BOLTZMANN ANT

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- Animal / insect baiting has been a favourite of physicist's pastimes
- we are all familiar with the dogs of Ehrenfest and their tenant fleas - the dog-flea model that describes the irreversible march toward equilibrium
- the Schrödinger cat and its innumerable kittens have gone into the folk-lore, we call quantum mechanics
- in very early times when mathematicians had difficulties in summing an infinite series - they in fact did not know how to do it - they had the arrogance - like only mathematicians can have - to say that a hare can never overtake a tortoise when the latter is given a handicap

- Maxwell dared a demon - now called the Maxwell demon - to extract work from an equilibrium system; Ever since Maxwell demon has given raise to several off-springs:
  - Szilard demon,
  - Bennet demon,
  - Landauer demon,
  - Zurek demon,
  - Caves demon and the most recent
  - Unruh demon
- time has now come to speak of ants:
  - ants in general and of
  - Boltzmann ant in particular

- Welcome to the story of Boltzmann ant
- Ants are natural allies to physicists
  - the blind ant of P. G. de Gennes,
  - the myopic ant of the Rosenbluths,
  - ant in a labyrinth,
  - ant in the fractal land, *etc.*
- In this talk I shall tell you of the Boltzmann ant
- Before we see what a Boltzmann ant is let us ask a general question:
- What does an ant do for the physicists ?
- Ans: an ant helps grow a RANDOM WALK (RW) and
- when the ant avoids its own trail it grows a Self Avoiding Walk (SAW)

- Boltzmann ant is an ant with perception;
- at every step it calculates a local partition function on the basis of energy change that would occur in each of the available moves at local growth temperature;
- it chooses randomly one of the available moves with a probability based on the calculated local partition function
- the self avoiding walk grown by the Boltzmann ant is given the name Interacting Growth Walk (IGW)
  S. L. Narasimhan, P. S. R. Krishna, K. P. N. Murthy and M. Ramanadham, Interacting Growth Walks: a new model for generating compact self avoiding walks, Physical Review E (Rapid Communications) **65** 010801 (2001)

Collaborators (who haven't yet avoided each other!!)

- S. L. Narasimhan, BARC, Mumbai; M. Ponmurugan, V. Sridhar, IGCAR, Kalpakkam; P. S. R. Krishna, BARC, Mumbai
- if you're interested, join the ant-team in their future explorations

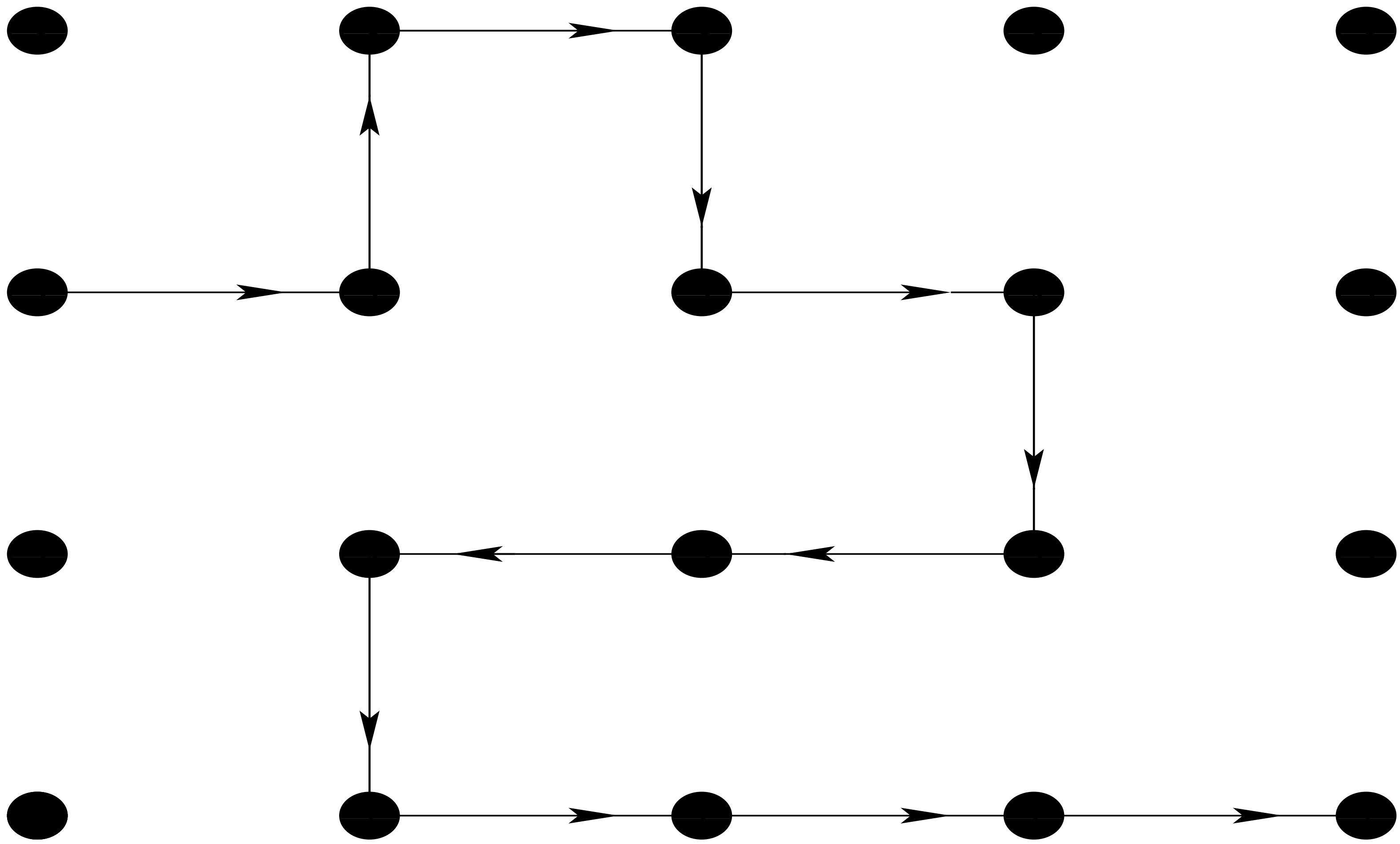
The ant story is based on:

- PRE **65** 10801(Rapid Communications)(2001)
- Physica A **320** 51 (2003); PRE **67** 11802 (2003)
- Physica A **371** 171 (2006); JCP (2007) to appear;
- PRE (2007)(submitted); PRE(L?)(on the anvil)(2007)

