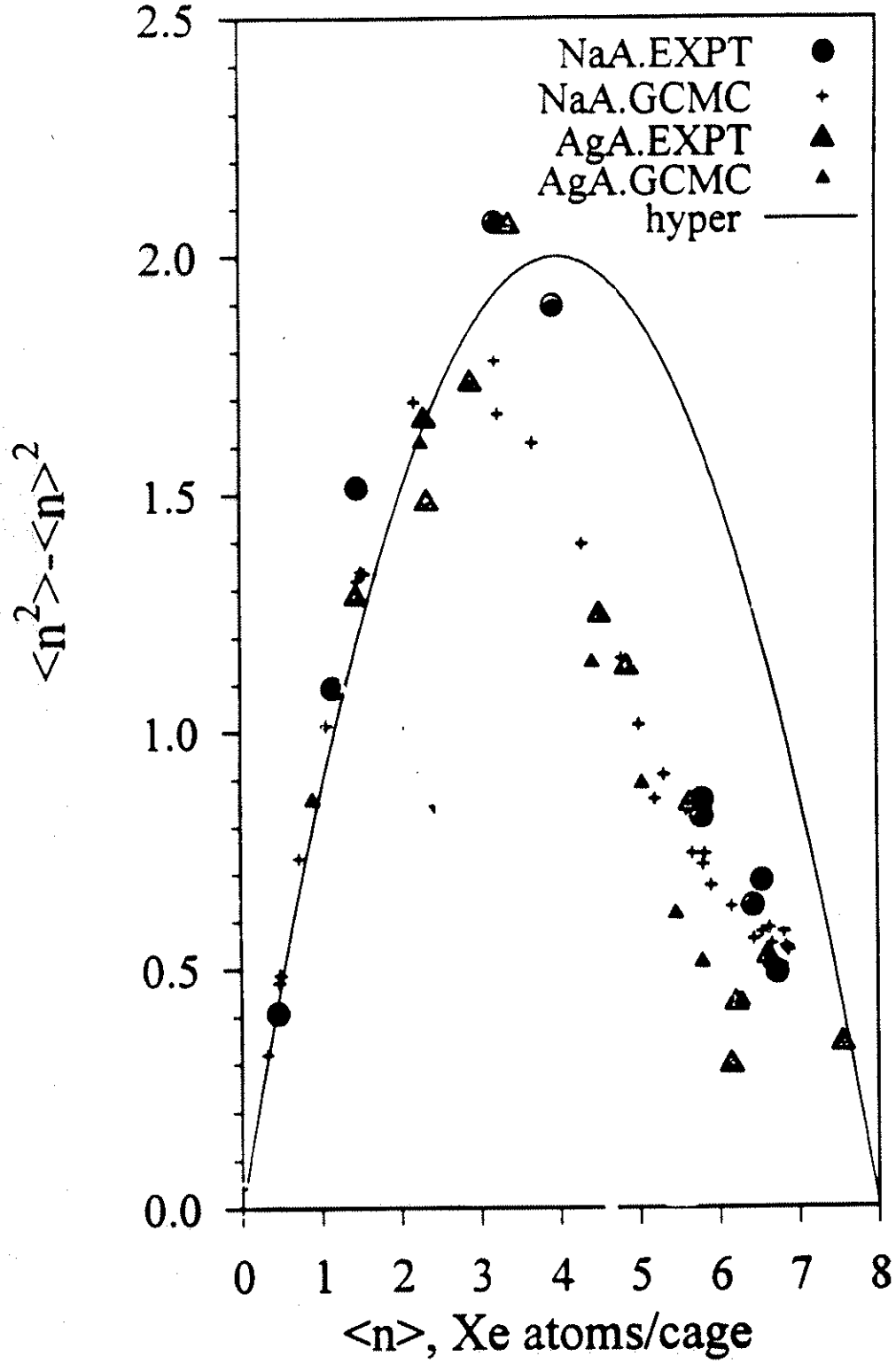
etc. $\langle \delta N^2\rangle_{\mu VT} = kT\left(\frac{\partial N}{\partial \mu}\right)_{VT} = \frac{N^2}{V}\, kT\, \beta_T$

