

# Lattice Polymers : SAW, ISAW, KGW, IGW and BFM

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- Thanks ..... **Gambo** ..... for the invitation
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# Polymer

- A polymer is a macromolecule
- formed by several sub-units of atomic groupings
- each grouping is called a monomer
- monomers are bonded by the same kind of linkages
- these monomers often form into a chain like structures
- the chemical reactions by which a giant molecule is formed from monomers is called polymerization
- number of monomers in a polymer chain is called the degree of polymerization
- A polymer can exist in various conformations
- The conformation has a direct bearing on the physical properties of a polymer

# Polymer Conformations

- Number of monomers and physical structure are two important factors that determine the macroscopic properties of a polymer
- the conformational statistics of polymer depend on the solvent
- Good Solvent:
  - Monomers in a segment prefer to be surrounded by the solvent rather than monomers from other segments;
  - there is an effective segment-segment repulsion
  - results in swollen coil conformation
  - called extended phase

# Interacting Polymer

- Poor Solvent
  - induces an effective interaction between two monomers belonging to different segments
  - different segments get dragged . . . one toward the other . . . by excluding the intervening solvent
  - results in a compact globular conformation
  - called collapsed phase
- quality of solvent is often parameterized by temperature
- Low temperatures correspond to poor solvent
- High temperatures correspond to good solvent
- when temperature decreases there occurs a transition from an extended to a collapsed phase

## Coarse grained models

- to study such phase transitions, coarse grained models are useful
- treats a group of chemical units as a bead - a monomer
- microscopic degrees of freedom, invariably present within a monomer, are completely ignored
- only basic features common to all polymers of the same chain topology are retained
- we incorporate only features like chain connectivity, excluded volume effect, monomer-monomer interaction *etc.*
- coarse grained models are suitable for studying universal properties of polymer systems

# Variety of Polymers

- depending on the chain connectivity we can have different kinds of polymers
- They are
  - linear polymer
  - branched polymer
  - cross-linked polymer
- on the basis of the monomers, polymers are classified as
  - HOMOPOLYMER; monomers are all of the same type
  - HETEROPOLYMER: monomers are of different types
- I shall talk about **linear homo polymer**

## linear homopolymer on a lattice

- lattice models have been employed in polymer studies for more than six decades
- See **C. Vanderzande**, **Lattice Models of Polymers**, Cambridge University Press (**1998**).
- lattice models are based on Self Avoiding Walks (SAW)
- A walk that does not visit a site it has already visited
- Self avoidance incorporates in a natural way the excluded volume effect
- SAW is generated by
  - blind ant or
  - non reversing blind ant



## Blind Ant

- An ant starts its random walk from a chosen origin on a lattice
- it chooses randomly and with equal probability one of the nearest neighbour sites and steps into that site
- if it finds that it had earlier visited the site it has just stepped into, it terminates its walk and starts all over again from the origin
- otherwise it continues its random walk until the walk gets terminated
- when the ant does not reverse its step, it is called a non-reversing blind ant

- Blind ant algorithm ensures equal a priori probability of polymer conformations
  - Let  $z$  be the coordination number of the lattice;  
 $z = 4$  for a two dimensional square lattice;  
 $z = 3$  for a two dimensional honeycomb lattice;  
 $z = 6$  for three dimensional cubic lattice  
*etc.*
  - Let  $N + 1$  be the number of monomers.
  - Then the probability of a polymer conformation  $C$  is
    - Blind ant :  $P(C) = z^N$
    - Non-reversing blind ant :  $P(C) = z \times (z - 1)^{N-1}$

## Blind → Myopic ant

- From the lattice polymers generated by the blind ant, we can
  - construct microcanonical ensembles by grouping in terms of energies,
  - estimate canonical ensemble averages by attaching Boltzmann weight based on energy
- a major problem with Blind ant : **sample attrition**
- Partial remedy : Rosenbluth-Rosenbluth walk based on myopic ant: **M N Rosenbluth and A W Rosenbluth, J Chem Phys 23 356 (1955)**
  - The ant selects one of the unoccupied nearest neighbour sites randomly and with equal probability.
- Sample attrition is considerably reduced, though not eliminated: Trapping does still occur.

# Rosenbluth-Rosenbluth Walks and Weights

- Major Problem with Myopic ant: The walks generated are not all equally probable. Hence we need

- RR weights ( $W$ ) for calculating microcanonical ensemble averages:

$$W_{RR}(N \text{ step RR Walk}) = \left(\frac{1}{4}\right) \left(\frac{1}{z^{N-1}}\right) \left(\prod_{i=1}^N n_i\right)$$

where

- $z$  is the coordination number of the lattice and
- $n_i$  is the number of unoccupied nearest neighbours available when the myopic ant takes its  $i$ -th step.
- RR weights, see above, and Boltzmann weights, see below, for calculating canonical ensemble averages.

$$W_B(N \text{ step RR walk}) = \exp[-\beta E(N \text{ step RR walk})]$$

where  $\beta = 1/[k_B T]$ :  $k_B$  is Boltzmann constant,  $T$  is absolute temperature and  $E$  is energy of the SAW, defined as follows.

## Interacting Self Avoiding Walk : ISAW

- In a SAW conformation, count the number of non-bonded nearest neighbour contacts,  $n$ .
- Energy of the SAW equals  $n\epsilon$ .  
See e.g. J Mazur and F L McCrackin, J Chem Phys 49 648 (1968)
- If  $\epsilon$  is negative the interaction is attractive;
- If  $\epsilon$  is positive, the interaction is repulsive.
- An SAW with well defined energy is called Interacting Self Avoiding Walk (ISAW).
- We take  $\epsilon = -1$  without loss of generality: attractive interactions.

# PERM, Flat-PERM

- RR weights fluctuate wildly.
- Besides sample attrition is present, though less.
- Long walks are difficult to generate.
- PERM: Pruned and Enriched Rosenbluth Model of Grassberger provides some remedy.  
[P Grassberger, Phys. Rev. E 56 3682 \(1997\)](#)
- PERM algorithm has further been improved to Flat-PERM
- Flat-PERM ensures that the energy histogram of generated conformations is flat.

