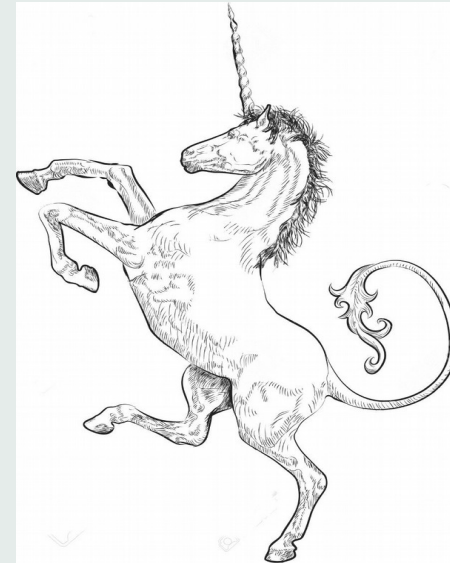
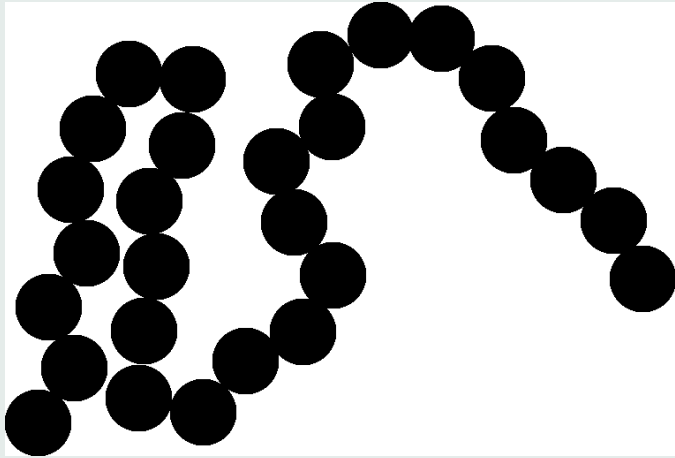