Self Avoiding Walk - SAW

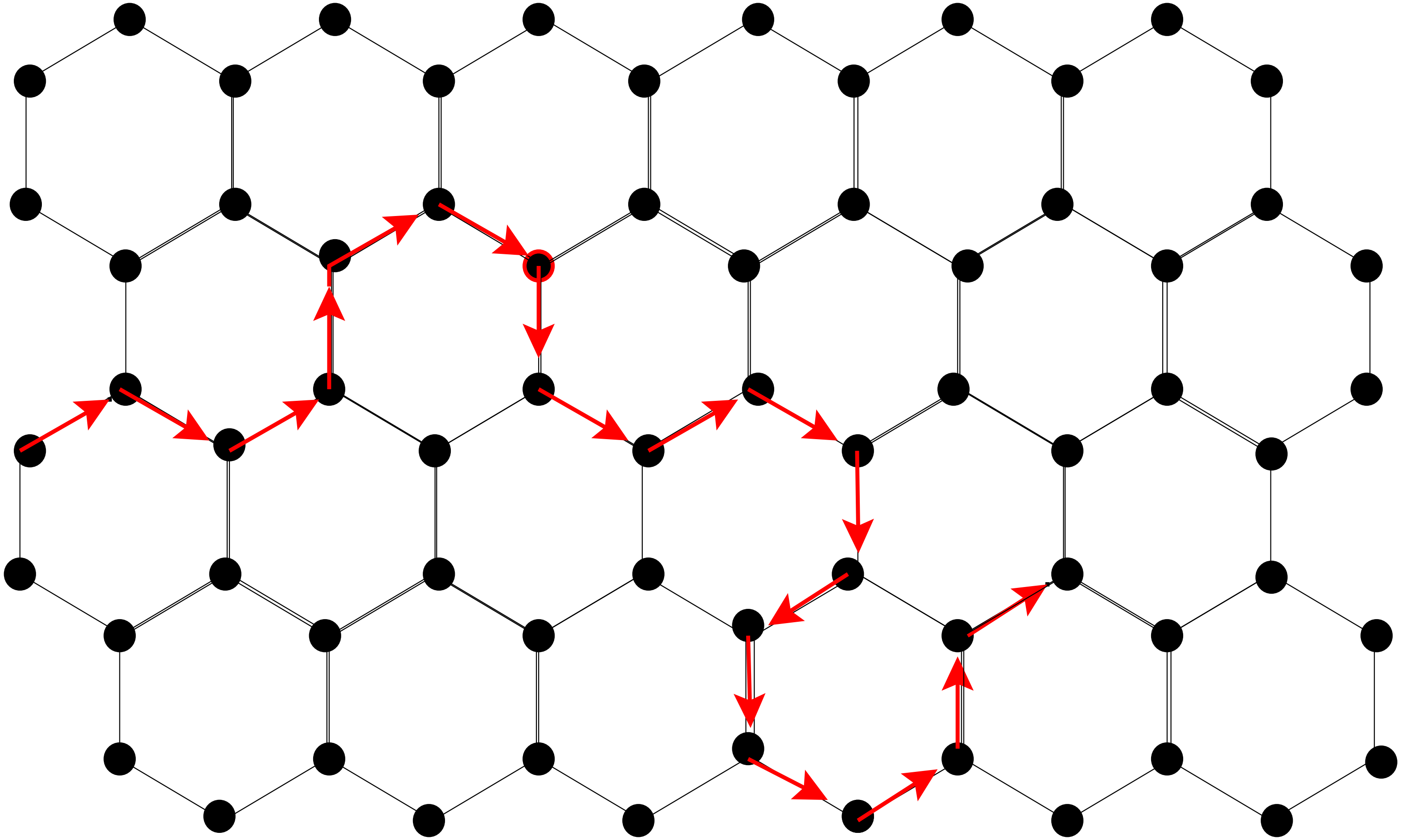
- Random Walk (RW) that does not intersect itself
- Walks on a lattice: SAW is RW that does not visit a site it has already visited
- self avoidance models excluded volume effect - hard core repulsion; it was Van der Wall who first introduced the notion in the context of ideal gas.
- for a given number of steps N, a SAW configuration is typically more extended than a RW.
- HOW DO WE GENERATE A SAW ?
- Collect a set of all possible distinct N-step random walks. Throw away those that intersect. What remains in the set are SAWs.

SAW on a Square lattice



$z = 4$

SAW on a Honey Comb lattice

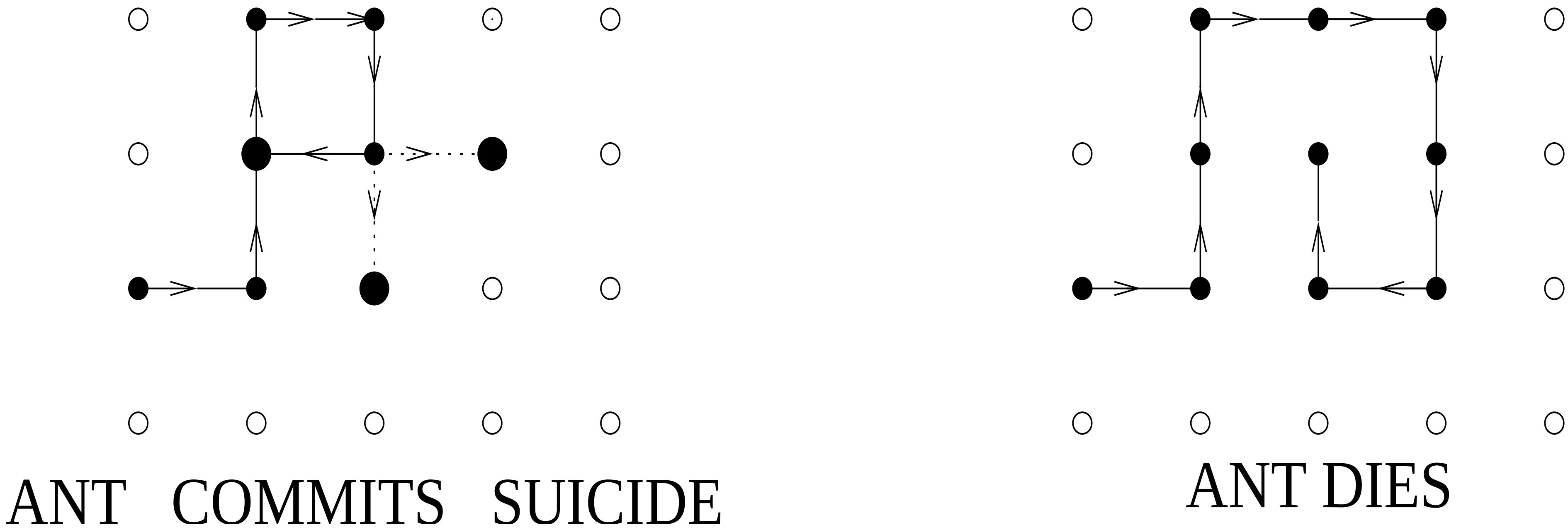


$z = 3$

BLIND ANT

- the ant starts from an origin
- it steps into one of the z Nearest Neighbour (NN) sites randomly and with equal probability.
- In any subsequent steps also, the walk selects one of z NN sites randomly and with equal probability and steps it it
- the ant checks if the site it has landed into has been visited by it earlier. (since the ant is blind it does the checking only after it lands into a site)
- If YES: the ant dies
- If NO: the ant proceeds further with its random walk

Sample attrition : death of an ant - by chance and by necessity



- left: the ant by chance (one-third probability) visits an already visited site; there are unvisited sites available; it could have lived with two-third probability.
- right: the ant by necessity can not escape visiting an unvisited site; it is sort of ambushed by its own trail; it dies.