$\beta_T$: isothermal compressibility


Chemical potential of Xe in NaA
-16000
-18000
-20000
-22000
-24000
-26000
-28000
-30000
-32000
-34000
mu, joule/mol
220 K
296 K
300 K
360 K
0
10
20
30
40
50
60
<N>

<n>=0.45
<n>=1.18
<n>=1.46
<n>=3.21
<n>=3.84
EXPT
GCMC
<n>=5.79
<n>=5.80
<n>=6.43
<n>=6.54
<n>=6.73
0.0
0.2
0.4
0.6
0 2 4 6 8
n

# Dispersion of distribution



Applications of fluctuations:

Light scattering — random fluctuations in concentration and density produce corresponding fluctuations in the refractive index of the medium. Light scattering occurs due to the instantaneous non-uniform refractive index n

$$\left(\frac{\partial(n^2)}{\partial g}\right)_{T,P}^2 g M_2 \frac{8\pi^3}{3\lambda^4} = \text{"turbidity"}$$

$g$ = concentration of solute in $g \cdot cm^{-3}$

$M_2$ = molecular weight of solute

Distribution of adsorbates within a porous solid or on the surface of a solid. [See figure]

## The random walk

1-D: Consider a random walk in one dimension. The walker makes $\nu$ jumps per unit time, each of length $l$ at random, in either the $+x$ or $-x$ direction.

Question: What is the probability that he will be a certain distance $x$ from the origin after time $t$?

The number of jumps is $N = \nu t$

One possible result of this random walk is that the number of jumps in the + direction is $m$. Then $\nu t - m$ = number of jumps in the − direction:

The mean or most probable value for $m$ is $\langle m \rangle = \nu t/2$.

The distance traveled for the case of $m$ forward jumps is

$$x = ml + (\nu t - m)(-l) = l(2m - \nu t) = 2l(m - \langle m \rangle)$$

forward backward

For a large number of jumps ($\nu t >> 1$) the probability of a given value of $m$ is given by (to be derived later)

$$P_N(m) = \left(\frac{2}{\pi N}\right)^{1/2} \exp -2(m - \langle m \rangle)^2/N$$

a Gaussian distribution

Let us see what this gives us for $\langle x^2 \rangle$:

Since the relation between the number of jumps in the forward direction and the distance travelled is given by

$x = 2l(m - \langle m \rangle)$ as shown above,

an interval $dm$ in the number of jumps corresponds to an interval $dx = 2l\,dm$ in the distance travelled. Therefore, the probability of the random walker being in the interval between $x$ and $x+dx$ after time $t$ is

$$p(x)dx = \left(\frac{2}{\pi \nu t}\right)^{1/2} \exp -2\left(\frac{x}{2l}\right)^2/\nu t \cdot \frac{dx}{2l}$$

$$= \left(\frac{1}{2\pi \nu l^2 t}\right)^{1/2} \exp -x^2/2l^2\nu t \; dx$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 p(x)\,dx = 2\int_0^\infty \sqrt{\frac{a}{\pi}}\, x^2 e^{-ax^2} dx = \frac{1}{2a} = l^2 \nu t$$

Therefore the mean square distance travelled is

$$\langle x^2 \rangle = l^2 \nu t$$

(The Gaussian distribution is $\left(\frac{1}{2\pi\langle x^2\rangle}\right)^{1/2} \exp -x^2/2\langle x^2\rangle$)

# Digression on the Gaussian distribution:

Problem: Consider $N$ boxes each containing $Q$ white balls and $R$ black balls.

One ball is taken from each box.

What is the probability $P_N(m)$ that $m$ of the balls will be white and $N-m$ black?

