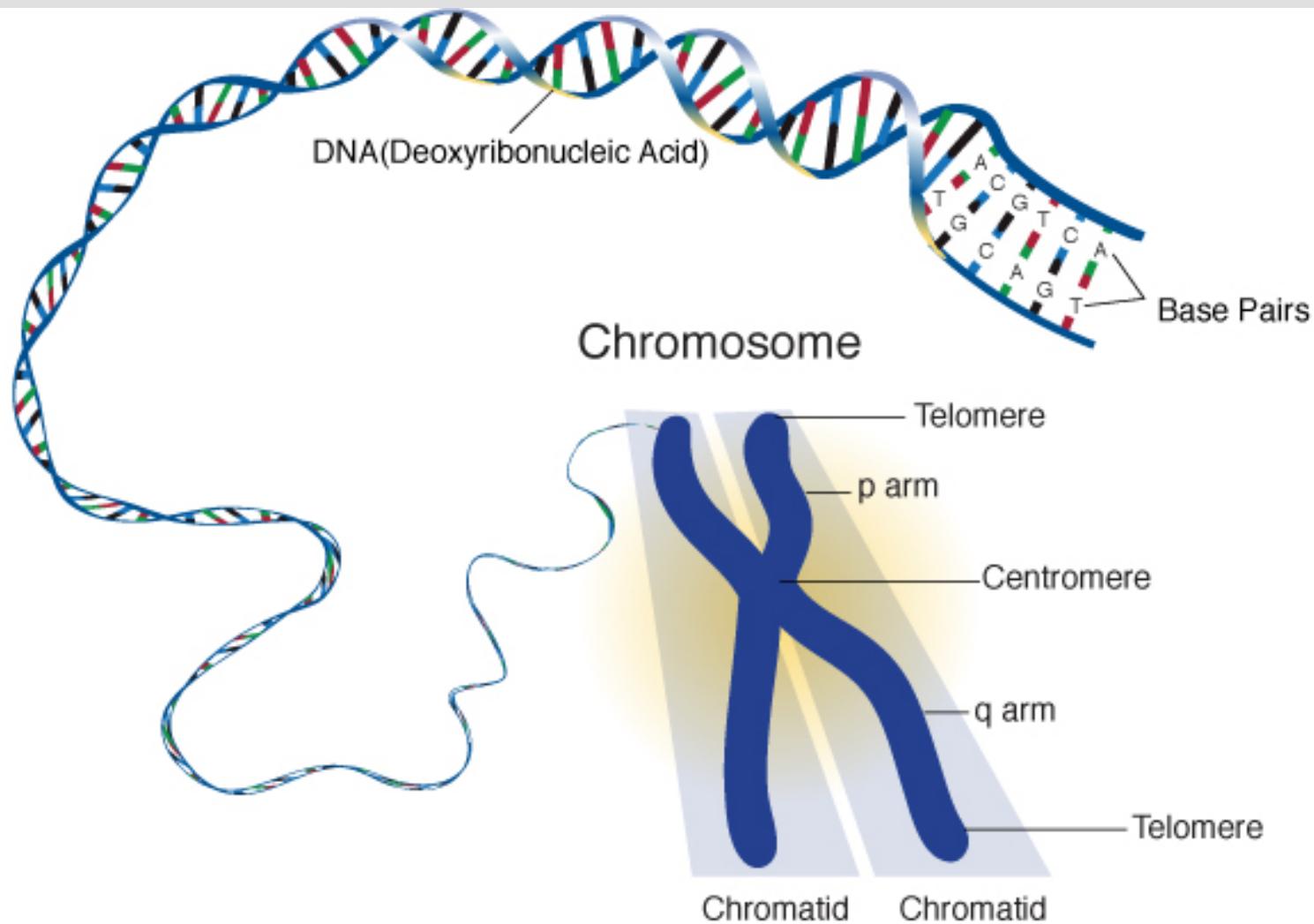


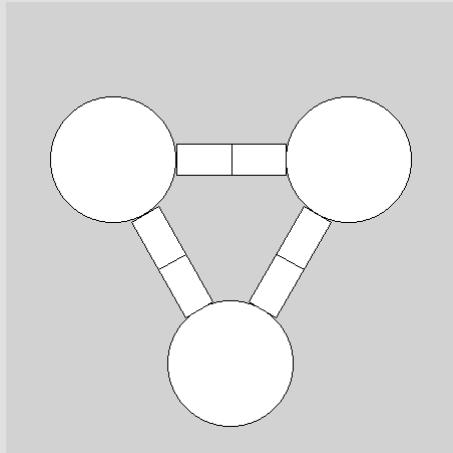
# A Monte-Carlo Study of Physical Properties of Molecules: Structure, Energy, and Thermal Dynamics

Presented by Lecheng Wang

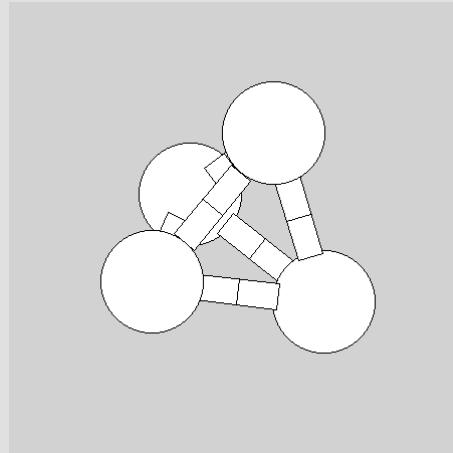
# I. Introduction – chromosome structures



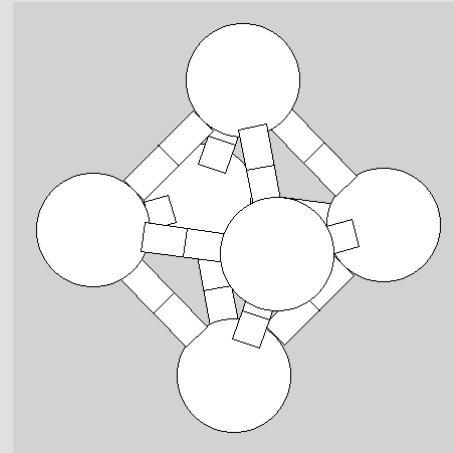
# I. Introduction – $(Ar)_N$ clusters' structure



$N=3$



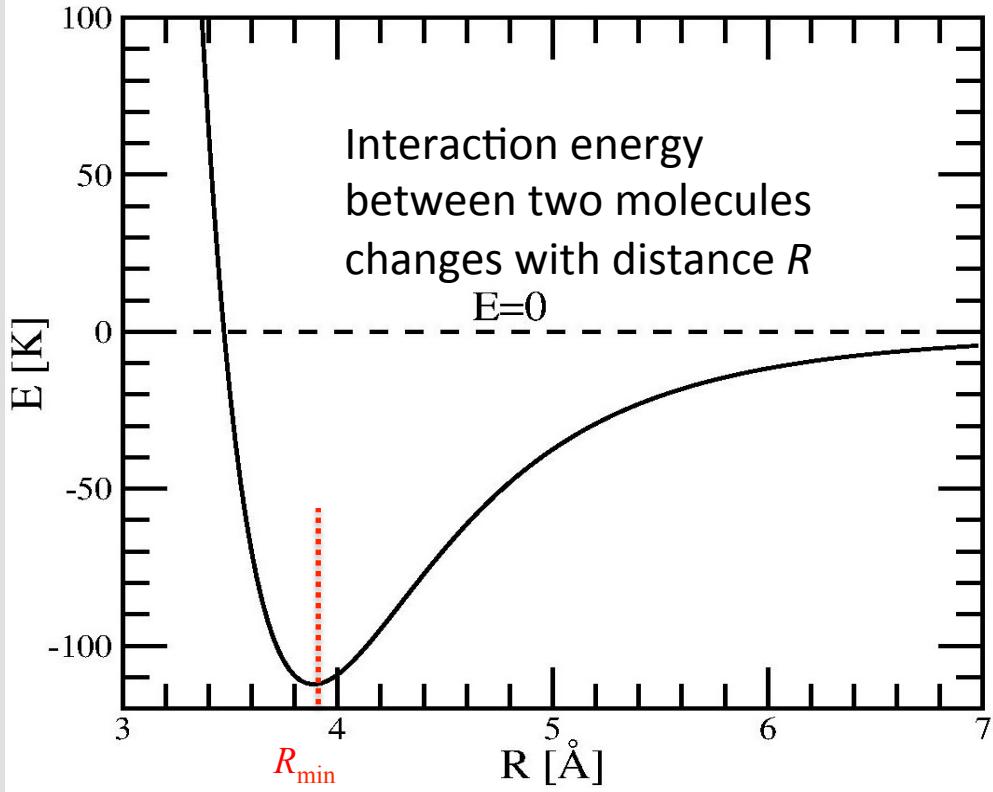
$N=4$   
Tetrahedron



$N=6$   
Octahedron

How about  $N$  continue increasing?