Problem of Sample Attrition

C_N: Number of distinct SAW on a 2-D square lattice

N	C_N	N	C_N (SAW)/ C_N (RW)
5	284	10	56%
10	$44,100$	20	19%
15	$6,416,596 \approx 6$ million	30	6%
20	≈ 900 million	50	0.6%
51	10^{22}	100	0.001 %

- For one SAW with $N = 100$, we need to generate ten thousand random walks: called sample attrition.
- the problem of sample attrition becomes exponentially severe with increase of N.

ANT WITHOUT REVERSE GEAR

- to reduce attrition we can disallow the ant from reversing its step:
- we then have an ant that does not have a reverse gear
- ADVANTAGE OF EMPLOYING BLIND ANT (with or without REVERSE GEAR):
- All N-step walks are generated with the same probability
- For a non-reversing blind ant

$$P(\omega_N) \propto \left(\frac{1}{z}\right)\left(\frac{1}{z-1}\right)^{N-1}$$

ω_N denotes an N-step SAW

ENTROPY OF SAW

$$C_N(\text{RW}) = \begin{cases} 4^N & \text{with reverse gear} \\ 4 \times 3^{N-1} & \text{without reverse gear} \end{cases}$$

$$C_N(\text{SAW}) \underset{N\to\infty}{\sim} \mu^N \text{ with } 2 < \mu < 3 \text{ for a square lattice}$$

μ is an effective coordination number of the lattice; $\mu = 2.641$ for 2D square lattice. It is easy to see that on a square lattice $2^N < C_N < 3^N$ (an ant that goes to the right or up is always self-avoiding and the number of such walks is 2^N)

$$C_N \equiv \mu^N N^{\gamma-1} \quad \gamma = \begin{cases} \text{4/3} & \text{2D} \\ \text{7/6} & \text{3D} \end{cases}$$

End-to-end distance or radius of gyration

- R - the average size of an N-step SAW: end-to-end distance..... radius of gyration
- $R \equiv N^\nu \quad \nu = 3/(2+d)$, where d is the embedding dimension
- Hand waving argument for estimating ν
- $P(r, N|\cdot) \sim N^{-d/2} \exp[-r^2/N]$
  Survival probability : $\mathcal{S}(r, N) \sim (1-\rho)^N \quad \rho << 1$. The chain density: $\rho \sim N/r^d$
- the walk that grows in a congested fashion (high chain density) has a less chance of survival; therefore $\mathcal{S} \sim (1-\rho)^N \sim \exp[-N\rho]$.

Hand Waving .....continued

Consider : $P(r,N|\cdot\ ) \times \mathcal{S}(R,N)$. It is given by

$$\begin{aligned} & \exp\left[-\frac{r^2}{N} - N\rho\right] \\ = & \exp\left[-F(r,N)\right] \end{aligned}$$

$$F(r,N) = \frac{r^2}{N} + \frac{N^2}{r^d}$$

extremizing F by setting the derivative of F with respect to r to zero. We get

$$\frac{r}{N} = \frac{N^2}{r^{d+1}}$$

which yields $r \sim N^{\nu}$ with $\nu = 3/(2+d)$.

Blind ant: useful for studying extended coil phase

- Blind ant generates extended walks - 'high temperature phase' - completely dictated by entropy;

$$R(\mathrm{RW}) \underset{N\to\infty}{\sim} N^{1/2}$$

$$R(\mathrm{SAW}) \underset{N\to\infty}{\sim} N^{3/4}$$

- SAW : good model for describing polymer configurations in a good solvent - for describing polymer configurations at high temperature
- SAW is NOT the best model for studying the low temperature globular phase or for investigating coil-globule phase transition
- Can we improve the situation?

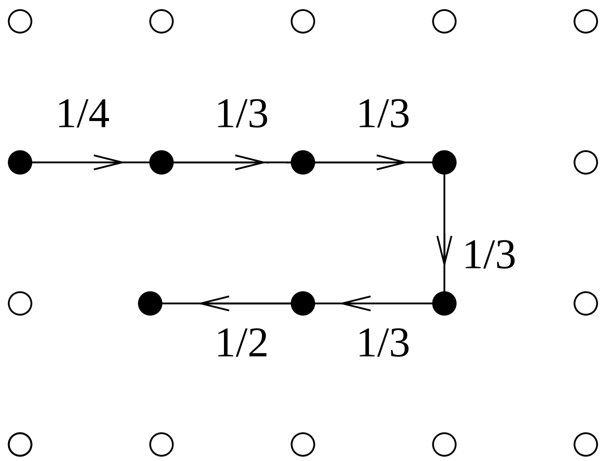
Sample Attrition - by chance and by necessity

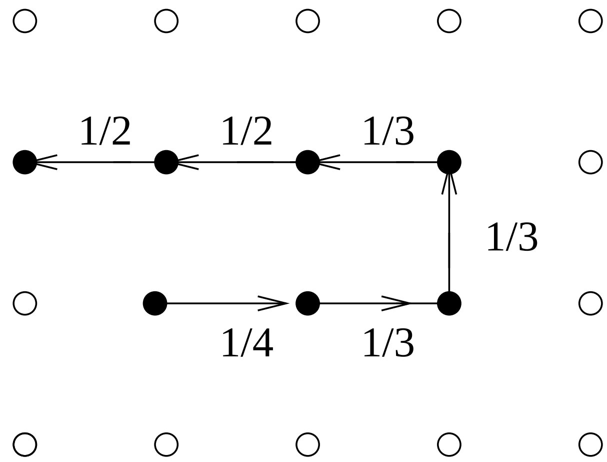
- Attrition: Only a very few of the attempts made result in long SAW when we employ a blind ant with or without reverse gear *e.g.* one of ten thousand attempts can lead to a hundred step self avoiding walk
- Attrition by chance: the ant being blind can step into a site it has already visited even when it has unvisited NN sites available; the ant commits suicide.
- Attrition by necessity: the ant does not have a choice; all its NN sites have already been visited. The ant is sort of ambushed with no escape route; it dies.
- We can reduce attrition : by preventing the ant from committing suicide. How ? make the ant MYOPIC INSTEAD OF BLIND.