## KGW, IGW and flat IGW

- KGW: If we ignore RR weights *i.e.* if we set RR weight to unity for all the walks, then we get Kinetic Growth Walk (KGW)
- KGW models a polymer that grows faster than it could relax.
- KGW does not generate equilibrium lattice polymer conformations
- All KGWs are not equally probable
- A KGW, grown in the forward way, does not have the same probability of then one grown in the reverse way
- A KGW belongs to the same universality class as SAW

## IGW and flat-IGW

- When kinetic growth occurs as per local Boltzmann weights - PERM-B with RR weight set to unity - we get Interacting Growth Walk (IGW), see [S L Narasimhan et al, Phys. Rev. E \(RC\) 65, 10801 \(2001\)](#)
- IGWs are not equi-probable
- An IGW and its reverse are not necessarily grown with the same probability
- IGW belong to the same universality class as ISAW
- IGW has been improved to Flat-IGW, see [M Ponmurugan et al, Comput. Mater. Sci. 44, 36 \(2008\)](#)
- Sokal provided an alternative to all Growth Walks:  
[A D Sokal](#), in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, Ed. K Binder, Oxford University Press (1995)



## Sokal algorithm

- Start with a lattice polymer of a given length.
- Make local changes employing pivoting, cranking, rotating in a self avoiding fashion to generate a trial configuration.
- Employ standard Metropolis algorithm to generate a Markov Chain of Polymer conformations.
- Asymptotic part of the Markov Chain corresponds to a canonical ensemble.
- Calculate the desired properties by averaging over the canonical ensemble
- Problem with Sokal algorithm is that local changes are difficult to make and time consuming

# Bond Fluctuating Model

- Bond Fluctuating Model retains the advantages of both the algorithms: L Carmesin and K Kremer, *Macromolecules* 21 2819 (1988)
  - we start with a conformation like in Sokal's algorithm
  - a randomly selected monomer is moved to its nearest site - like in growth algorithm a monomer is placed at a nearest neighbour site
  - the price we pay is the bond can get stretched when a monomer is moved
- A move is legal only if the following conditions are fulfilled
  - self avoidance
  - no bond crossing during a move
  - no bond stretching beyond a prescribed limit

## Bonds in Two Dimensional Square lattice

- We consider bond fluctuating lattice polymer model on a two dimensional square lattice
- lattice constant is taken as unity
- each monomer occupies four lattice sites of a unit cell
- each lattice site can at best be part of only one monomer - self avoidance condition.
- Let  $l$  denote length of a bond.
- minimum value of  $l$  is 2
- If we take  $l < 3$ , then possible bond lengths are 2,  $\sqrt{5}$  and  $\sqrt{8}$
- If we take  $l < 4$ , then possible bond lengths are 2,  $\sqrt{5}$ ,  $\sqrt{8}$ , 3,  $\sqrt{10}$ , and  $\sqrt{13}$ .