## II. Theory – A little physics



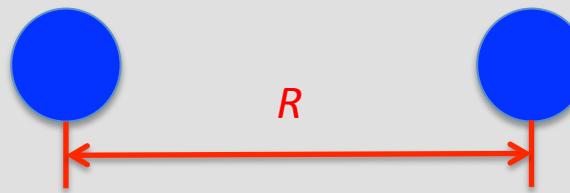
Boltzmann distribution:

$$P(R = r) \propto \exp(-E(R)/kT)$$

$k$ : Boltzmann constant.

$T$ : temperature.

$E(R)$ : Energy as a function of intermolecular distance  $R$ , as shown below



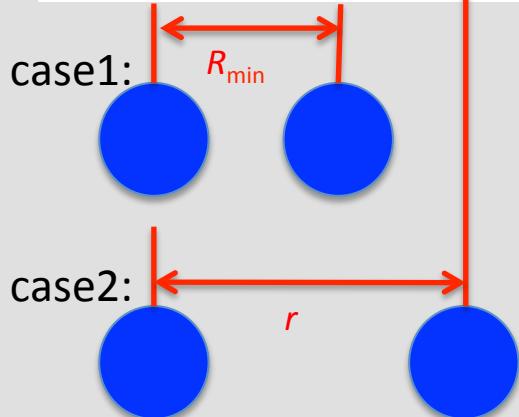
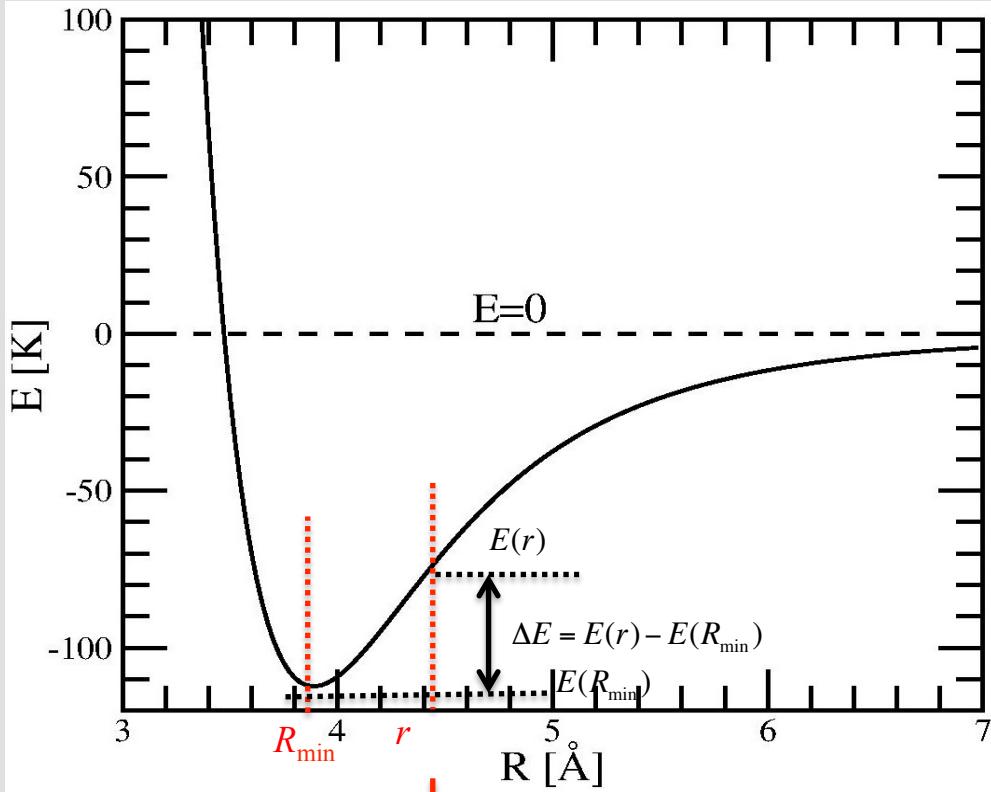
$R_{\min}$ : The distance between two molecules where the interaction is minimal (most stable, optimized).

$\rho(R)$  is probability density function (PDF) of  $R$ , and the expectation values:

$$\bar{R} = \int_0^{\infty} dR \times R \rho(R), \quad \bar{E} = \int_0^{\infty} dR E(R) \rho(R)$$

$$\rho(R) = P(R = r) = \frac{\exp(-E(R)/kT)}{\int_0^{\infty} dR \exp(-E(R)/kT)}, \quad \bar{R} = \frac{\int_0^{\infty} dR \times R \exp(-E(R)/kT)}{\int_0^{\infty} dR \exp(-E(R)/kT)}, \quad \bar{E} = \frac{\int_0^{\infty} dR E(R) \exp(-E(R)/kT)}{\int_0^{\infty} dR \exp(-E(R)/kT)}$$

## II. Theory –Monte Carlo random walk



How to determine  $\rho(R)$  ?

$$\rho(R) = P(R = r) = \frac{\exp(-E(R)/kT)}{\int_0^\infty dR \exp(-E(R)/kT)}$$

By Monte Carlo random walk.

What is the ratio of the probability between case 2 (with  $r$ ) and case 1 (with  $R_{\min}$ )?

$$P(R = r) \propto \exp(-E(R)/kT)$$

So:

$$\frac{P(R = r)}{P(R = R_{\min})} = \frac{\exp(-E(r)/kT)}{\exp(-E(R_{\min})/kT)} = \exp(-\Delta E/kT)$$

What is the probability of a Monte Carlo move from case 1 to case 2 is accepted?

$$P(\text{Accept case 1} \rightarrow \text{case 2}) = \frac{P(R = r)}{P(R = R_{\min})} = \frac{\exp(-E(r)/kT)}{\exp(-E(R_{\min})/kT)} = \exp(-\Delta E/kT)$$

Observation: if  $\Delta E \leq 0$ ,  $\exp(-\Delta E/kT) \geq 1$ : always accept  
 if  $\Delta E > 0$ ,  $\exp(-\Delta E/kT) < 1$ : accept with probability  $\exp(-\Delta E/kT)$

## II. Theory – Algorithm

Exactly the same as the Monte Carlo introduced in class:

$x_1$ : for transition function

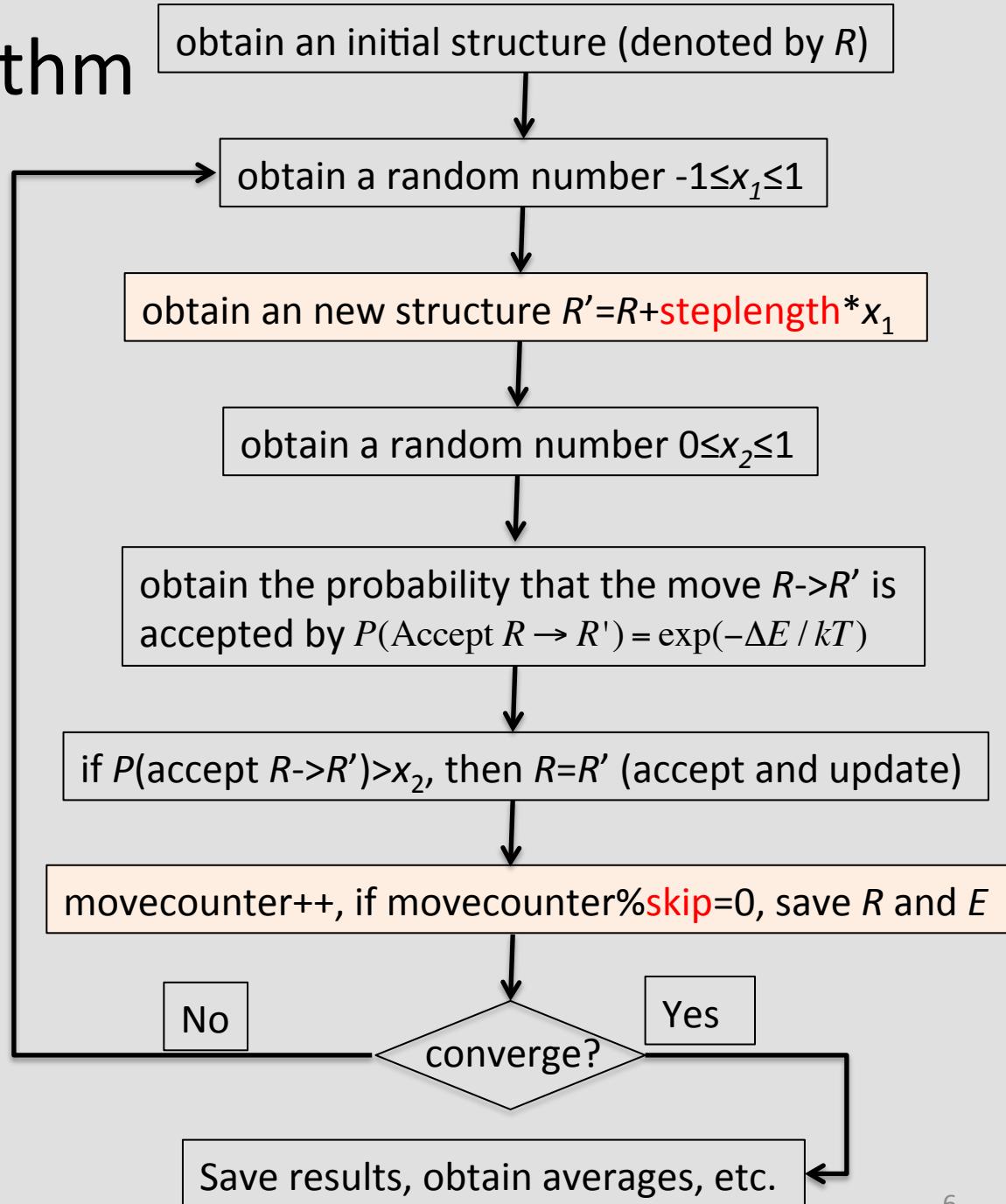
$x_2$ : for acceptance probability

Little difference:

**steplength**: controlling the length of random walk, to ensure an acceptance probability between 0.3-0.6

**skip**: controller when the sampling result will be saved.

Since consecutive steps tend to be ‘similar’, thus no need to save all steps.

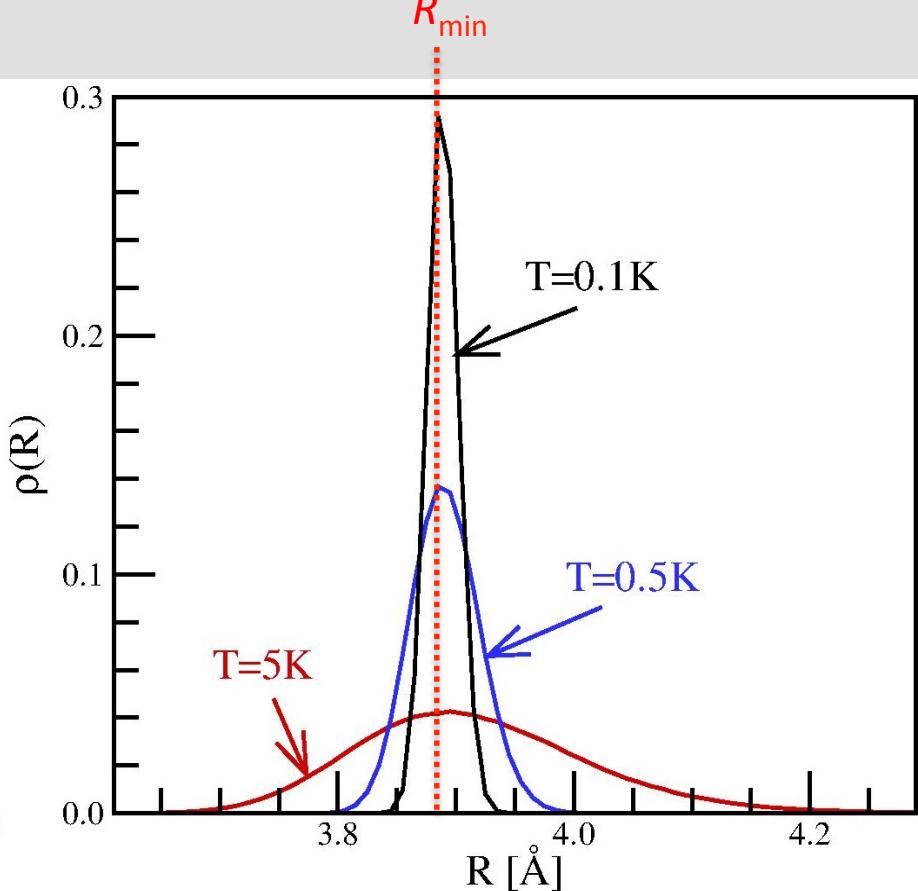
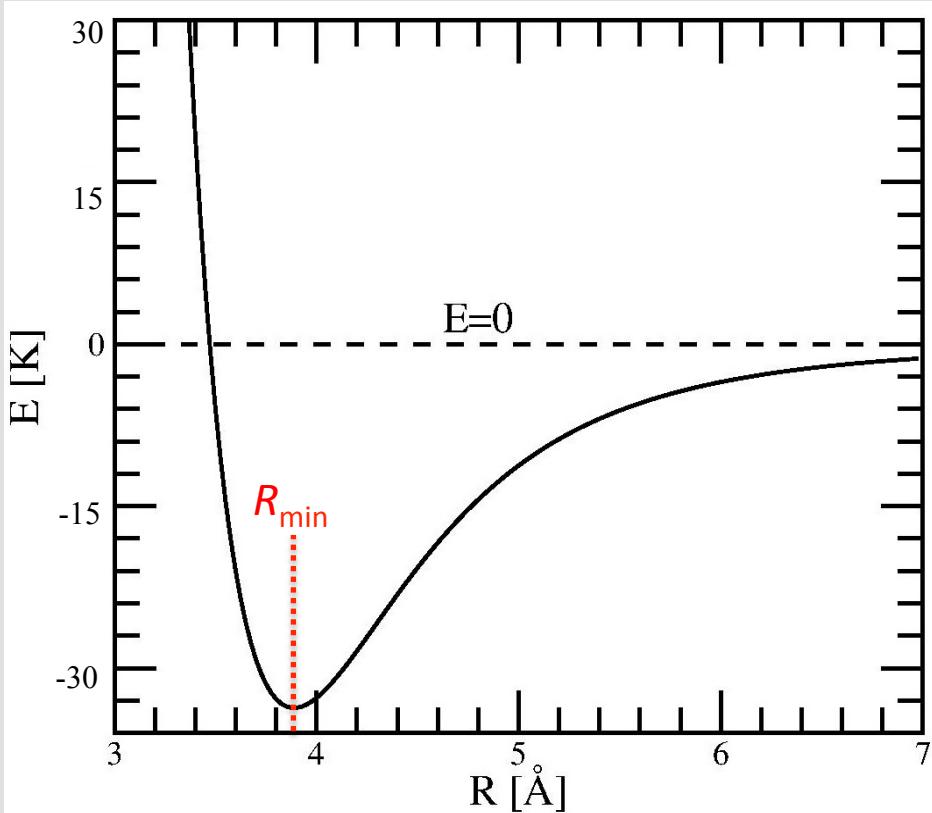