MYOPIC ANT

- A myopic ant has a short vision. It peers into the NN sites and finds what amongst them it has visited earlier; it avoids those NN sites in its next step.
- Thus a myopic ant selects one of the unvisited NN sites randomly and with equal probability and steps into it.
- Attrition by *chance* is completely eliminated
- But attrition by *necessity* still persists
- What is the price we have to pay for employing a myopic ant instead of blind ant ?
- the walks generated by a myopic ant are not equi-probable
- we require additional Rosenbluth-Rosenbluth weight (RR weight) for calculating macroscopic properties

Myopic ant does not generate equi-probable SAW





- Probability of SAW on the left : $\frac{1}{4}\left(\frac{1}{3}\right)^4\frac{1}{2}$
- Probability of SAW on the right: $\frac{1}{4}\left(\frac{1}{3}\right)^3\left(\frac{1}{2}\right)^2$
- the walk and its reverse do not have the same probability; the growth is irreversible.

What is Rosenbluth-Rosenbluth weight - W_{RR} ?

- W_{RR} is set to unity at the beginning of the walk and is constantly updated at every step, see below
- Let a_n denote the number unvisited NN sites available at the n-th step then $W_{RR} = W_{RR} \times a_n/(z-1)$
- this weight is employed while calculating averages of N-step walks in addition to other weights like Boltzmann weight
- RR weight usually fluctuates heavily from walk to walk: MC statistics become poor
- we need advanced algorithm like PERM - Pruned and Enriched Rosenbluth Method - proposed by Grassberger to take care of the problem

Kinetic Growth Walk - KGW

- Let us call RR-weighted walks as RR walks
- What if we do not attach RR weight to the walk generated by the myopic ant ?
- *i.e.* simply do not employ the RR weight while calculating ensemble averages.
- Pretend as if all the N-step walks generated by the myopic ant are equi-probable.
- such walks are called KINETIC GROWTH WALKS - KGW
- Can we physically justify KGW ?
- Answer: YES

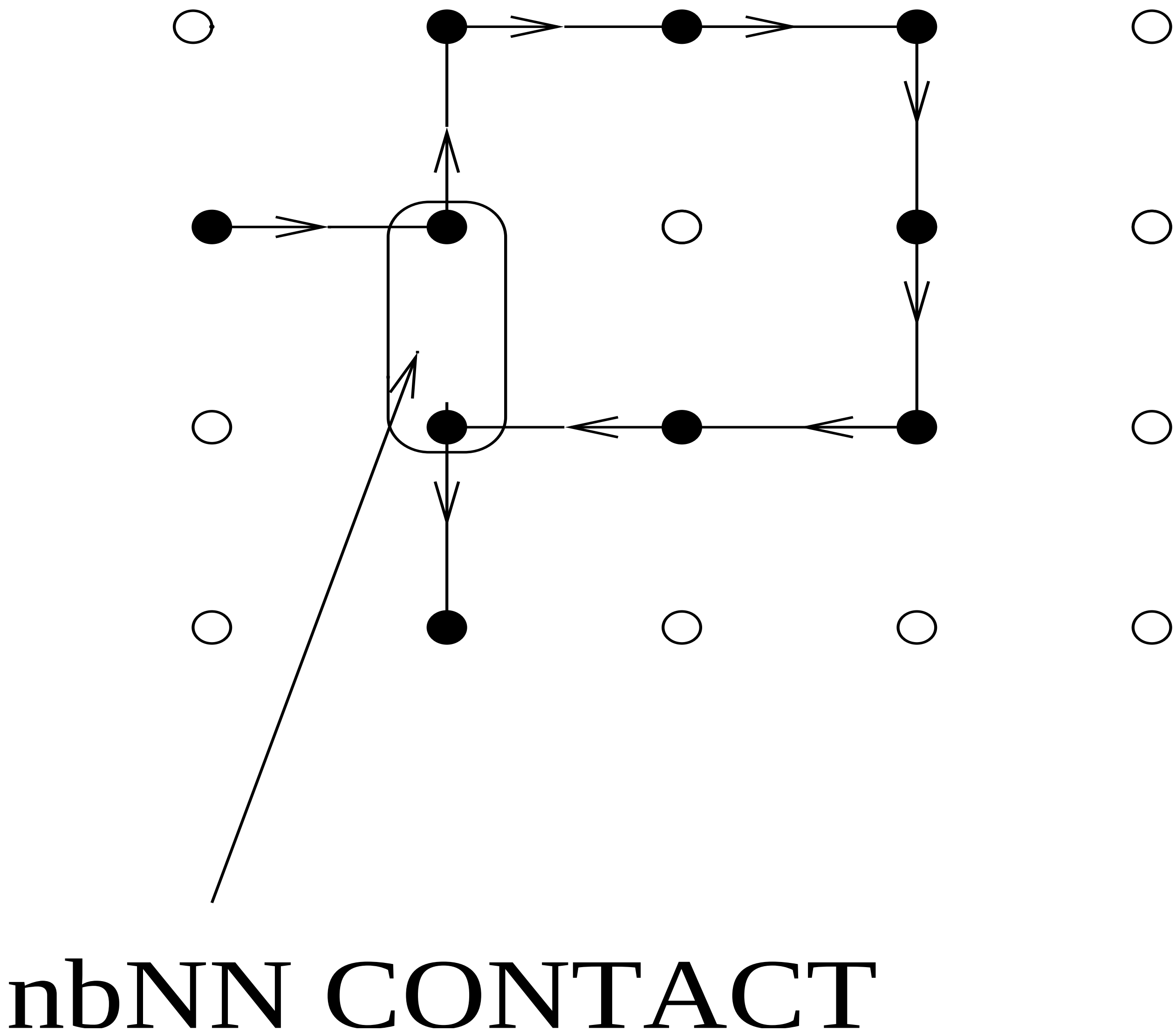
KGW

- KGW: Majid *et al.*, PRL, 52, 1257 (1984)
- KGW is a walk that describes a polymer that grows faster than it could relax.
- Describes situations when polymerization is faster than relaxation process
- relaxation time is very large compared to polymerization time
- Hence the adjective *kinetic* is attached to these walks
- KGW belong to the same universality class as SAW
- KGW is also an extended object and hence is suitable for studying high temperature coil phase and not low temperature globule phase or coil-globule phase transition

Thermal to athermal walks

- SAW and KGW are athermal objects: no energy is defined for a walk
- to make it thermal, we need to define an interaction energy when a segment of a polymer comes close to another segment of the same polymer.
- in a lattice the closest any two segments can come to, is a single lattice space apart
- two adjacent sites visited by the ant but not consecutively constitute non-bonded nearest neighbour (nbNN) contact pair or simply a contact.
- each contact is associated with an energy ϵ