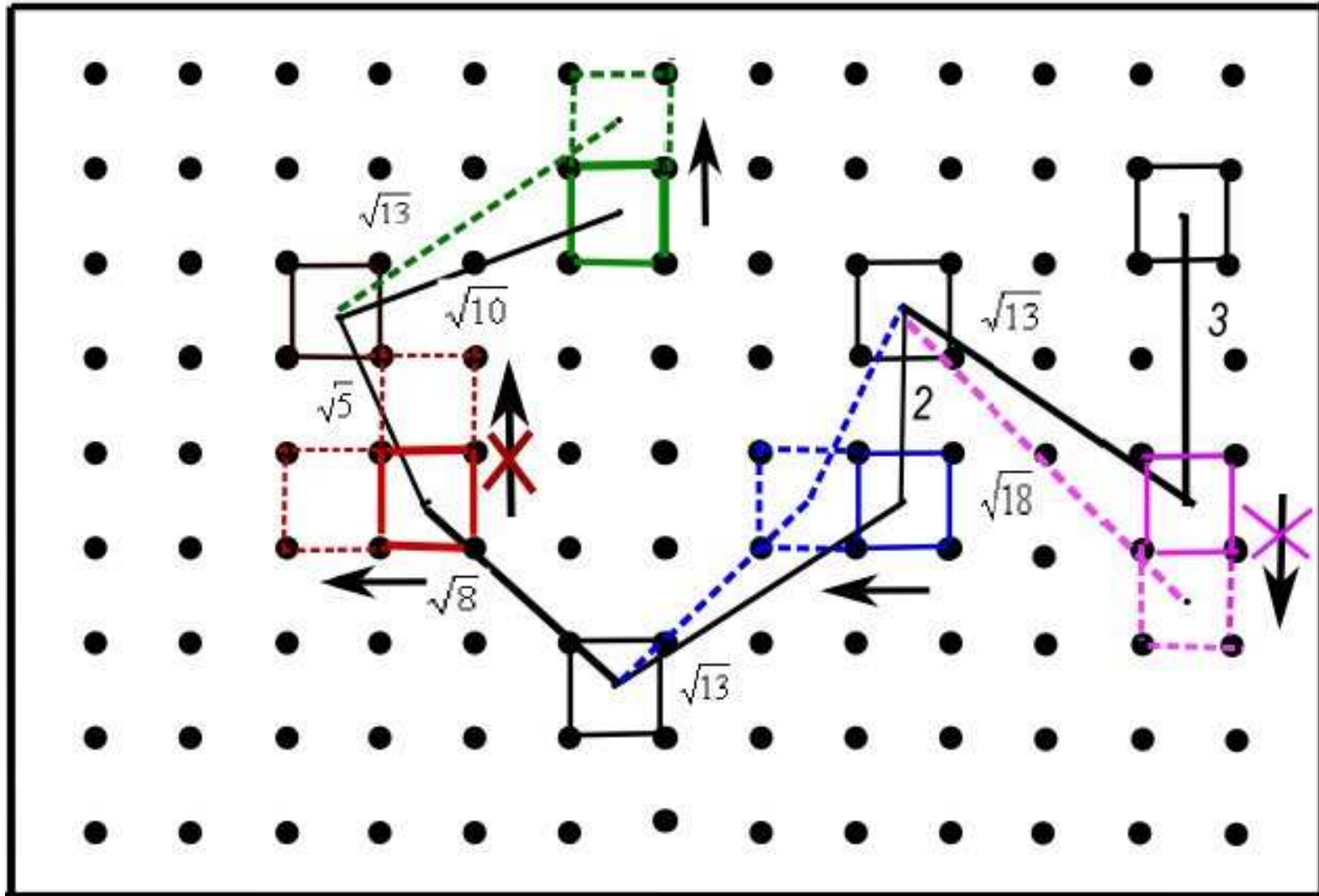


## Dynamics in Bond Fluctuating Model

- a monomer is selected randomly
- it tries to move by a distance of one lattice unit into one of the four lattice directions chosen randomly
- if the move complies with both self avoidance and bond length restriction it is considered legal
- if the attempted move turns out be illegal, select a monomer randomly and attempt to move it.
- and so on
- if we restrict  $l < 4$ , then bond cuts are avoided automatically
- in our simulation we restrict  $l < 3$
- In fact we consider bonds of length 2 and  $\sqrt{8}$  by moving a monomer always by two lattice units.

## A bond fluctuating polymer on a two dimensional square lattice

Moves that are legal and moves that are not legal are shown



# Entropic Sampling

- we have simulated Bond Fluctuation model on a two dimensional square lattice employing entropic sampling
- **Entropic Sampling**
  - Let  $C$  denote a lattice polymer conformation
  - $P(C) \propto \exp[-\beta E(C)]$
  - $P(E) \propto D(E) \exp(-\beta E)$
  - we sample polymer conformations such that  $P(E) \propto D(E) \times g^{-1}(E)$  where  $g(E) > 0 \forall E$
  - if  $g(E) = D(E)$  then  $P(E)$  is same for all  $E$
  - strategy is to start with an initial guess  $g^{(0)}(E)$ . e.g.  $g^{(0)}(E)dE = dE \forall E$ .
  - iteratively update it  
 $g^{(0)}(E) \rightarrow g^{(1)}(E) \rightarrow \dots \rightarrow g^{(n)}(E) \rightarrow \dots$

## Acceptance / Rejection in entropic sampling

- Let  $C_t$  be a trial conformation obtained from the current conformation  $C_i$  employing bond fluctuating model
- Let  $E_i = E(C_i)$  and  $E_t = E(C_t)$ .



$$C_{i+1} = \begin{cases} C_t & \text{with probability } p \\ C_i & \text{with probability } 1 - p \end{cases}$$

$$p = \min \left( 1, \frac{g^{(n)}(E_i)}{g^{(n)}(E_t)} \right)$$

- generate an ensemble of conformations and extract from it the energy histogram  $h(E)$



## Density of states

- when the histogram becomes flat stop the iteration and update the density of states as follows

$$g^{(n+1)}(E) = \begin{cases} g^{(n)}(E) \times h(E) & \text{if } h(E) \neq 0 \\ g^{(n)}(E) & \text{if } h(E) = 0 \end{cases}$$

- employ  $g^{(n+1)}(E)$  in the next stage and iterate
- In the limit  $n \rightarrow \infty$ , we get  $g^{(n)} = g(E) = D(E)$  over the energy interval in which the histogram is flat
- $S(E) = k_B \ln g(E)$  up to a constant.
- From the microcanonical entropy we can get other properties employing standard thermodynamic machinery