### III. Results: structure of $(H_2)_2$ dimer

The structure of  $(H_2)_2$  cluster is totally decided by  $E(R)$

$$\rho(R) = P(R = r) = \frac{\exp(-E(R)/kT)}{\int_0^\infty dR \exp(-E(R)/kT)}$$

- The  $R$  corresponding to largest probability density function (on the right) the same as the  $R_{\min}$  of the interactions (on the left).
- $\rho(R)$  is delocalized as  $T$  increase.

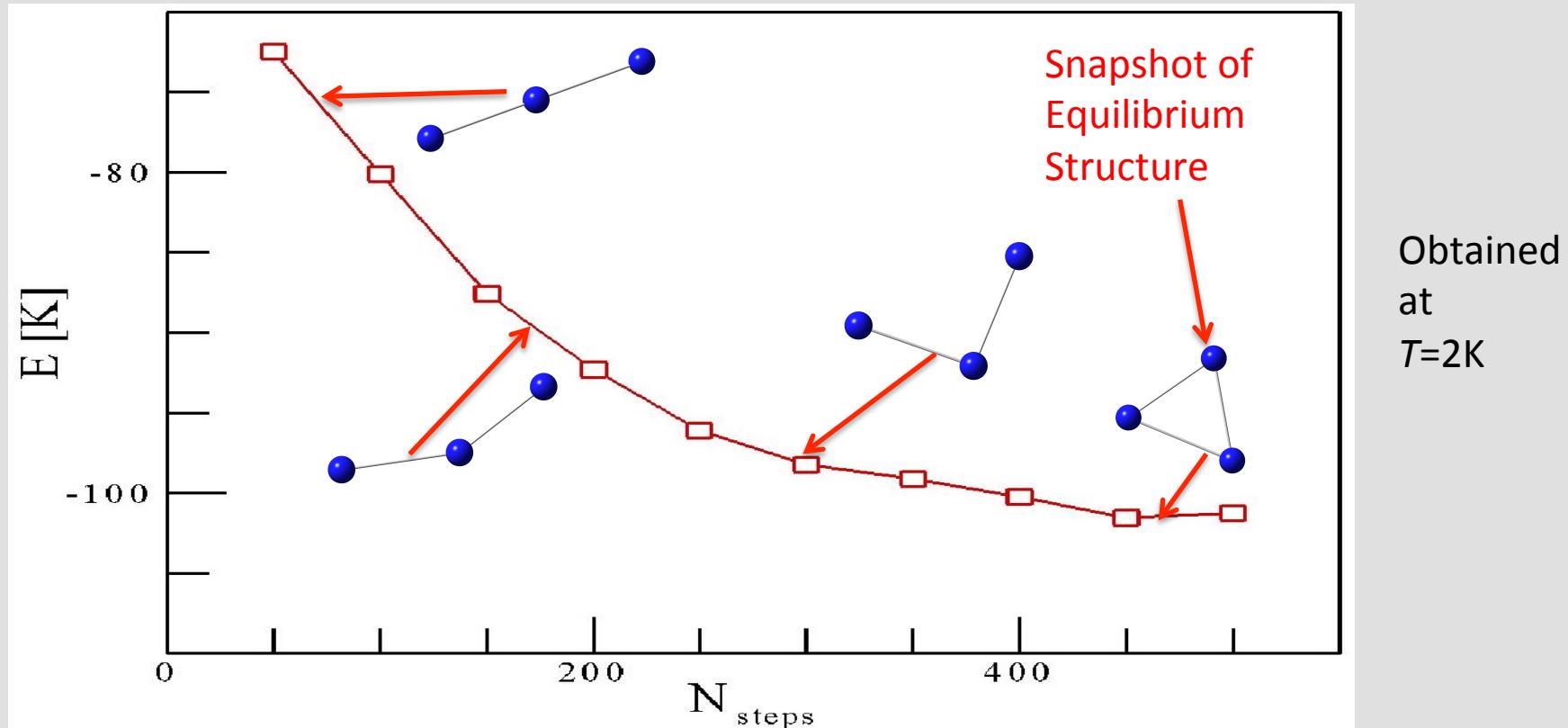


### III. Results: structure change of $(H_2)_3$

For clusters containing  $N H_2$  molecules:

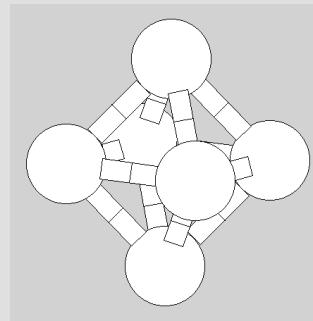
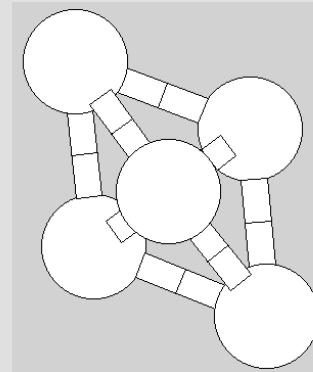
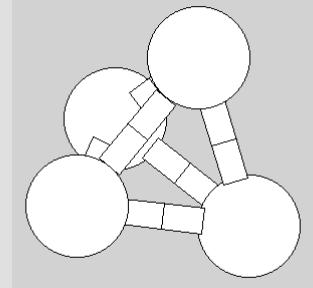
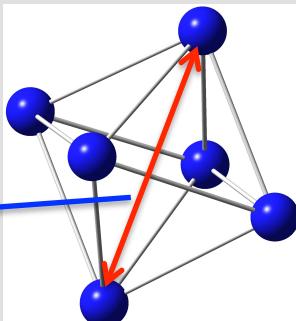
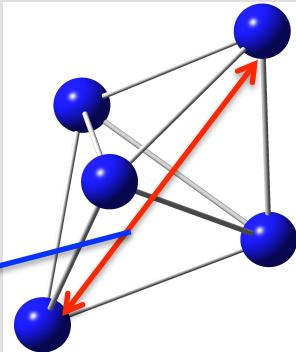
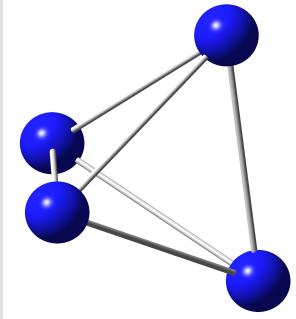
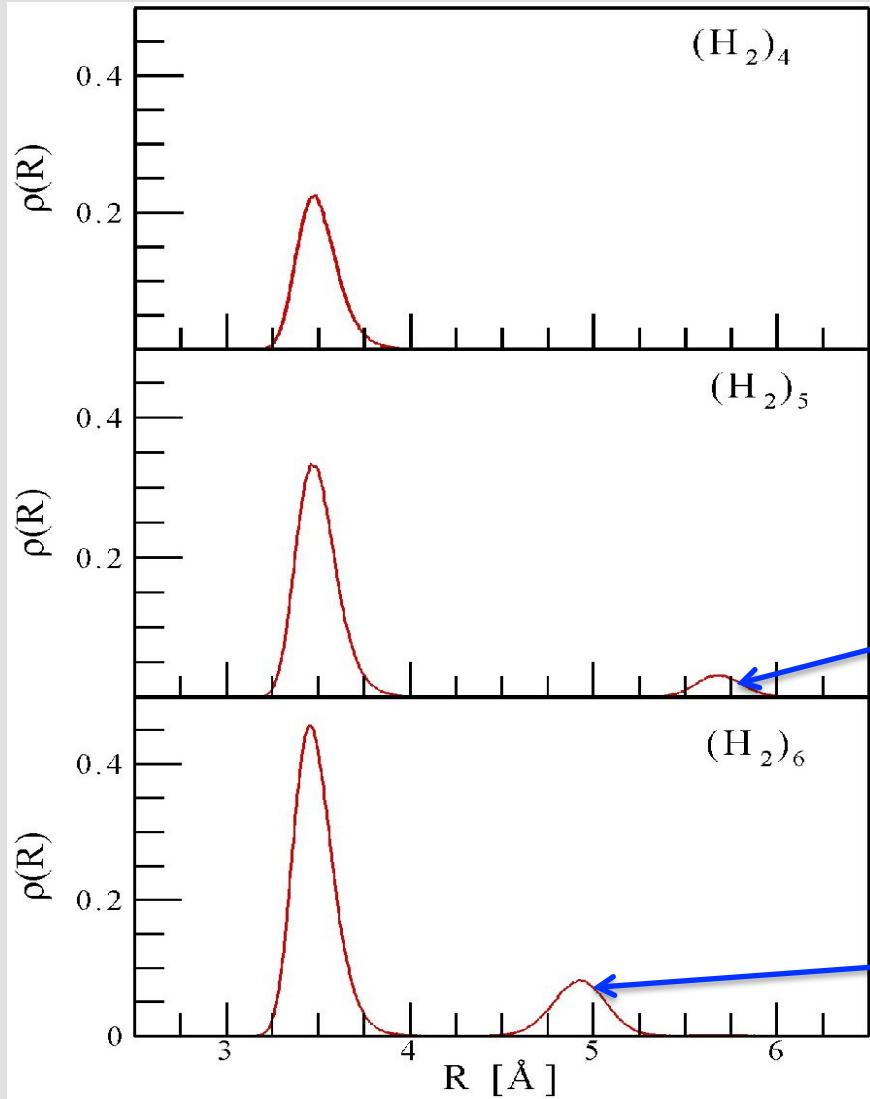
$$E_{total} = \sum_{0 < i < j \leq N} E(R_{i,j}) \quad (\text{Pairwise Additive})$$