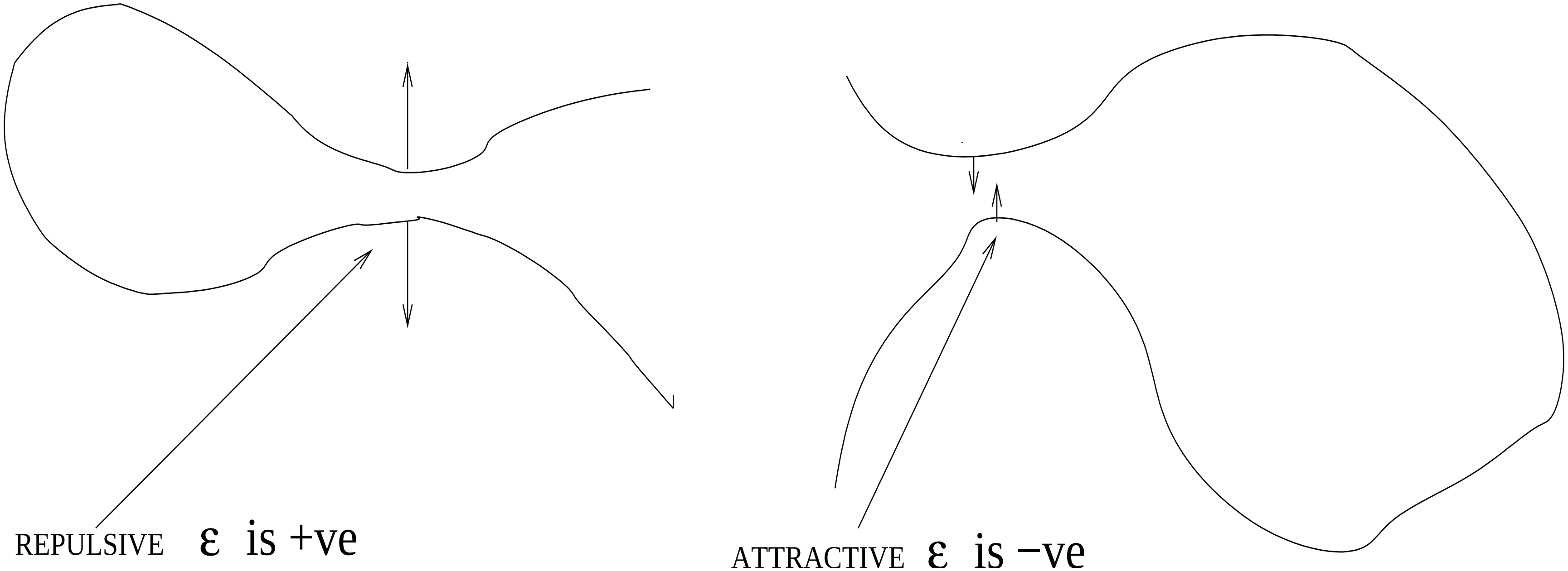
Non-bonded Nearest Neighbour Contact



Interacting Self Avoiding Walks (ISAW)

- if there are n contacts in an SAW, ω_N then its energy is $E(\omega_N) = n(\omega_N)\epsilon$
- an SAW with energy defined as above is called an Interacting Self Avoiding Walk (ISAW).
- An SAW ω_N with an energy $E(\omega_N)$ has a probability $\propto \exp[-\beta E(\omega_N)]$ of occurrence in a closed system in equilibrium with a heat bath at inverse temperature β.
- thus an SAW in the limit $N \to \infty$ is a macroscopic / thermodynamic /statistical mechanics object.
- $Z(\beta, N) = \sum_{\omega_N} \exp[-\beta E(\omega_N)$ where the sum is taken over all possible distinct SAWS.
- With energy thus defined, we can define temperature (change of entropy for unit change of energy)$^{-1}$, and study statistical mechanics of an SAW.

Non-bonded Nearest Neighbour Contact



ISAW

- end-to-end distance or radius of gyration in the thermodynamic limit of $N \to \infty$ - an ISAW is a statistical mechanical object with a well defined energy E and number of microscopic constituents N.

$$\begin{aligned} \langle r(N) \rangle &= \frac{1}{Z(\beta, N)} \sum_{\omega} r(\omega) \exp[-\beta n_{nbNN}(\omega) \epsilon] \\ &= N^{\nu} \end{aligned}$$

- ISAW $\underset{T\to\infty}{\sim}$ SAW (extended coil phase), with $\nu = 3/2 + d$.
- ISAW $\underset{T\to 0}{\sim}$ Globule (collapsed) phase with $\nu = 1/d = 1/2$ (2-dimensional)

Digression: Calculation of Entropy

- How does one calculate entropy S ?
- Entropy like energy, magnetization, volume, size *etc* is a macroscopic variable.
- Example: In statistical mechanics E is defined for each microstate.
- E fluctuates from one microstate to the other of a closed system
- thermodynamic energy U is defined as average of statistical mechanical energy E over
  (a) uniform ensemble Ω_{UE} with Boltzmann weight or
  (b) a canonical ensemble Ω_{CE} with constant weight, say unity, see below:

Entropy sits on a pedestal

$$U = \langle E \rangle = \frac{\sum_{\omega \in \Omega_{\rm UE}} E(\omega) \exp[-\beta E(\omega)]}{\sum_{\omega \in \Omega_{\rm UE}} \exp[-\beta E(\omega)]}$$

$$= \frac{\sum_{\omega \in \Omega_{\rm CE}} E(\omega)}{\sum_{\omega \in \Omega_{\rm CE}} 1}$$

- Can we calculate S like we calculate E ? No (?) Why?
- S is not defined for a single microstate.
- S is the property of a collection of microstates.
- To be precise S is logarithm of number of distinct microstates accessible to/accessed by the system
- thus S, though a macroscopic variable like E, it enjoys a special status - it sits on a pedestal

Entropy defined for a microstate

- In an astounding paper
  PRL, **92**,120602 (2004),
  Prellberg and Krawcsyk discovered a a NEW meaning of Rosenbluth-Rosenbluth weight :
  M.N.Rosenbluth, A.W. Rosenbluth,
  J. Chem. Phys. **23**, 356 (1955)
- These authors define a random variable called ATMOSPHERE : a
- Let a_i denote the number of unvisited NN sites available for the myopic ant when it takes its i-th step.
- $a = \prod_{i=1}^{N} a_i$ where N is the numb of steps.
- $a = W_{RR} \times (z \times z^{N-1})$