Solution:

The probability of drawing a white ball from a box is $q = \frac{Q}{R+Q}$

The probability of drawing a black ball from a box is $r = \frac{R}{R+Q} = 1-q$

The probability of drawing $m$ white balls from $m$ particular boxes and $(N-m)$ black balls from the $(N-m)$ other boxes is

$$q^m r^{(N-m)}$$

But there are $\frac{N!}{m!(N-m)!}$ ways of selecting $m$ boxes out of $N$ boxes. Therefore the total probability of drawing $m$ white balls is

$$P_N(m) = \frac{N!}{m!(N-m)!} q^m r^{(N-m)}$$

and of course $\sum_m P_N(m) = 1$

→ example

Now we are interested in the approximation for the case where both $N$ and $m$ are large.

Example: when m and N are small enough:

An application of this formula is in determining the fraction of a particular isotopomer when N exchangeable equivalent hydrogens are replaced by deuteriums. For example,

$[Co(NH_3)_6]^{3+}$ has 18 exchangeable equivalent hydrogens

The fraction of the Co complex ion that is in the form containing m deuteriums and (N-m) hydrogens is for $N = 18$

$$P(m) = \frac{18!}{m!\,(18-m)!}\, d^{m}(1-d)^{18-m}$$

where d is the deuterium fraction in the $H_2O/D_2O$ solvent that was used to dissolve the salt. $d = \frac{\text{no. of D atoms}}{\text{no. of (D + H) atoms}}$

fraction of $H_{16}D_2$ isotopomer in a 15% $D_2O$ solution $= \frac{18!}{2!\,16!}(0.15)^2(0.85)^{16}$

$= 0.2556$

fraction of $H_{12}D_6$ $= \frac{18!}{6!\,12!}(0.15)^6(0.85)^{12}$

$= 0.030$

.0536 $H_{18}$
.1704 $H_{17}D$
.2556 $H_{16}D_2$
.2406 $H_{15}D_3$
.1592 $H_{14}D_4$
.07866 $H_{13}D_5$
.0300 $H_{12}D_6$
.0090 $H_{11}D_7$
.006 $H_{10}D_8$