Where  $E(R_{i,j})$  is the interaction between the  $i^{\text{th}}$  and  $j^{\text{th}}$   $H_2$  molecule, which depends on their distance  $R_{i,j}$

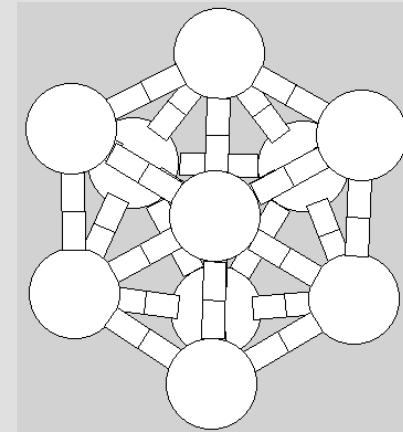
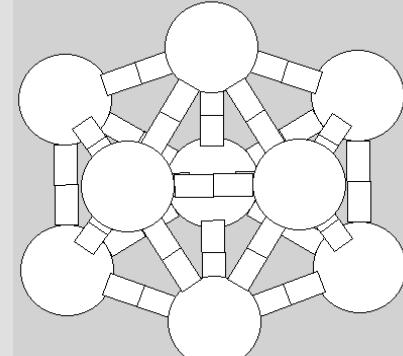
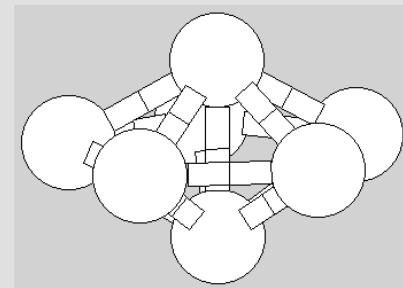
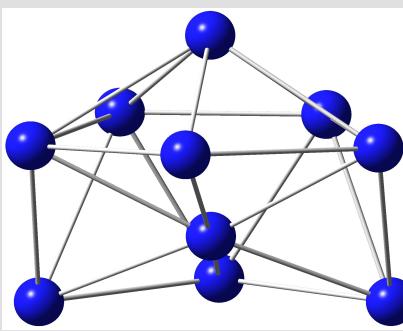
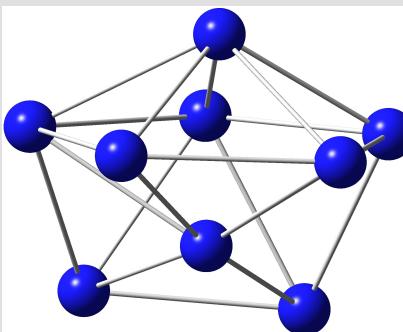
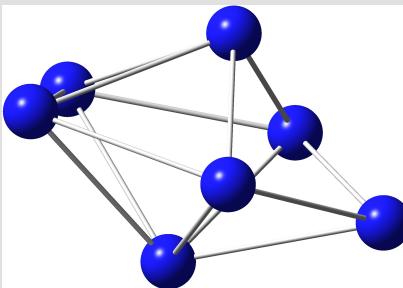
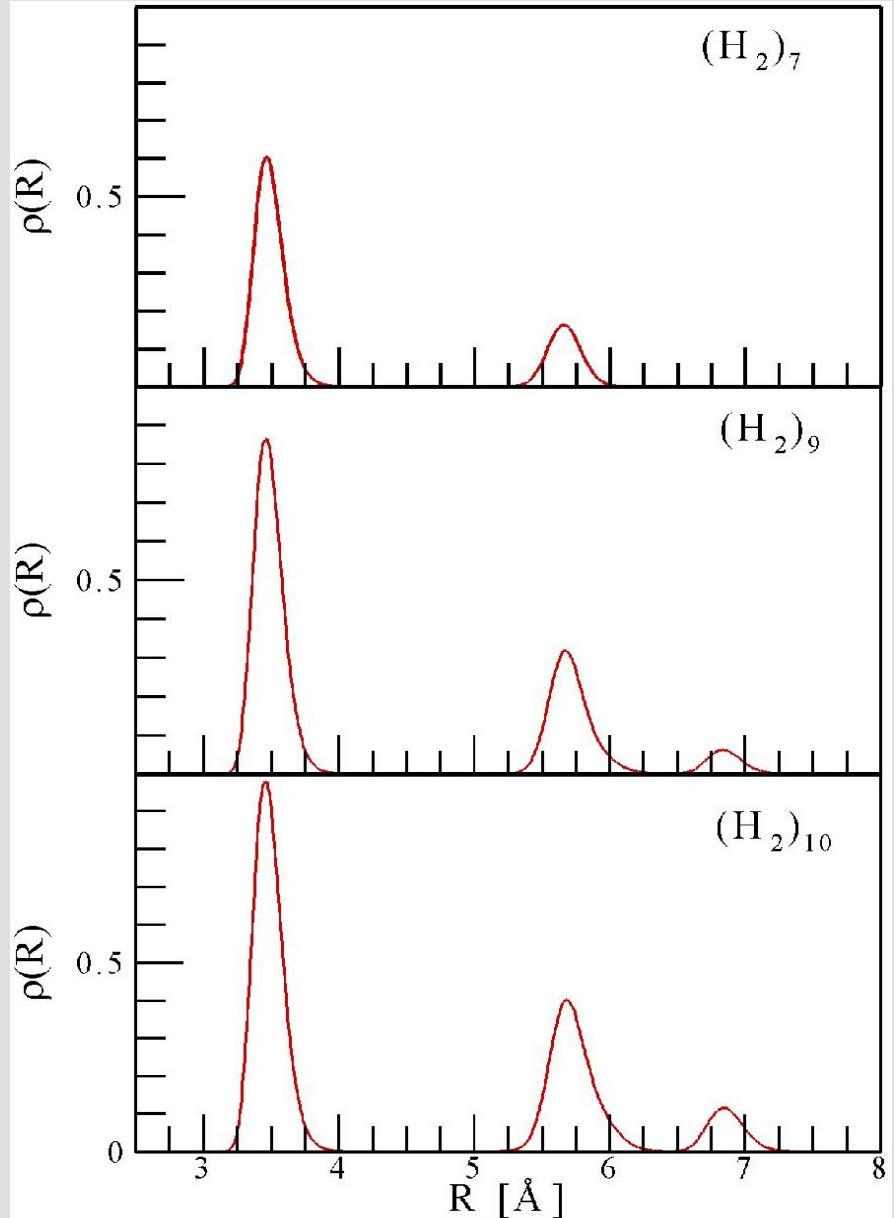