Folding in small polyethylene systems: Single chains and few chains

Timur Shakirov and Wolfgang Paul



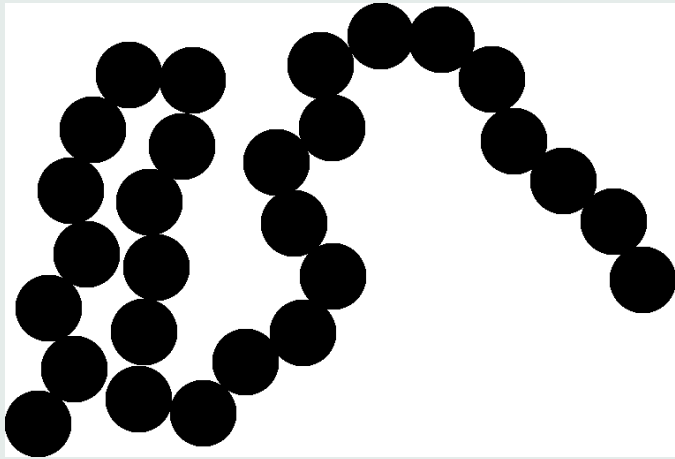
Folding



**Local
stiffness**



Folding

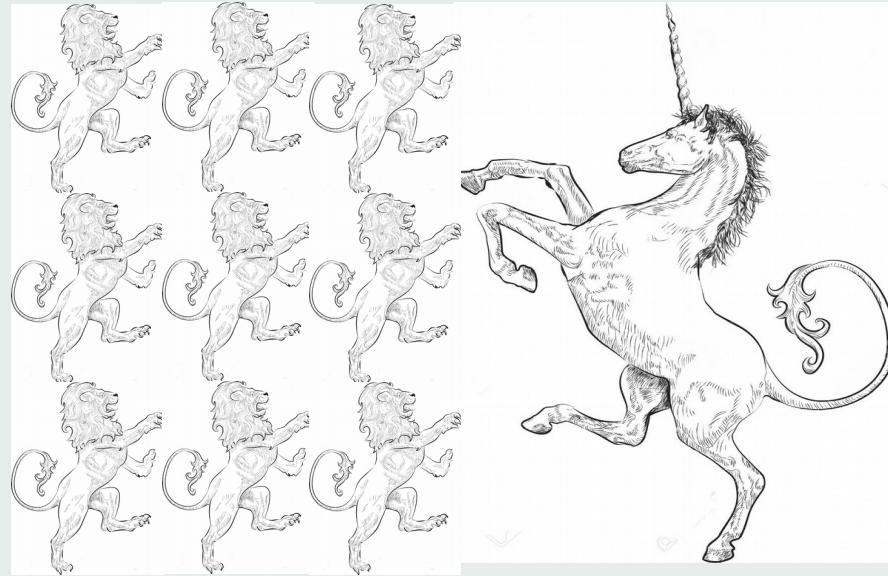
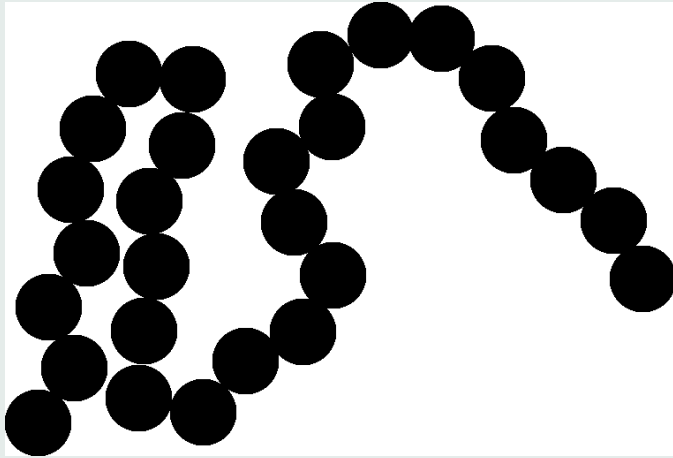


Attraction

**Local
stiffness**



Folding

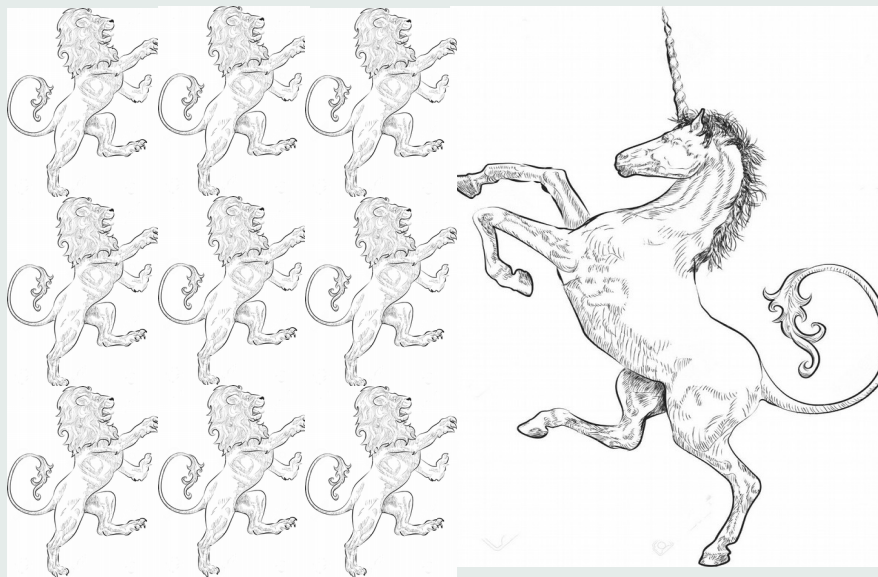
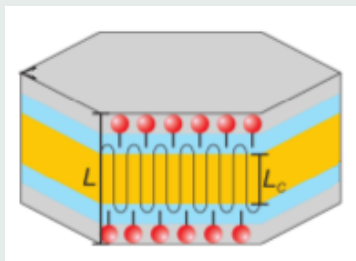