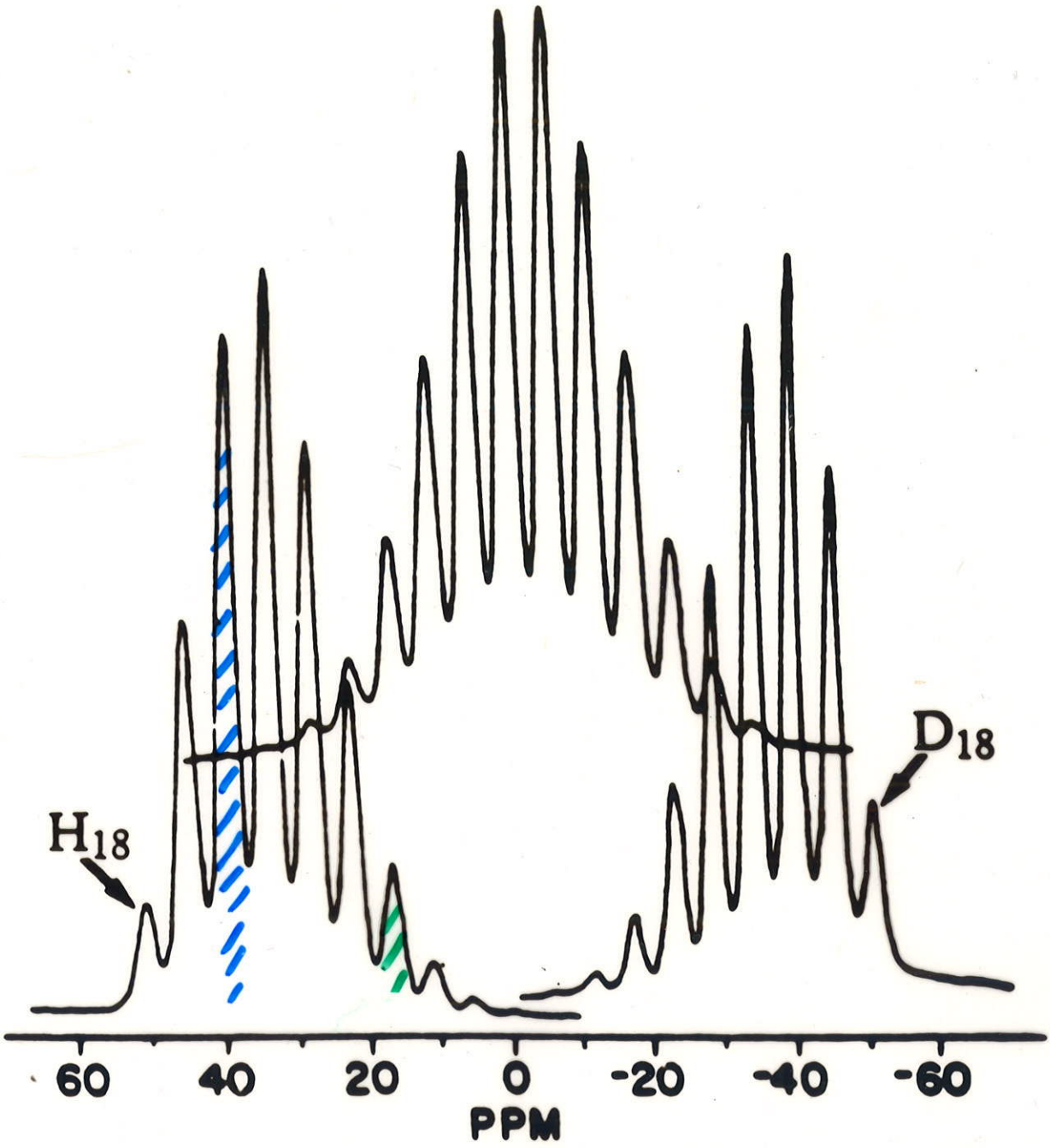
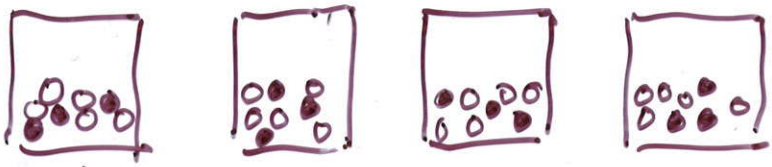



Fig. 3. The $^{59}Co$ NMR spectrum of $[Co(NH_3)_6]^{3+}$ ion in $D_2O/H_2O$ solvent. The spectra, from left to right, are for 15%, 50%, 85% $D_2O$

# The Gaussian Distribution

$N$ boxes



each has
$Q$ ○
$R$ ●

$$q = \frac{Q}{R+Q} \qquad r = \frac{R}{R+Q} = (1-q)$$

One ball is taken from each box

**What is the probability $P_N(m)$ that $m$ of the balls will be ○ and $(N-m)$ will be ●.**

Answer:

$$P_N(m) = \frac{N!}{m!\,(N-m)!}\, q^{m}\, r^{(N-m)}$$

When both $m$ and $N$ are very large, use Stirling's approximation

$$\ln N! = \tfrac{1}{2}\ln 2\pi N + N\ln N - N$$

$$\ln P_N(m) = \tfrac{1}{2}\ln\frac{N}{2\pi m(N-m)} + N\ln N - m\ln m - (N-m)\ln(N-m) + m\ln q + (N-m)\ln r$$

$$N\ln N = m\ln N + (N-m)\ln N$$

$$\ln P_N(m) = \tfrac{1}{2}\ln\frac{N}{2\pi m(N-m)} - m\ln\left(\frac{m}{Nq}\right) - (N-m)\ln\left(\frac{N-m}{Nr}\right)$$