### III. Results: structures of $(H_2)_N$ , $N=4,5,6$

Only the probability distribution function  $\rho(R)$  make sense!



### III. Results: structures of $(H_2)_N$ , $N=7,9,10$



# III. Results: energy of $(H_2)_N$ , $N=2$ to 10

Energy obtained Monte Carlo study:

$$\bar{E} = \frac{\int_0^{\infty} dR E(R) \exp(-E(R)/kT)}{\int_0^{\infty} dR \exp(-E(R)/kT)}$$

and compared with database values.

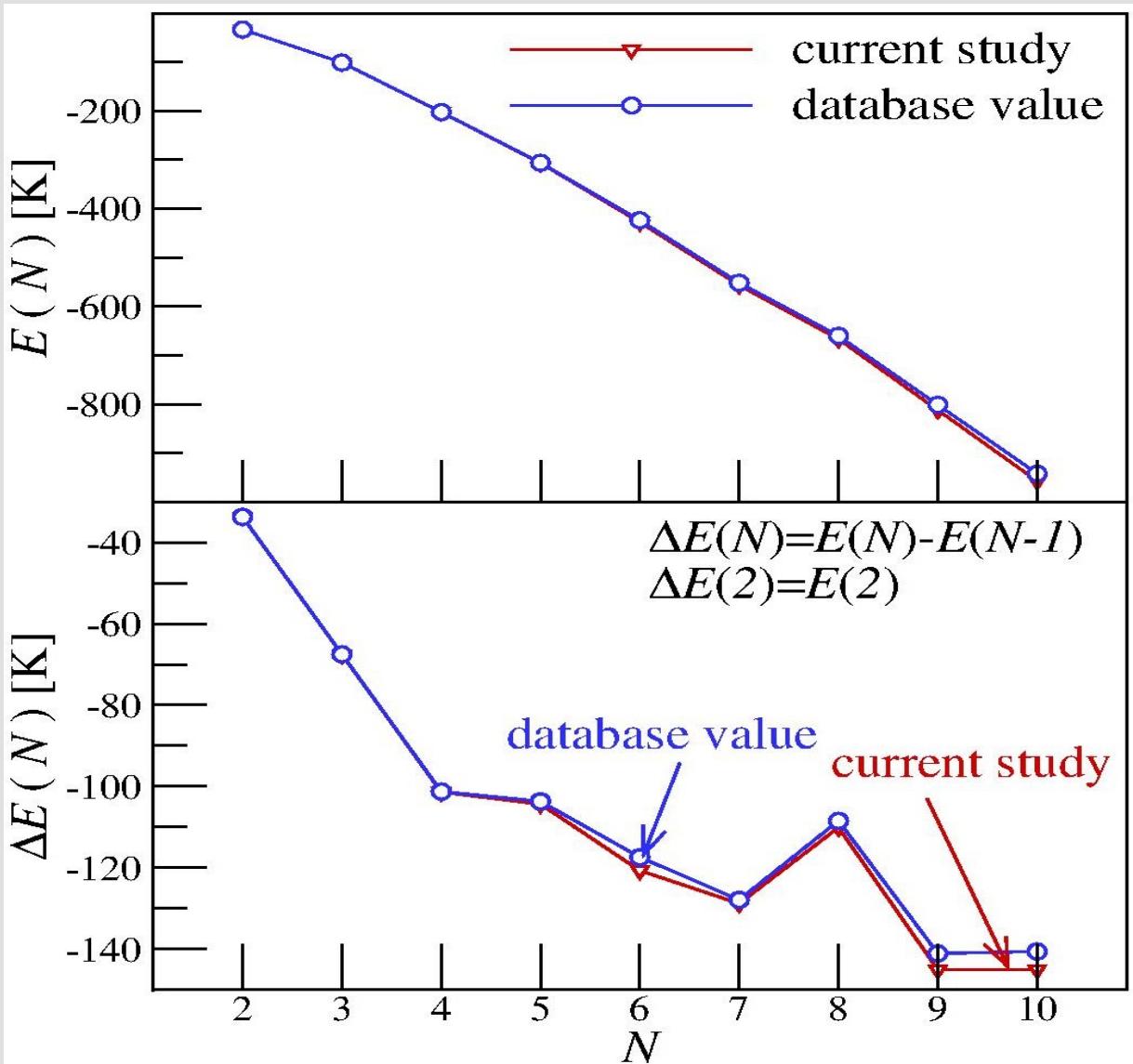
For better comparison, we compare:

$$\Delta E(N) = E(N) - E(N-1)$$

Reason:

$\Delta E(N)$  is of the same scale for all  $N$ .

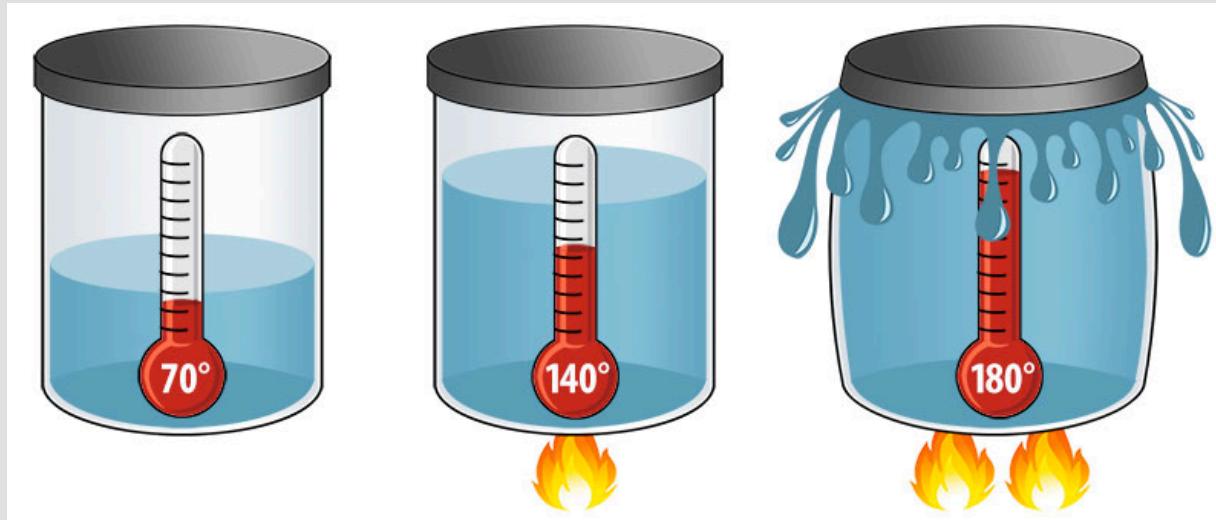
The error bars are smaller than symbols thus not shown.