Attraction

**Local
stiffness**



Folding of alkanes

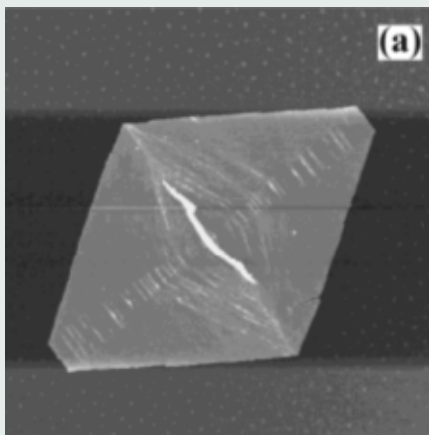
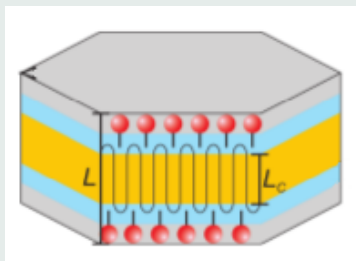


Attraction

**Local
stiffness**

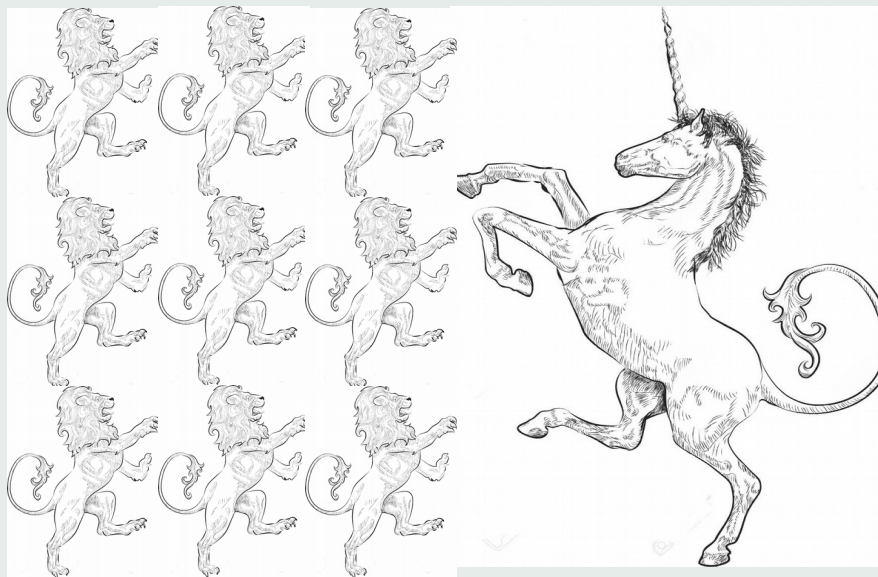


Folding of alkanes



Single crystal of polyethylene from atomic force microscopy

*)