Note that $\langle m \rangle = Nq$

Let us introduce a variable $x$ which will measure deviation from the mean in units of the rms deviation

Let $x = \dfrac{m - \langle m \rangle}{\sqrt{N}}$ so that values of $x$ are close to 1.0

$$m = \langle m \rangle + x\sqrt{N} = Nq + x\sqrt{N}$$
$$= Nq\left(1 + \frac{x}{q\sqrt{N}}\right)$$

$$N - m = N - [Nq + x\sqrt{N}] = N(1-q) - x\sqrt{N}$$
$$= Nr - x\sqrt{N}$$
$$= Nr\left(1 - \frac{x}{r\sqrt{N}}\right)$$

Since $\dfrac{x}{q\sqrt{N}} << 1$, in ↓ use approximation $\ln(1+y) \approx y - y^2/2 \cdots$

$$\ln m = \ln Nq + \ln\left(1 + \frac{x}{q\sqrt{N}}\right)$$
$$\cong \ln Nq + \frac{x}{q\sqrt{N}} - \frac{1}{2}\left(\frac{x}{q\sqrt{N}}\right)^2$$

$$\ln N - m = \ln Nr + \ln\left(1 - \frac{x}{r\sqrt{N}}\right)$$
$$\cong \ln Nr - \frac{x}{r\sqrt{N}} - \frac{1}{2}\left(\frac{x}{r\sqrt{N}}\right)^2$$

$$\therefore \ln \frac{m}{Nq} \simeq \frac{x}{q\sqrt{N}} - \frac{1}{2}\frac{x^2}{Nq^2}$$

$$\ln \frac{(N-m)}{Nr} \simeq \frac{-x}{r\sqrt{N}} - \frac{1}{2}\frac{x^2}{Nr^2}$$

substitute these into

$$\ln P_N(m) = \frac{1}{2}\ln \frac{N}{2\pi m(N-m)} - m\ln\left(\frac{m}{Nq}\right) - (N-m)\ln\left(\frac{N-m}{Nr}\right)$$

and much algebra thereafter

⋮

$$\ln P_N(m) \simeq -\frac{1}{2}\ln(2\pi N q r) - \frac{x^2}{2qr}$$

$$\text{or } P_N(m) = \left(\frac{1}{2\pi N q r}\right)^{1/2} e^{-\frac{x^2}{2qr}}$$

Now put back $x^2 = \dfrac{(m-\langle m\rangle)^2}{N}$

$$P_N(m) = \left(\frac{1}{2\pi N q r}\right)^{1/2} e^{-(m-\langle m\rangle)^2/2Nqr}$$

Example: When $r = q = 1/2$ as in tossing a coin $N$ times.

$$P_N(m) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-2(m-\langle m\rangle)/N}$$

average: $\langle m\rangle = Nq = \frac{N}{2}$

mean square deviation: $\left\langle (m-\langle m\rangle)^2 \right\rangle = ?$

$$\left\langle (m-\langle m\rangle)^2 \right\rangle = \int_{-\infty}^{+\infty} P_N(m)\,(m-\langle m\rangle)^2\, d(m-\langle m\rangle)$$

$$= \left(\frac{2}{\pi N}\right)^{1/2} \int_{-\infty}^{+\infty} (m-\langle m\rangle)^2 e^{-2(m-\langle m\rangle)^2/N}\, d(m-\langle m\rangle)$$

is of the form

$$\int_{-\infty}^{+\infty} y^2 e^{-ay^2}\, dy = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

where $a = 2/N$

$$= \left(\frac{2}{\pi N}\right)^{1/2} \cdot \frac{1}{4/N}\sqrt{\frac{\pi N}{2}} = \frac{N}{4}$$