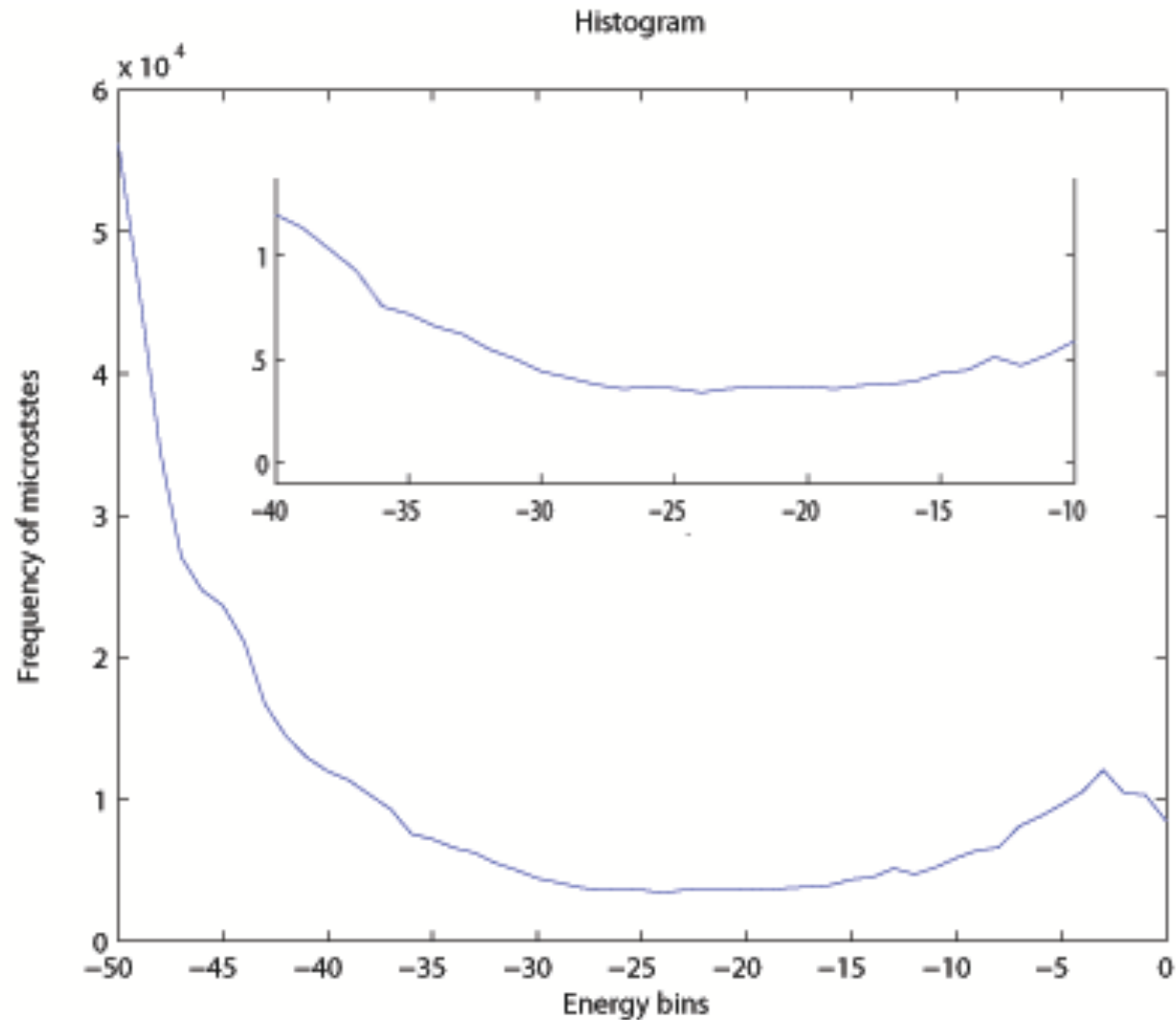
# Entropic Ensemble

- alternately generate an entropic ensemble employing  $g(E)$ .
- Calculate un-weighting-cum-re-weighting factors for each conformation of the entropic ensemble. It is given by  $W(C) = g(E(C)) \exp[-\beta E(C)]$ .
- Use this weight and obtain canonical ensemble average of desired properties from the entropic ensemble

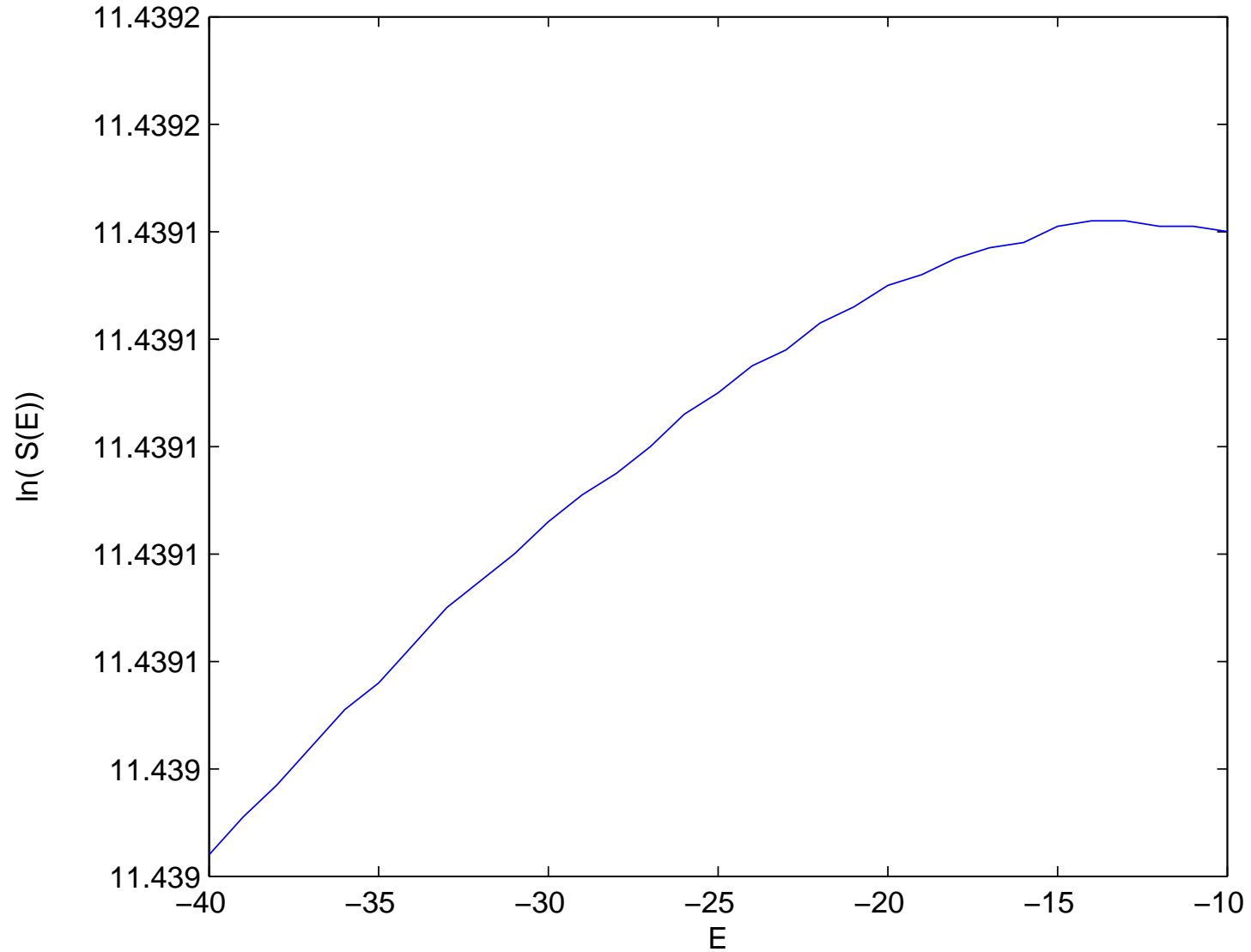
$$\langle \eta(\beta) \rangle = \frac{\sum_C \eta(C) W(C)}{\sum_C W(C)}$$

- The sum runs over all the conformations of the entropic ensemble

$h(E)$  versus  $E$ . Histogram is not flat over the entire range of energy. Inset shows histogram for  $-40 \leq E \leq -10$ . In this range the histogram is reasonably flat. All subsequent calculations are carried out with polymer conformations belonging to this range of energy