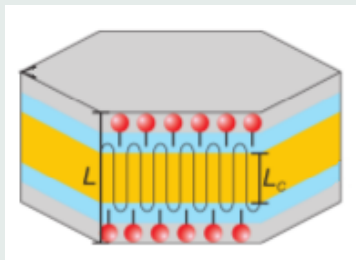
Attraction

Local stiffness

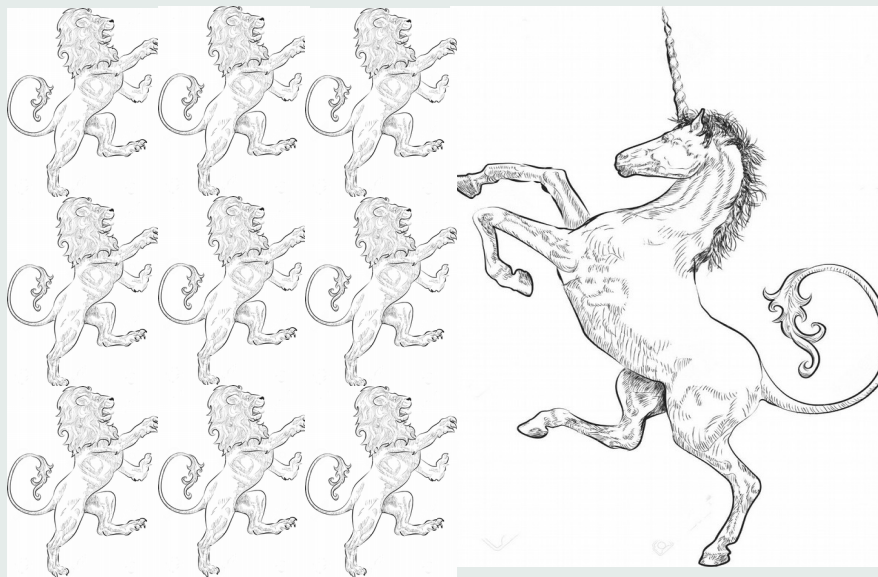
*) Tian et al., Macromolecules, Vol. 37, No. 4, 2004



Folding of alkanes



Computer simulation

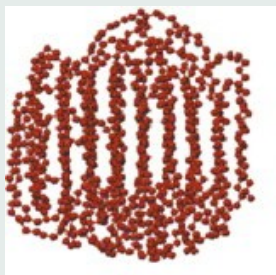
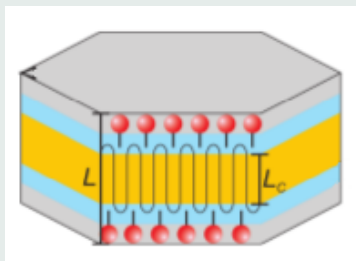


Attraction

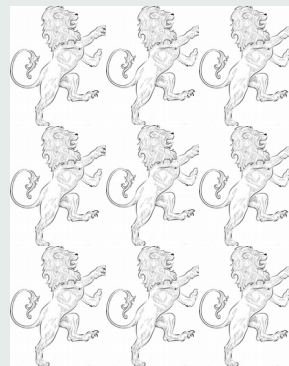
Local stiffness



Folding of alkanes



Computer simulation



Attraction



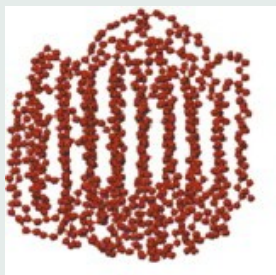
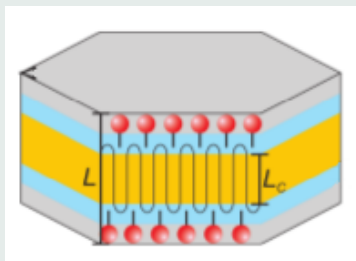
Local stiffness

How to cook it?