Gaussian distribution:

$$P(x) = \left[\frac{1}{2\pi \langle x^2 \rangle}\right]^{1/2} e^{-\frac{x^2}{2\langle x^2 \rangle}}$$

in this example

$$x = m - \langle m \rangle$$

$$\langle x^2 \rangle = N/4$$

# Diffusion and random walk

Random walk on a square lattice, N steps:

a) $k = 0$

$\underset{\sim}{r}(0) = 0$ (origin)

b) Choose a random number I between 1 and 4

c) $\underset{\sim}{r}(k+1) = \underset{\sim}{r}(k) + \underset{\sim}{v}(I)$

where $\underset{\sim}{v}(1) = (1,0)$

$\underset{\sim}{v}(2) = (0,1)$

$\underset{\sim}{v}(3) = (-1,0)$

$\underset{\sim}{v}(4) = (0,-1)$

d) If $k+1 = N$, $\underset{\sim}{rr} = \underset{\sim}{r}(k+1)$ end-to-end distance of the walk

e) Else $k = k+1$, go to b)

This is a reasonable model for hopping conduction in solids, diffusion processes on ideal lattices. To get a statistically valid average end-to-end distance, one should do the above a large number of times (CYCLES), accumulate the end-to-end distances and divide by the number of cycles to get the average.

Try a random walk in 3 dimensions (SC). Let the rate constant be 0.31 per second for the hopping rate. Loop through $N = 40$ time steps. Use 1500 samples or cycles to obtain the mean square distance from the origin. Repeat for $N = 100$ and $N = 200$. This is a model for the diffusion of a Xe

atom in zeolite NaA. The mean square end-to-end distance is

$$\langle R_N^2 \rangle = \langle [\underset{\sim}{R}_N(N) - \underset{\sim}{R}_N(0)]^2 \rangle$$

Find the relationship between k and the self-diffusivity. The diffusion coefficient (the self-diffusivity $D_S$) is obtained by

$$D_S = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle [\underset{\sim}{R}(t) - \underset{\sim}{R}(0)]^2 \rangle$$

Random walks are not a good model for obtaining the size of an N-step chain, for example a string of N beads. We need self-avoidance. In diffusion the random walk intersects itself and folds back on itself, whereas beads have mutual exclusion, that is, there cannot be two beads occupying a lattice site. Therefore, a simple random walk can not be used. What we need is a self-avoiding walk, that is if the step will lead to a lattice site that has already been visited, stop the walk and start all over again.

## Self-avoiding Random Walks —

Characteristics of an N-step chain

a) mean square end-to-end distance

$$\langle R_N^2 \rangle = \langle [\underset{\sim}{R}_N(N) - \underset{\sim}{R}_N(0)]^2 \rangle$$

b) mean square radius of gyration (mean sq. distance between 2 beads)

$$\langle S_N^2 \rangle = \frac{1}{2N^2} \sum_{n,m=0}^{N} \langle [\underset{\sim}{R}_N(m) - \underset{\sim}{R}_N(n)]^2 \rangle$$

($\underset{\sim}{R}_N(m)$: position vector of the $m^{th}$ bead in an N-step chain)

The restriction of self-avoidance is equivalent to the introduction of a memory into the random walk scheme, which makes exact calculations impossible.

c) distribution function of the end-to-end vector $P_N(\underset{\sim}{R})$ is the number of possibilities of an N-step chain to have an end-to-end vector $\underset{\sim}{R}$ divided by the total number of N-step chains to normalize. For a simple random walk and for $N >> 1$, this distribution is Gaussian, as we have shown. However, for SAW (self-avoiding walks) the distribution deviates from a Gaussian. In any case the mean square end-to-end distance is the SECOND MOMENT of this distribution function,

$$\langle R_N^2 \rangle = \int_0^\infty R^2 P_N(\underset{\sim}{R}) \, d\underset{\sim}{R}$$

A simple sampling algorithm for self-avoiding walks:

To study SAWs of N steps on the square lattice choose a finite lattice (e.g., of dimension $2N \times 2N$)

b) introduce occupation variables $c_i$ for each lattice site $i$. Initialize with $c_i = 0$ for all $i$.

c) Generate a walk

But $c_i = 1$ if it visits site $i$

Generate an array labeling the lattice sites which have $c_i = 1$ in the order in which they have been visited.