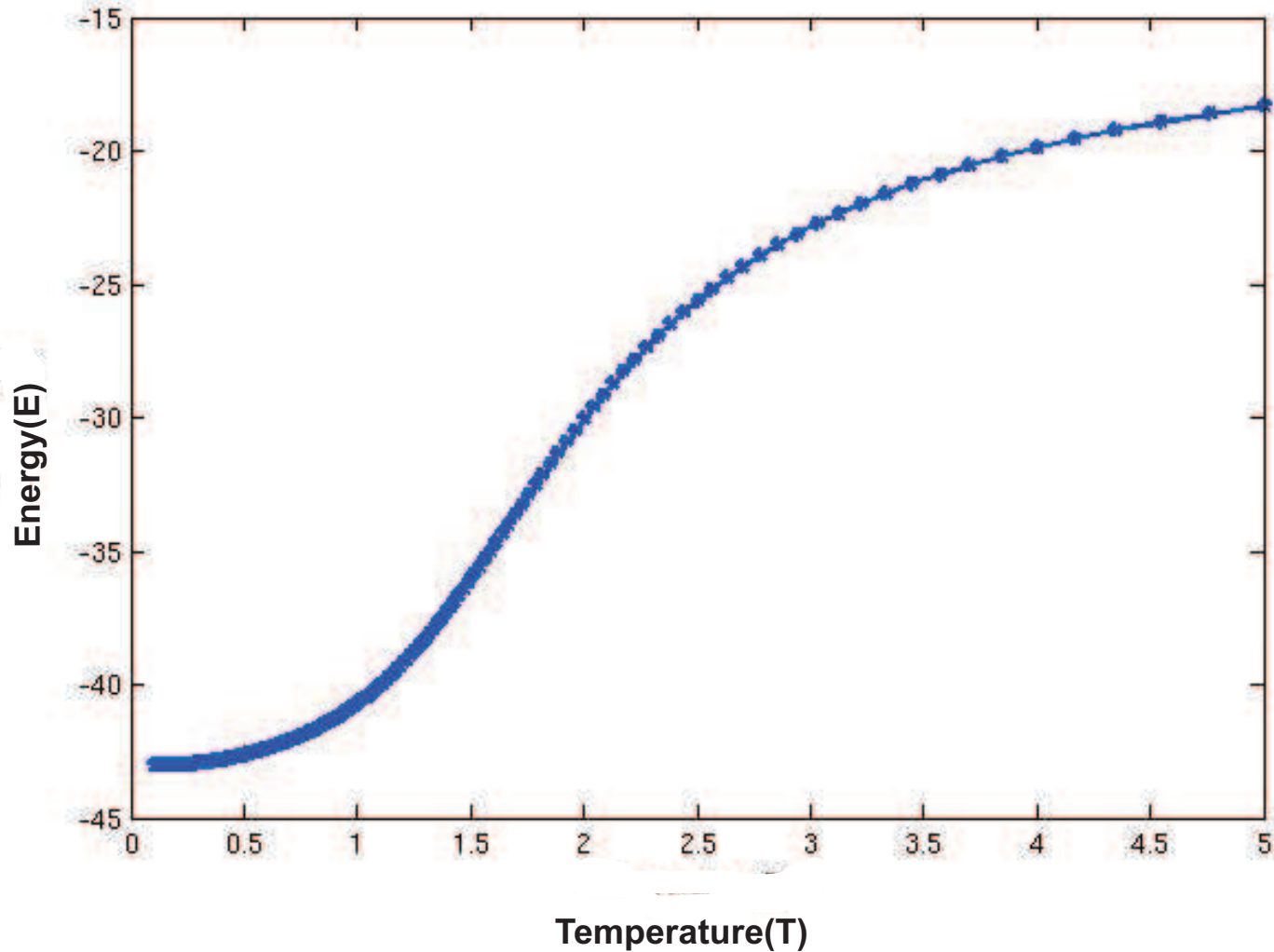


*lnS(E) versus E*

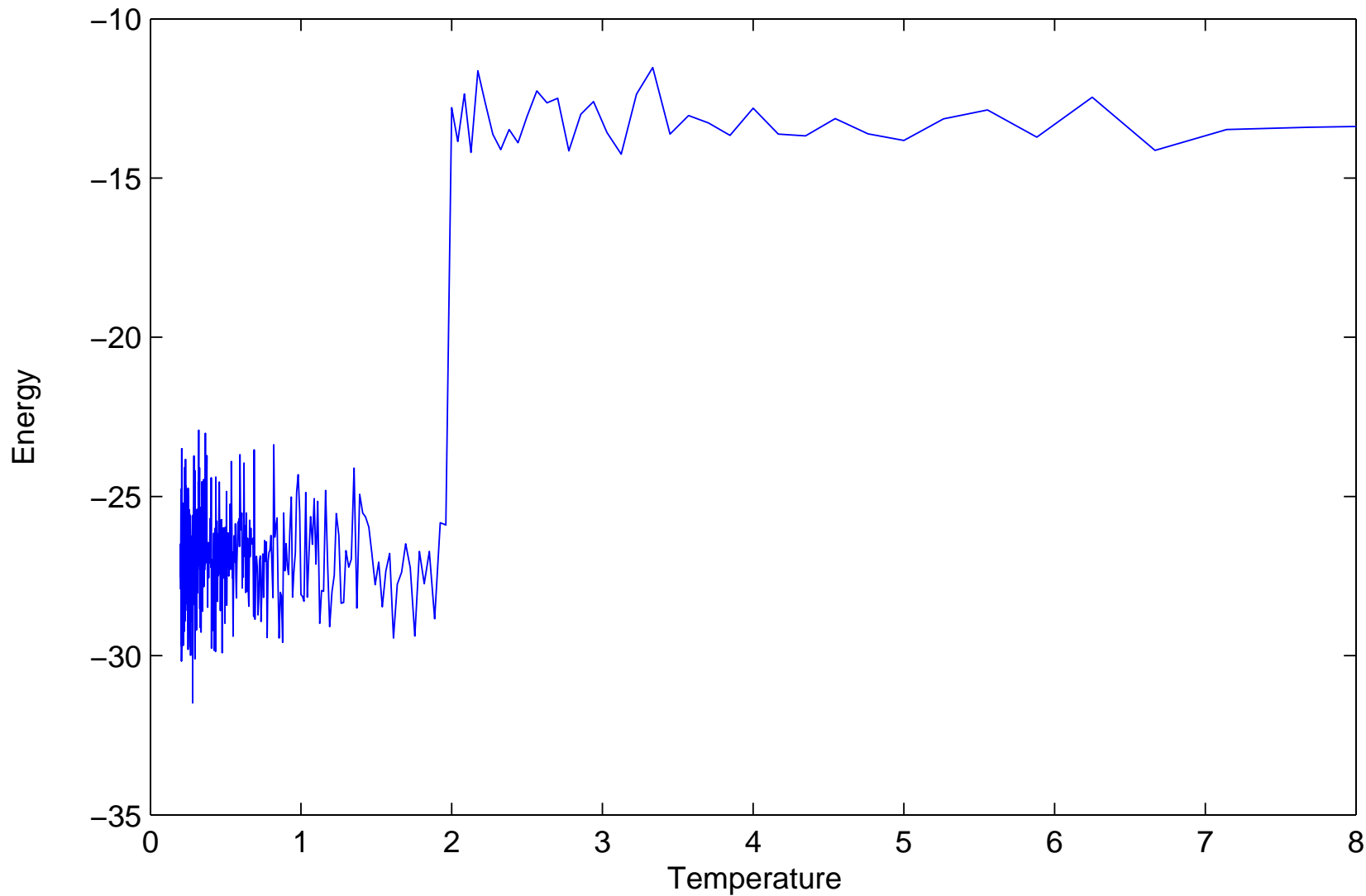


$$\langle E \rangle = \frac{\int dE E g(E) \exp(-\beta E)}{\int dE g(E) \exp(-\beta E)}.$$