Just make attraction
(much) weaker

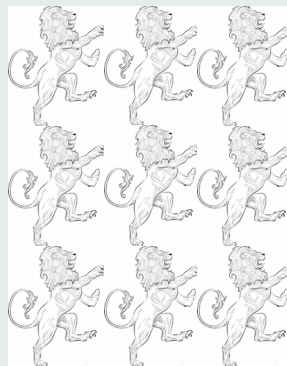


Folding of alkanes

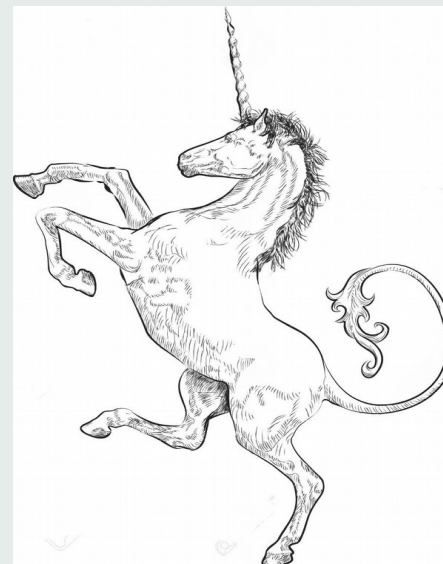


Computer simulation

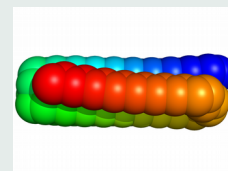
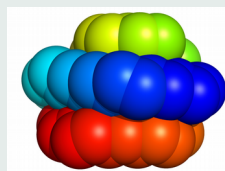
How to cook it?
Just make attraction
(much) weaker