Atmosphere and augmented ensemble

- Ω_N: set of all possible N step KGWs
  Ω_k^{ATT} set of all possible KGWs that could not proceed beyond $k \le N-1$ steps due to trapping.
  Augmented ensemble: $\Omega = \Omega_N \cup_{k \le N} \Omega_k^{ATT}$
  atmosphere for a walk that could not proceed beyond N steps is zero when we consider N-step walks - makes sense
- $S = \log \langle a \rangle_\Omega$
- atmosphere is defined for each microstate; it fluctuates from one microstate to the other;
- we average atmosphere over an augmented ensemble of microstates and take its logarithm which gives entropy

Entropy and Free energy from atmosphere and KGW

- entropy can thus be calculated exactly like any other thermodynamic variable by ensemble averaging.
- we can calculate microcanonical entropy:

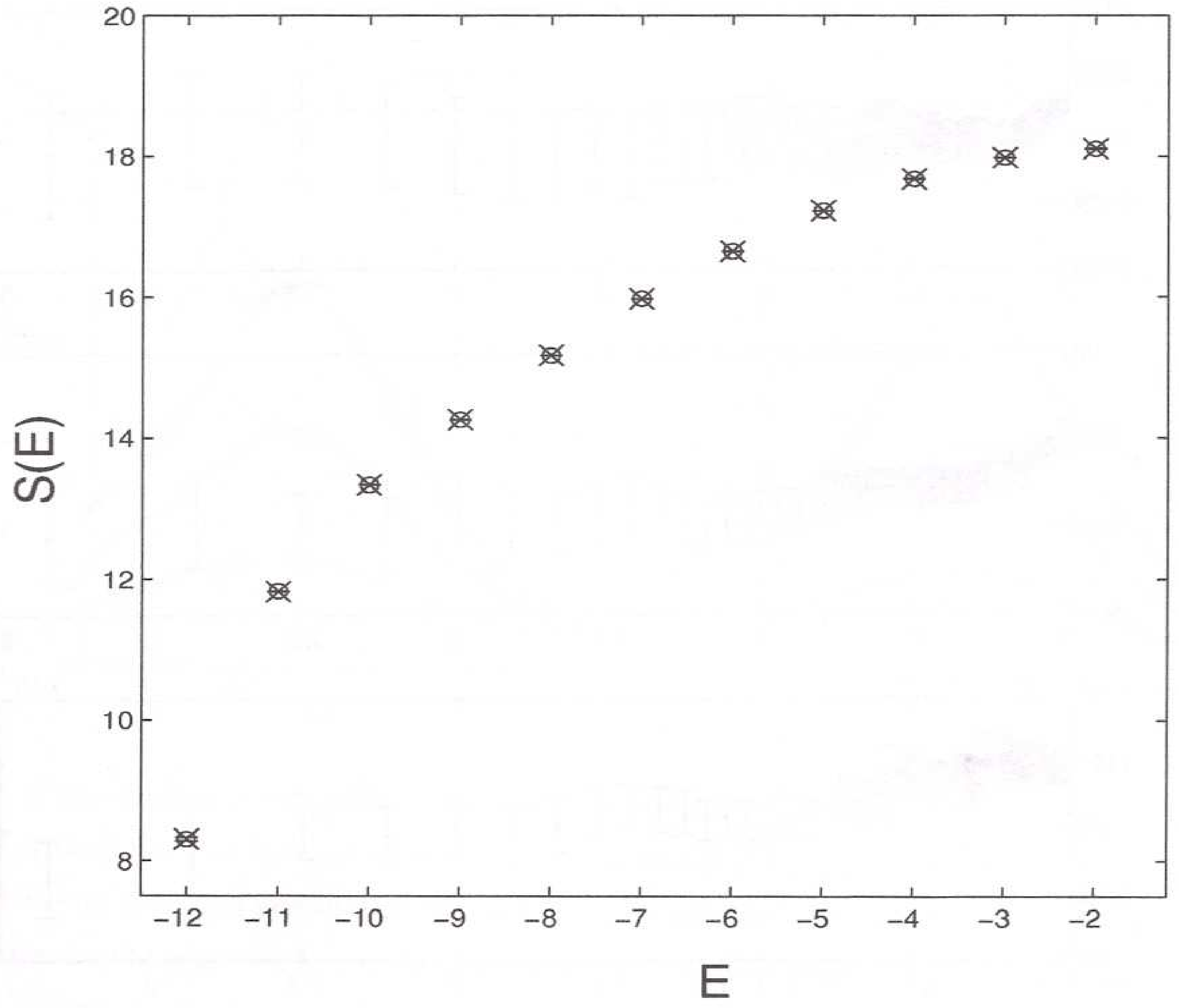
$$S(E,N) = \langle a_{E,N} \rangle_\Omega$$

- Free energy:

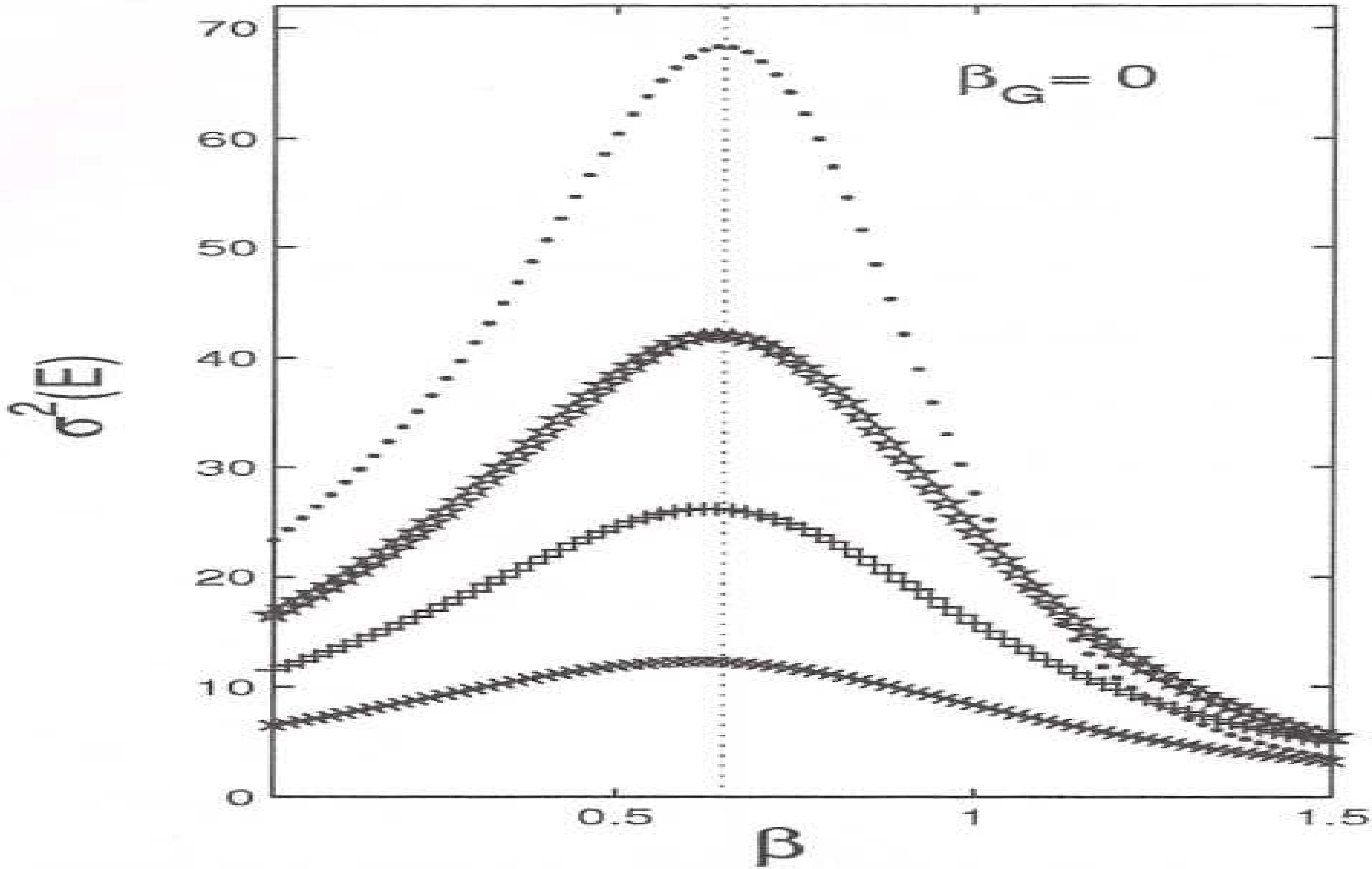
$$\begin{aligned} F(E,N) &= E - TS(E,N) \\ T &= \frac{1}{\left(\frac{\partial S(E,N)}{\partial E}\right)_N} \end{aligned} \quad (1)$$