# IV. Simulating thermal expansion

Thermal expansion is the tendency of matter to change in shape, area, and volume in response to a change in temperature.

In macroscopic view (a organic solvent):

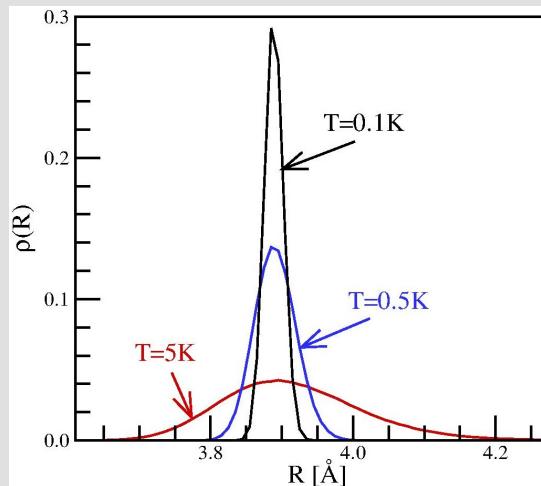


taken from Phy101 lecture slides,  
by Dr. Zhang, New York University

In microscopic view:

- Delocalization at high temperature
- Localization at low temperature
- $\bar{R}$  increases as  $T$  increases

$$\bar{R} = \frac{\int_0^{\infty} dR \times R \exp(-E(R)/kT)}{\int_0^{\infty} dR \exp(-E(R)/kT)}$$



$$\bar{R}(T = 0.1\text{K}) = 3.881 \text{ \AA}^{\circ}$$

$$\bar{R}(T = 0.5\text{K}) = 3.893 \text{ \AA}^{\circ}$$

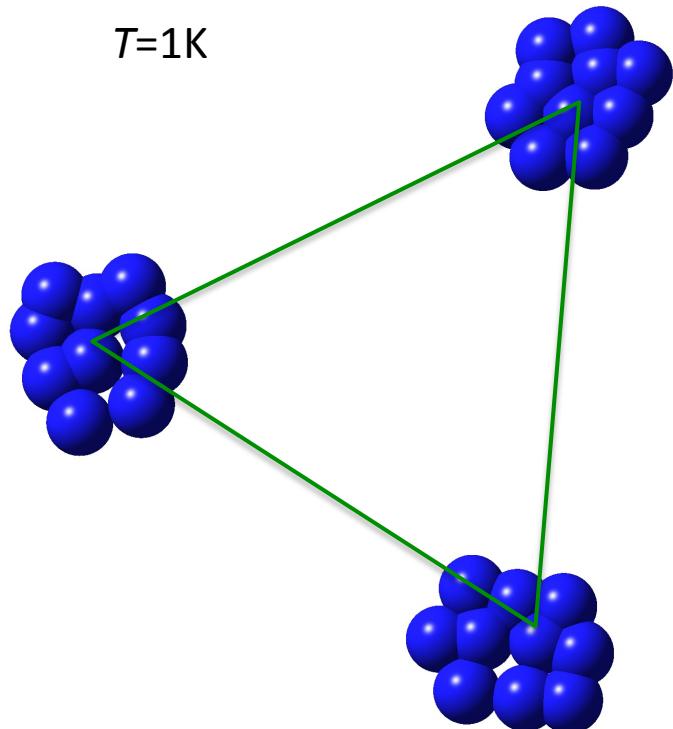
$$\bar{R}(T = 5\text{K}) = 3.909 \text{ \AA}^{\circ}$$

# IV. Simulating thermal expansion

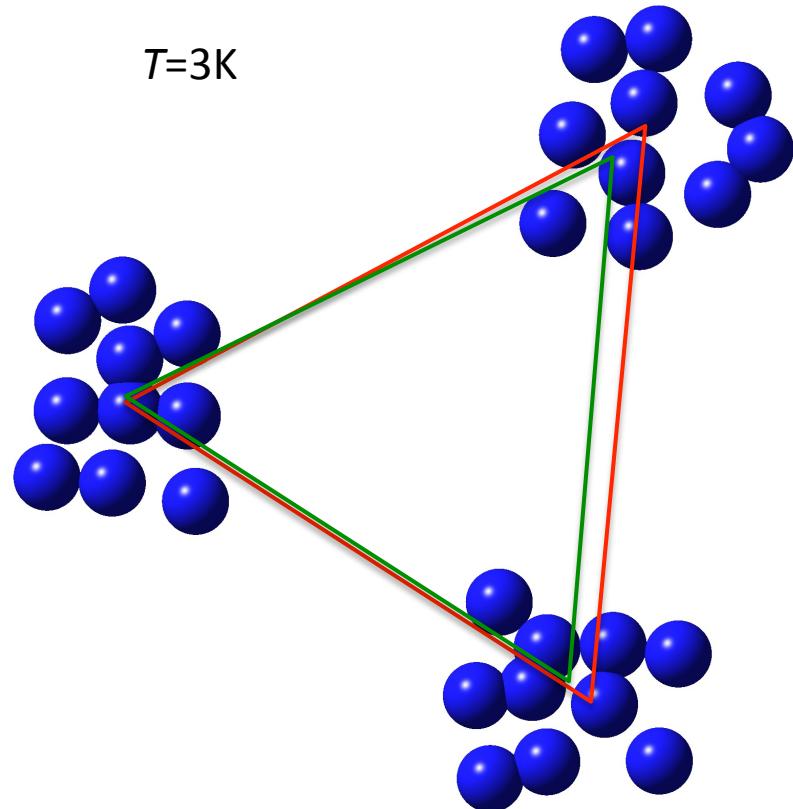
Ten snapshots of the structure of  $(H_2)_3$  clusters in Monte Carlo simulation, obtained at 1K and 3K, correspondingly.

The triangles illustrate the approximate average structures at different temperature.

$T=1K$



$T=3K$



# V. Simulating boiling of materials

What happens if the thermal expansion continues, and temperature increase? **Boiling**