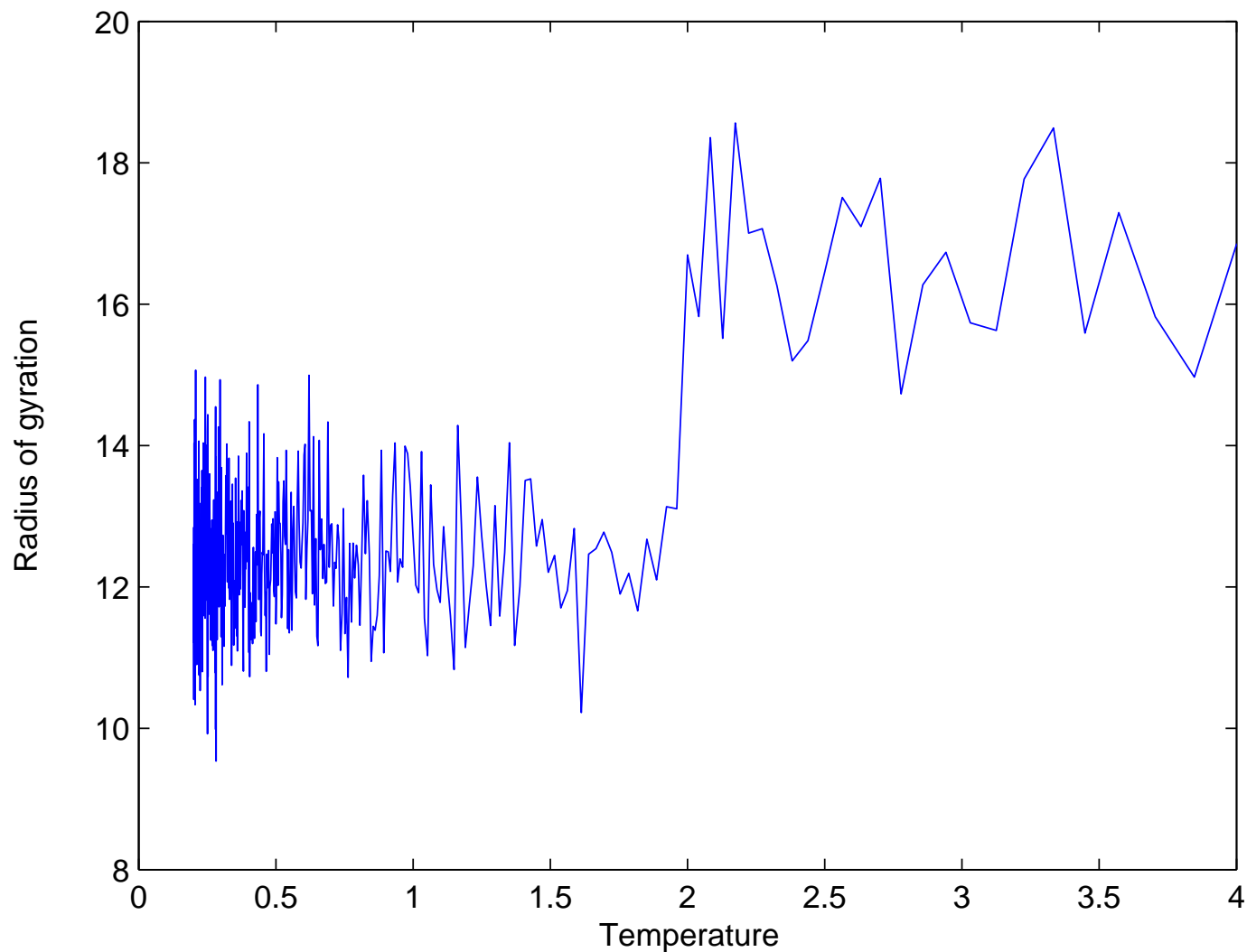
## Energy Vs Temperature



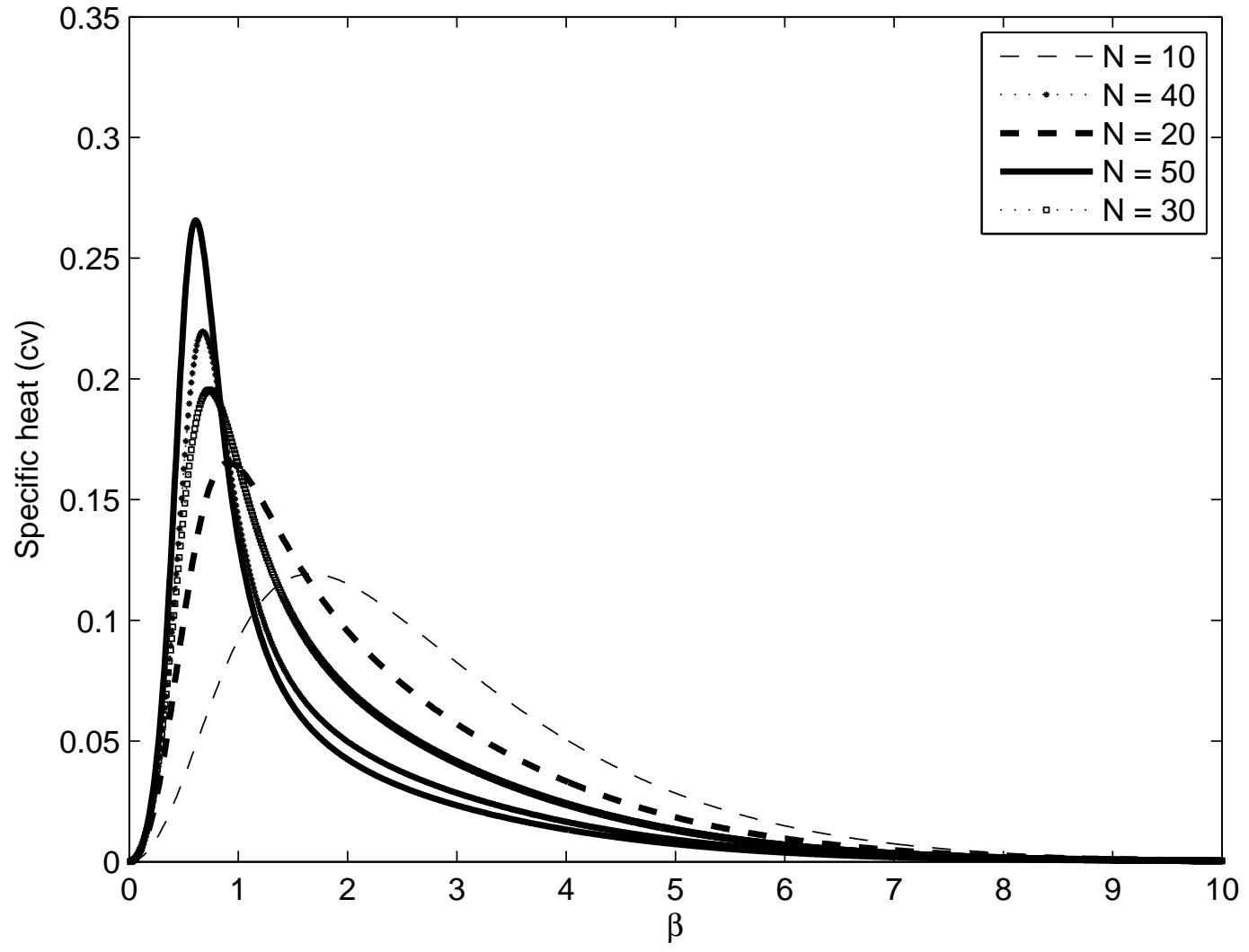
Energy *versus* temperature calculated from a small entropic ensemble generated in the production run with converged density of states



Radius of gyration *versus* temperature calculated from a small entropic ensemble generated in the production run with converged density of states



Specific Heat *versus*  $\beta$  for different polymerization





# Free Energy: Thermodynamics : Closed System

- **Closed System:**
- Natural variable for free energy is  $T$ .
- We start with  $U \equiv U(S, \cdot)$  where  $\{\cdot\}$  stands for other thermodynamic variables relevant for the description of the system under study. For example
  - $\{\cdot\}$  stands for  $V, N$  for a simple fluid.
  - $\{\cdot\}$  stands for  $M, N$  for a magnetic system.
  - *etc.*
- Legendre transform:  $S \rightarrow T$  and  $U \rightarrow F$ .

$$F(T, \cdot) = U(S, \cdot) - T(S, \cdot)S$$

$$T(S, \cdot) = \left( \frac{\partial U}{\partial S} \right)_{\{\cdot\}}$$

# Free Energy: Thermodynamics : Isolated System

- **Isolated System:**
- Microcanonical Free energy:

$$F \equiv F(U, \cdot)$$

- Start with  $S \equiv S(U, \cdot)$ . For example
  - Entropic sampling gives us an estimate of entropy as a function of energy up to an additive constant.
- Microcanonical Free Energy is then given by

$$F(U, \cdot) = U - T(U, \cdot)S(U, \cdot)$$
$$\frac{1}{T(U, \cdot)} = \left( \frac{\partial S}{\partial U} \right)_{\{\cdot\}}$$

## Free Energy : Statistical Mechanics

- Free energy for a closed system is related to canonical partition function as follows