- *etc* *etc*.

Entropy versus energy from atmosphere-KGW



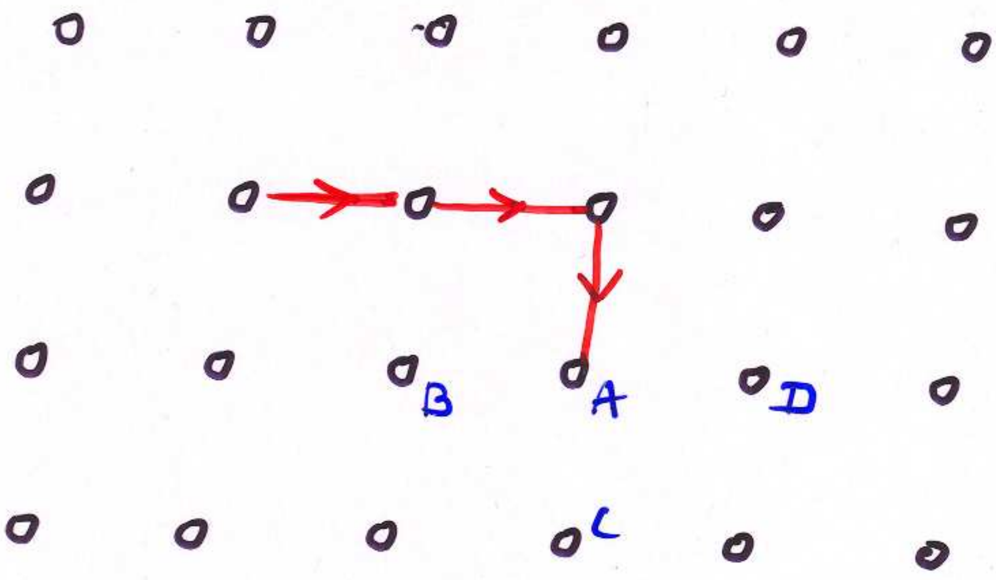
Energy Fluctuations - Myopic ant - KGW -Atmosphere - entropy



Boltzmann Ant

- the walks generated by a myopic ant are typically extended and hence are suitable for studying low temperature globule phase or coil-globule phase transition
- can we improve upon the myopic ant ?
- Narasimhan in 2001 proposed a Boltzmann ant
- Boltzmann ant selects an unvisited NN site with a local Boltzmann probability unlike the myopic ant which selects with equal probability
- we have a the so-called growth temperature that tunes the nature of the walk

Boltzmann ant



inverse groo
temperatu

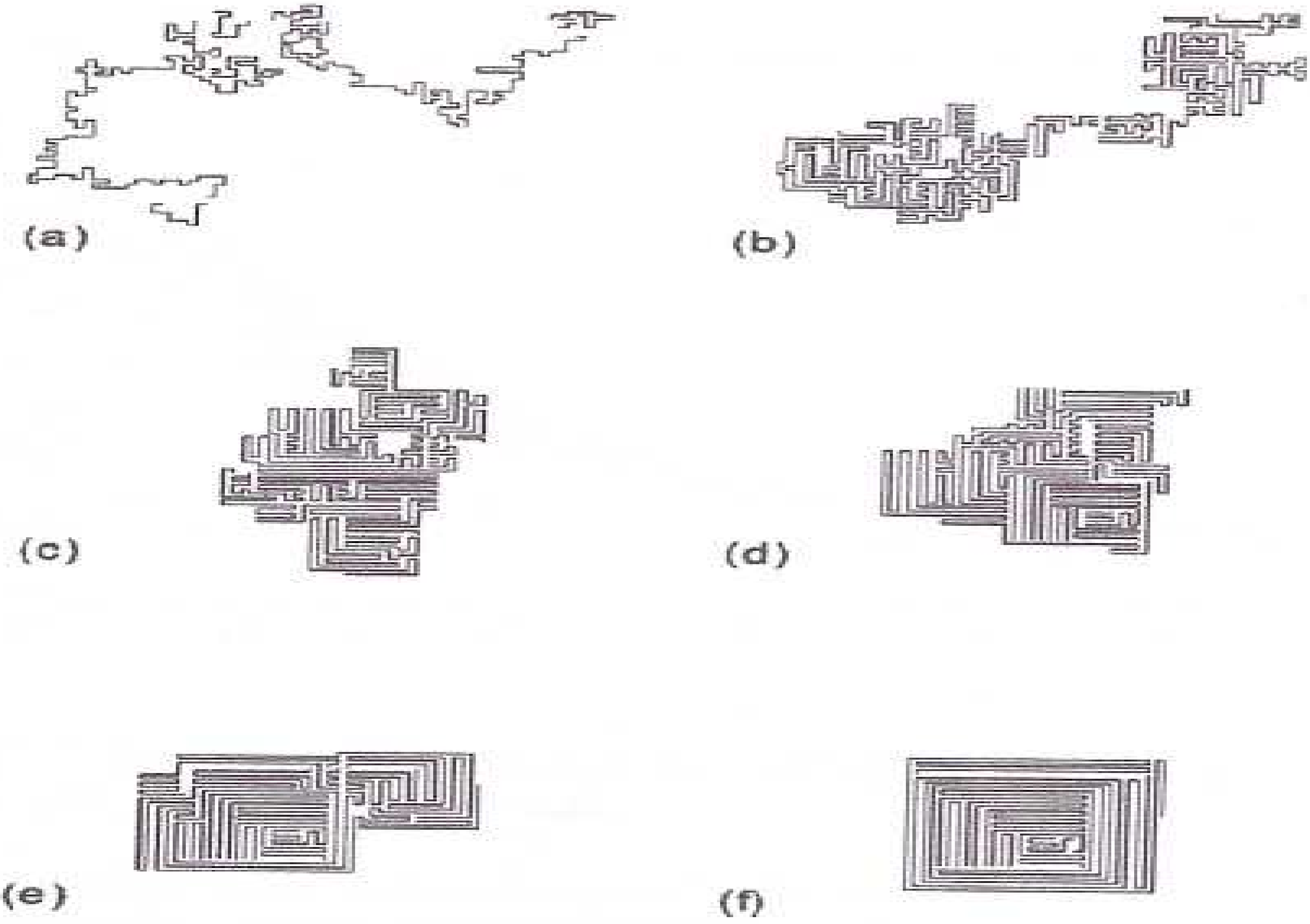
$$P(A \to B) = \frac{e^{-\beta_G E}}{1+1+e^{-\beta_G E}} = \frac{e^{-\beta_G E}}{Z(\beta_G)}$$