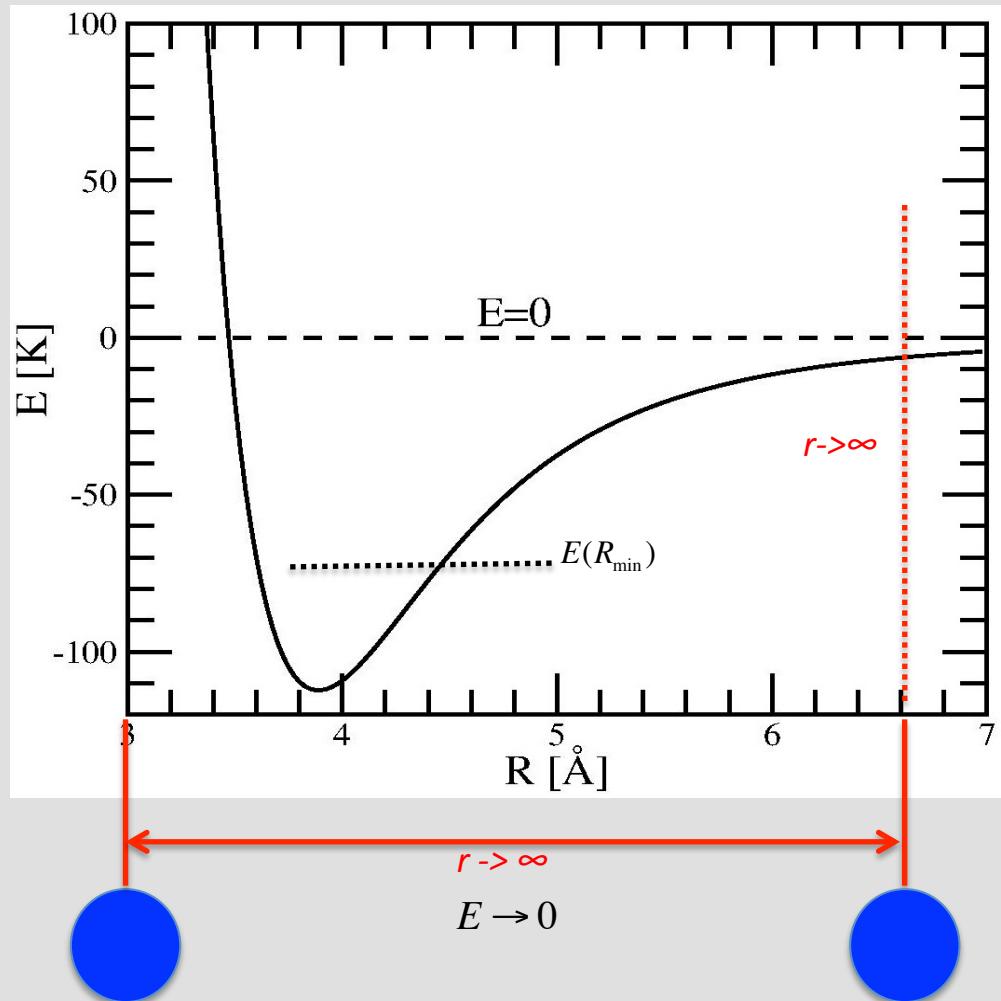


Boiling in microscopic: temperature is high enough (approaching infinite), so that for any moves:

$$\lim_{T \rightarrow \infty} P(\text{Accept moves}) = \lim_{T \rightarrow \infty} \exp(-\Delta E / kT) = 1$$

Thus

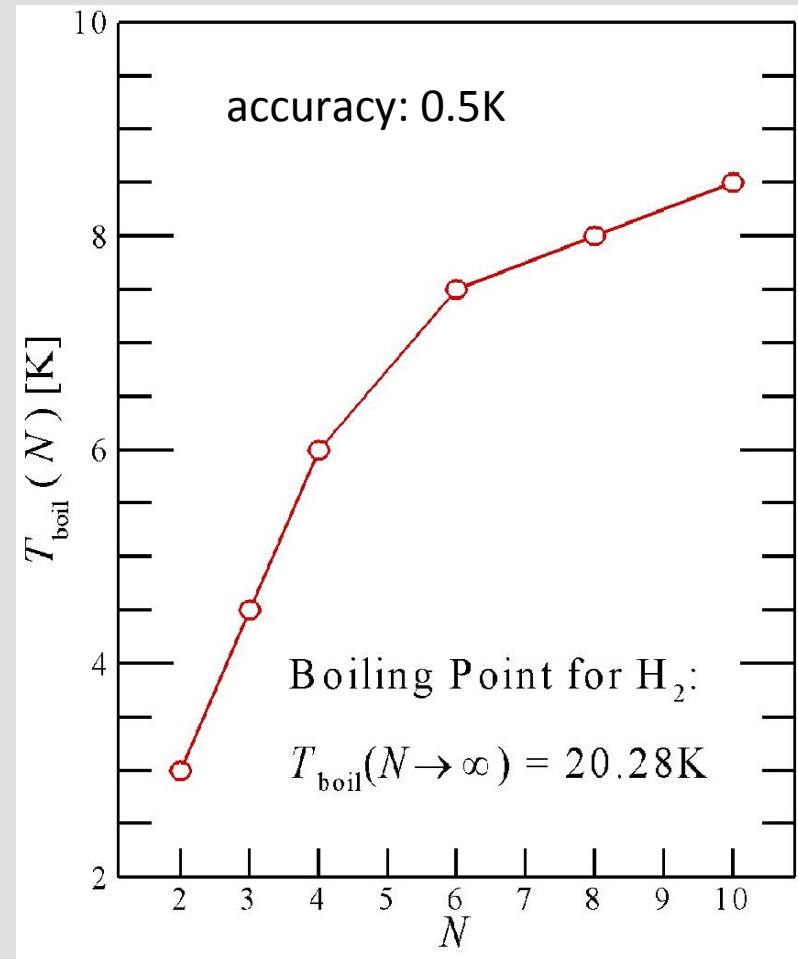
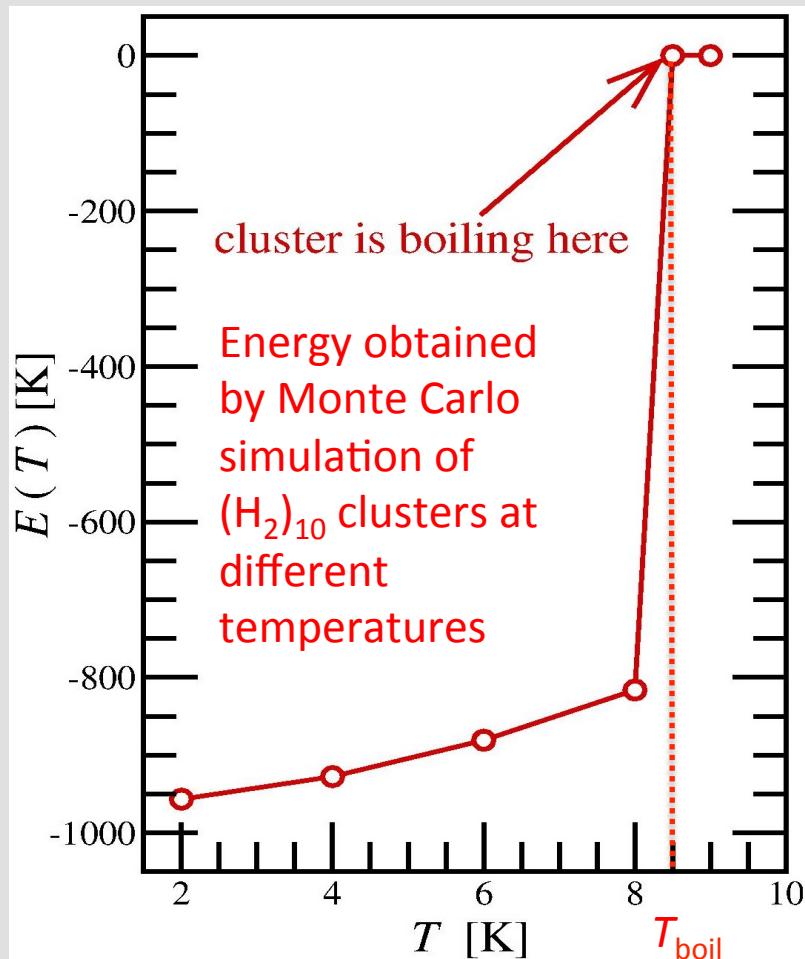
- All moves will be accepted
- The system will be **dissociated**
- The total interaction will become  **$E=0$**  due to dissociation



# V. Simulating boiling of materials

Boiling temperature increases as  $N$  increases, and will approach the true boiling point of  $\text{H}_2$  when  $N$  approaches infinitely large

Reason:  $P(\text{Accept moves}) = \exp(-\Delta E / kT)$ ,  $\Delta E$  increases as  $N$  increase. Thus  $T$  should increase so that  $\lim_{T \rightarrow \infty} P(\text{Accept moves}) = \lim_{T \rightarrow \infty} \exp(-\Delta E / kT) = 1$



# VI. Conclusions and Lookouts

Conclusion:

- Monte Carlo Simulation can satisfingly predict the structure of materials
- Monte Carlo Simulation can satisfingly predict the energy of materials
- Using Monte Carlo Simulation at different temperatures can satisfingly reproduce the thermal expansion of materials
- Using Monte Carlo Simulation at different temperatures can simulate the boiling of materials and predict the boiling points, but require more computation efforts.

Future works:

- Doped clusters.
- Incorporating quantum mechanics to better simulate the microscopic environment.
- Parallelization of sampling process.

Thank You!

Comment and questions?