$$F(T, \cdot) = -k_B T \ln Q(T, \cdot)$$
$$Q(T, \cdot) = \sum_C \exp[-\beta E(C)]$$

where the sum extends over all microstates  $C$  belonging to the closed system at temperature  $T = 1/[k_B\beta]$

- The energy of the closed system is given by

$$U(T, \cdot) = \langle E \rangle = \frac{1}{Q(T, \cdot)} \sum_C E(C) \exp[-\beta E(C)]$$

## Free Energy is not all that free !

- $F$  is either a function of **Energy** (for an isolated equilibrium system) or a function of **Temperature** (for a closed equilibrium system)
- For any equilibrium system, isolated or closed,  $F$  **can not be** simultaneously a function of both Energy and Temperature.
- This is because,
  - An isolated system with fixed Energy has a unique Temperature
  - A closed system at a given Temperature has a unique Energy
- Can we define a **phenomenological** free energy, denoted by  $F_L$ , as a function of both Energy and Temperature ?

# Phenomenological Free Energy

- Let us call  $F_L$  as phenomenological free energy. It resembles
  - Landau Free Energy (originally proposed to describe continuous phase transition) or
  - Ginzburg-Landau free energy (proposed in the context of superconductivity) or
  - Landau-de-Gennes free energy (in the context of liquid crystals)
- **Question:** Why are we interested in defining such a free energy ?
- **Answer:** We want to estimate the price, in terms of excess free energy, we need to pay if want to keep a closed system in a (non-equilibrium ?) state with an energy, different from equilibrium energy.