local partiti
function

$$P(A \to C) = 1/Z$$

$$P(A \to D) = 1/Z .$$

Boltzmann ant

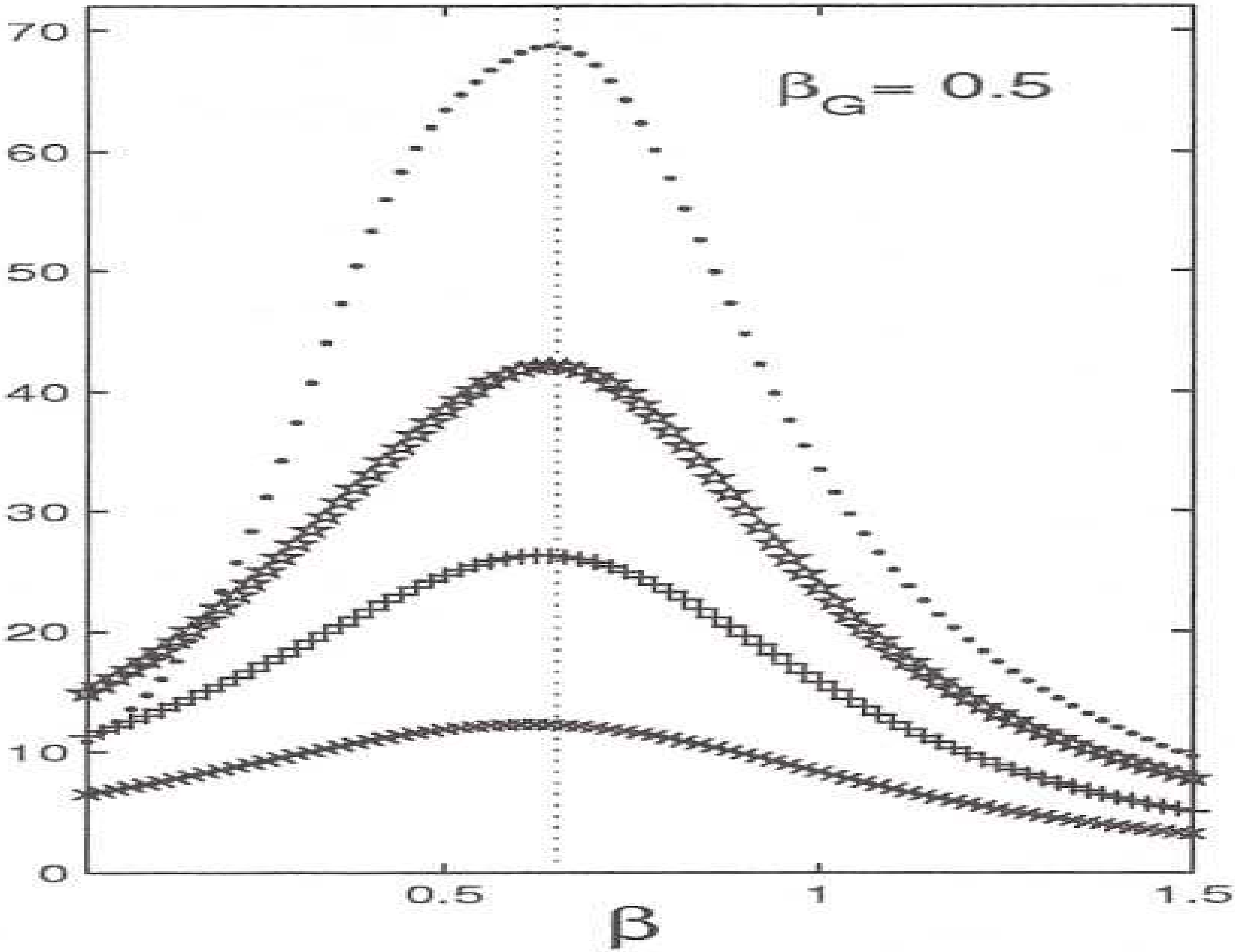


β_G= (a) 0 (IGW) (b) 2 (c) 3 (d) 4 (e) 5 (F) 300

Boltzmann ant

- KGW is SAW of a Myopic ant without RR weights
- IGW is SAW of Boltzmann ant (PERM-B algorithm of Grassberger) without RR weight/PERM-B weight
- We can extend the notion of atmosphere to IGW: Let a_i denote the reciprocal of the probability of the i-th step taken by the Boltzmann ant.
- atmosphere of an N-step SAW is given by $\prod_{i=1}^{N} a_i$
- we calculate the average of atmosphere over an augmented ensemble like we did for the KGW and take logarithm of it to get entropy

Energy fluctuations calculated from Boltzmann ant



FLAT HISTOGRAM IGW MONTE CARLO

- We can interpret β_G of the Boltzmann ant as a parameter and allow it to fluctuate in a controlled way to produce a flat histogram of energy of polymer conformations
- then the number of walks belonging each energy that generates flat histogram gives the density of states from which microcanonical entropy can be estimated.
- from microcanonical entropy we can calculate all other thermodynamic properties of ISAW
- this work is in progress
- THANKS