Excluded volume condition is satisfied by checking at each step whether $c_i = 0$ still at the next site to be visited.

d) After termination of the construction go through the array of sites which have been visited to replace $c_i = 1$ by $c_i = 0$ again

e) start the next construction.

Save constructions that terminate at some value say 20. Analyze the chains that are 20-long. All other terminated constructions can be used for analysis of shorter chains.

# Self-avoiding random walks (SAW) on a simple cubic lattice

Use simple sampling method for SAWs to generate polymers of length $N$ (that is having $N+1$ monomers on it). Let us now find the $\langle R_N^2 \rangle$ :

$$\langle R_N^2 \rangle = \int_0^\infty R^2 P_N(\underline{R}) \, d\underline{R}$$

For SAW the distribution deviates from Gaussian. How to get $P_N(\underline{R})$, the normalized number of SAW configurations of $N$ steps with the $N^{th}$ point being at vector position $\underline{R}$ starting from the origin?

Consider $N=1$ ●—● 6 such configurations all with $R^2 = 1$

$$\langle R_1^2 \rangle = 1$$

Consider $N=2$ There would be $6^2$ RW configurations but not all of them are self-avoiding.

Two unique arrangements

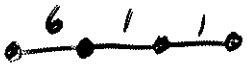

6 of these $R^2 = 4$


24 of these $R^2 = 2$

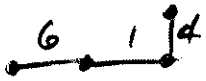
30 SAWs only (the 6 reversing walks included in the 36 configurations generated by RW are not allowed)

$$\langle R_2^2 \rangle = \frac{6 \times 4 + 24 \times 2}{30} = 2.4$$

Consider $N=3$ There would be $6^3 = 216$ RW configurations, of which only 150 are SAWs.



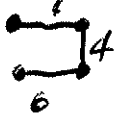

6 of these $R^2 = 9$



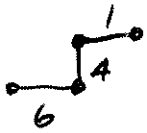

24 of these $R^2 = 5$

same if both ends are same

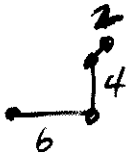

24 of these $R^2 = 5$




24 of these $R^2 = 1$




24 of these $R^2 = 5$



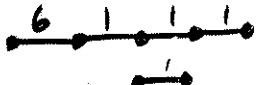

48 of these $R^2 = 3$

150 altogether SAW configurations

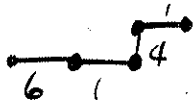
$$\langle R_3^2 \rangle = \frac{6\times 9 + 48\times 5 + 24\times 1 + 24\times 5 + 48\times 3}{150} = 3.88$$

would have been 3.0 for RW

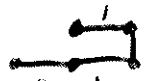
Consider $N=4$ There would be $6^4 = 1296$ RW configs. of which I found only 678 are SAWs.