## $F_L(E, T)$

- The function  $F_L(E, T)$  should have the following property:
  - $F_L(E, T) \geq F(T) \forall E$
  - In the above equality obtains when  $E = \langle E \rangle = U(T)$  ( $\langle \cdot \rangle$  denotes an average over a canonical ensemble at temperature  $T$ ).
- Thus the system has to incur a free energy penalty, if it wants to be in a macroscopic state with an energy different from equilibrium energy; the penalty is given by,

$$\Delta F = F_L(E \neq U(T)) - F_L(T)$$

- How does one calculate  $F_L(E, T)$  ?
- In thermodynamics, start with  $S(U)$  and calculate  $F_L(U, T) = U - TS(U)$ , assuming  $U$  and  $T$  to be independent of each other !

## $F_L(E, T)$ : Statistical Mechanics

- In statistical mechanics we define  $F(T)$  as

$$F(T) = -k_B T \ln \sum_C \exp[-\beta E(C)]$$

Where the sum is taken over all microstates (denoted by  $C$ ) of the closed system.

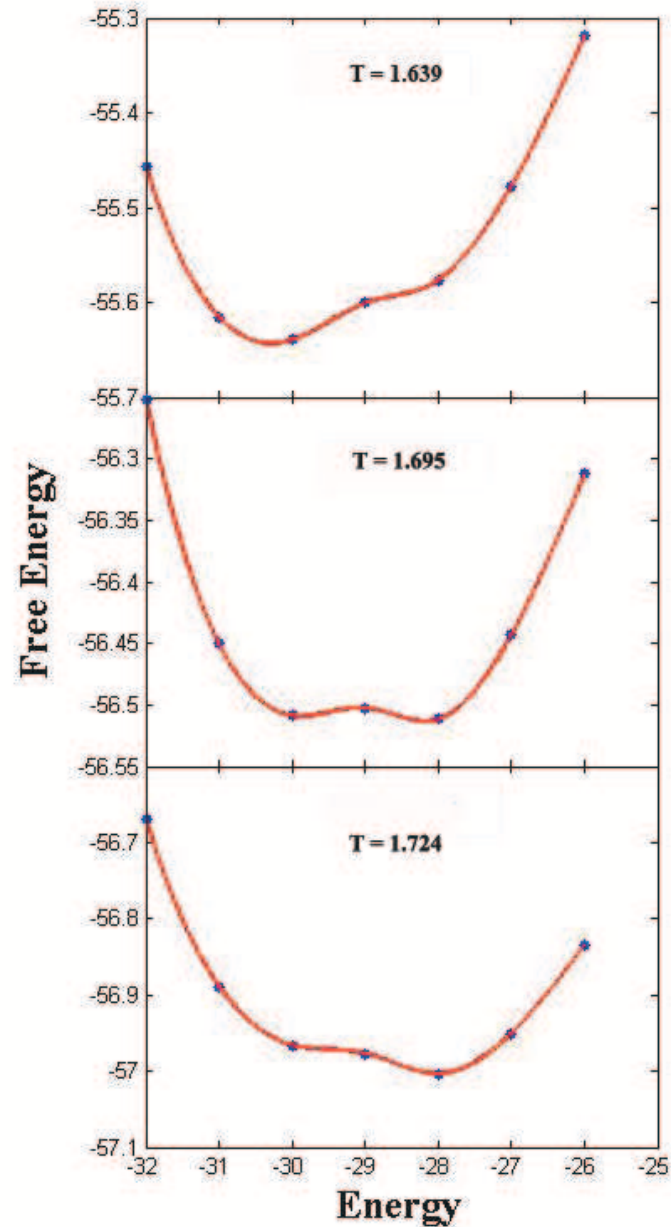
- However, for a given temperature  $T$ , the contribution to the partition sum comes predominantly from conformations having energy  $E = \langle E \rangle = U(T)$ . Hence we can express free energy as

$$F(T) = -k_B T \ln \sum_C \delta(E(C) - U(T)) \exp[-\beta E(C)]$$

In the above if we replace  $U(T)$  by  $E$ , we get Landau free energy,

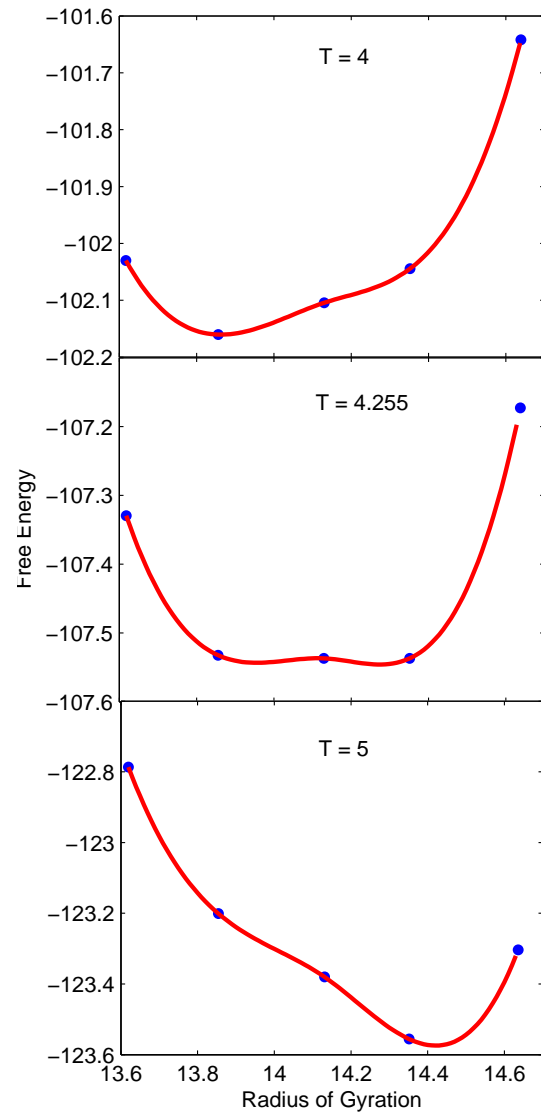
$$F_L(E, T) = -k_B T \sum_C \delta(E(C) - E) \exp[-\beta E(C)]$$

$F_L$  versus  $E$ .  $N = 50$ .  $T = 1.639 < T_c$ .  $T = 1.695 = T_c$ .  $T = 1.724 > T_c$





$F_L$  versus  $R_g$ .  $T_c = 4.255$ . Larger than the one from  $F_L$  versus  $E$  curve.



*THANKS*