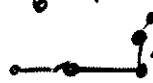

6 of these $R^2 = 16$



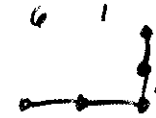

24 $R^2 = 10$




24 $R^2 = 2$

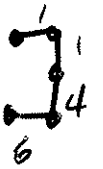



48 $R^2 = 6$

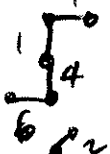



24 $R^2 = 8$

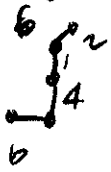
24 $R^2 = 10$



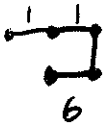
24 $R^2 = 4$



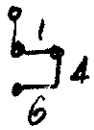
24 $R^2 = 8$



48 $R^2 = 6$

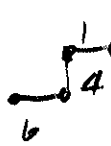


24 $R^2 = 2$

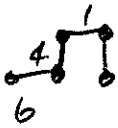


24 $R^2 = 4$

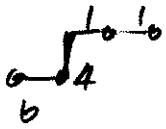
48 $R^2 = 2$



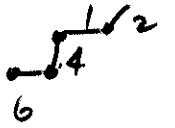
24 $R^2 = 8$



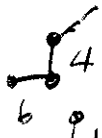
24 $R^2 = 4$



24 $R^2 = 10$

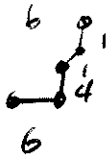


48 $R^2 = 6$

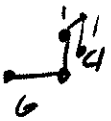


24 $R^2 = 6$

analogous alt



24 $R^2 = 6$



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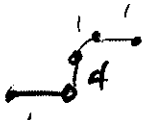
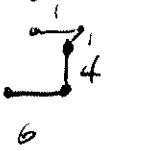


24 $R^2 = 6$



24 $R^2 = 2$

$$\langle R_4^2 \rangle = \frac{16\times6 + 72\times10 + 72\times8 + 264\times6 + 72\times4 + 192\times2}{678}$$

$$= 5.3805$$

would have been 4.0 for RW

Recently ( J. Chem. Phys. 99, 3976 (1993) Eizenberg and Klafter published the results for self-avoiding walks on a simple cubic lattice using an algorithm (not simple sampling!) which extend the chain length up to 7168 steps on a simple cubic lattice.

They find

$$\langle R_N^2 \rangle = A_R N^{2\nu}$$ where $\nu = 0.5909$, $A_R = 1.159$

RW would have been $\nu = 1/2$, $A_R = 1$

## Thermal averages by the simple sampling method

Consider the model of a polymer chain in which there is an additional energy $-\epsilon$ for every nearest-neighbor contact (non-bonded). For example


$-2\epsilon$ $\qquad$ $-3\epsilon$ $\qquad$ $N = 8$

$$\langle E \rangle^T = \frac{\sum_n (-n\epsilon) \exp^{-(-n\epsilon)/k_B T} P_N(n)}{\sum_n \exp^{-(-n\epsilon)/k_B T} P_N(n)}$$

$$\langle R^2 \rangle^T = \frac{\sum_n \sum_{\underset{\sim}{R}} R^2 \exp^{-(-n\epsilon)/k_B T} P_N(n, \underset{\sim}{R})}{\sum_n \exp^{-(-n\epsilon)/k_B T} P_N(n)}$$

Specific heat per bond of the chain can be obtained by the fluctuation relation we derived earlier

$$\frac{C}{k_B} = \frac{1}{N} \frac{\partial(\langle E \rangle^T)}{\partial(k_B T)} = \frac{\langle E^2 \rangle^T - (\langle E \rangle^T)^2}{N k_B^2 T^2}$$

Advantages of simple sampling:

(1) In one simulation run we obtain information on the full range of values for chain length $N$ up to some maximum length, and for a broad range of temperatures

(2) The individual configurations of the walks are statistically independent of each other, and therefore standard error analysis applies

Suppose $M$ configurations of $N$-step walks have been generated successfully.

$$\langle R^2 \rangle_{T=\infty} \simeq \frac{1}{M} \sum_{l=1}^{M} (R_l^2)$$

↑ end-to-end distance squared for $l^{th}$ configuration

the error in $\langle R^2 \rangle$ is

$$\sigma(\langle R^2 \rangle_{T=\infty}) \simeq \frac{1}{M(M-1)} \sum_{l=1}^{M} \left[ R_l^4 - \langle R^2 \rangle^2 \right]$$

What's wrong with simple sampling?

It does not sample well enough those regimes of phase space that contribute important terms to the thermal average. If $N$ is large, simple sampling will not generate all the configurations. Therefore, a poor thermal average will be obtained for those properties which are different from a simple arithmetic average over configurations.