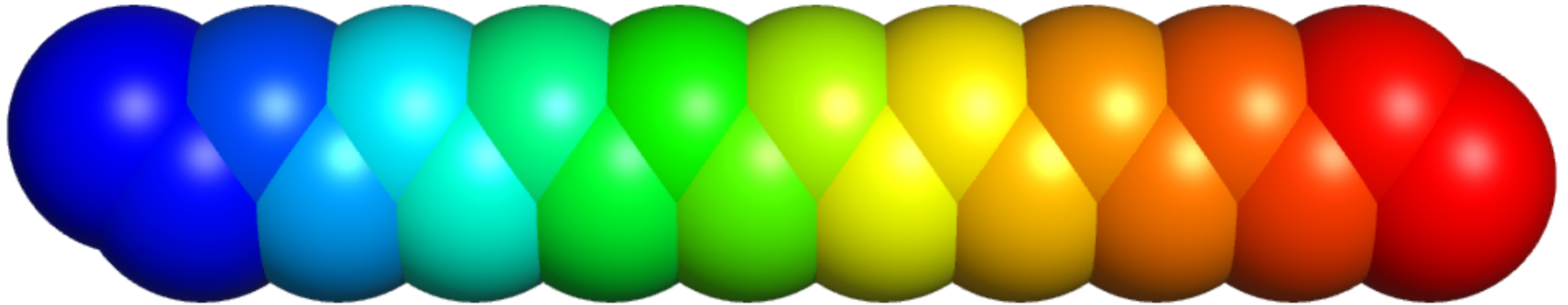
Attraction



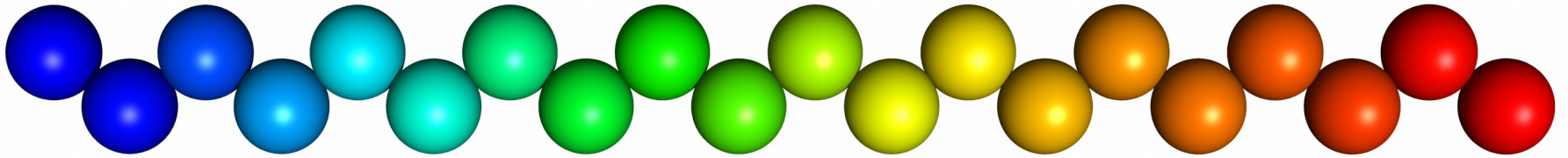
Local stiffness



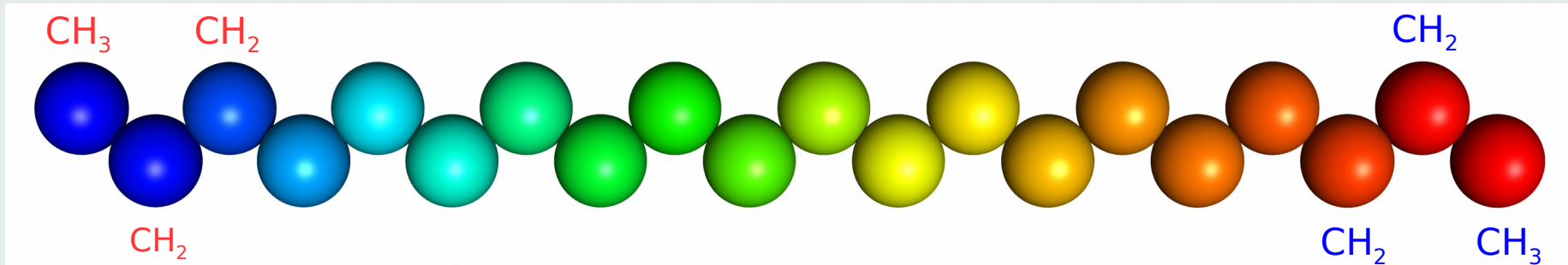
United atom model of polyethylene



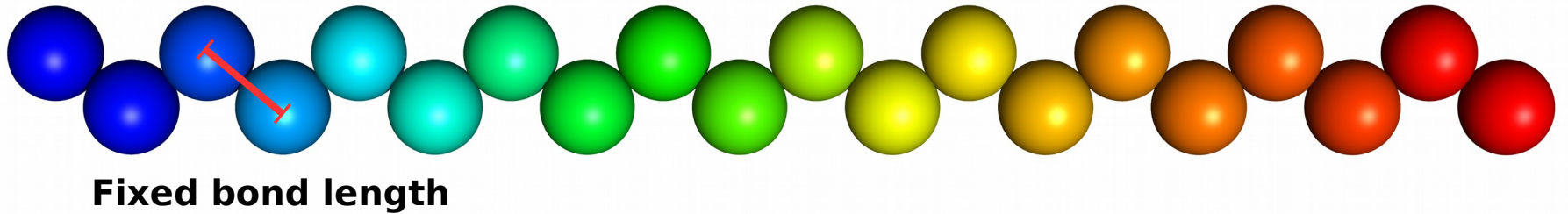
United atom model of polyethylene



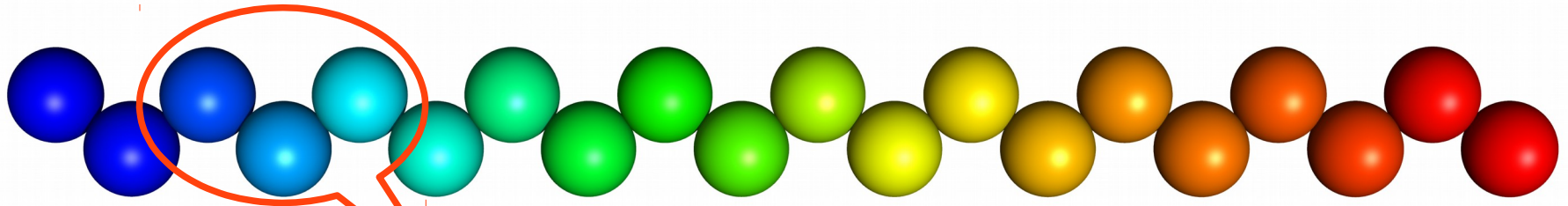
United atom model of polyethylene



United atom model of polyethylene



United atom model of polyethylene



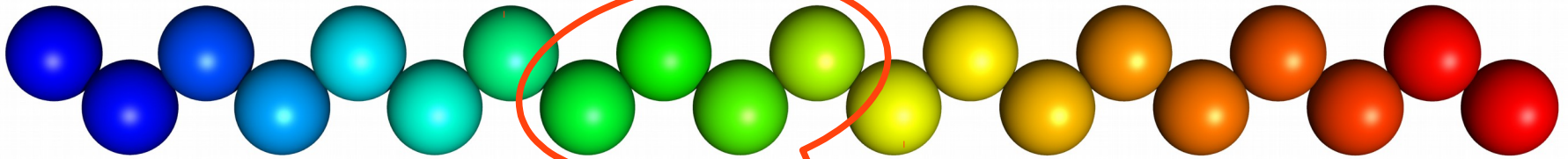
$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i)$$

$$V_{bond}(\theta) = k_{\theta}(\cos \theta - \cos \theta_0)^2$$

$$k_{\theta} = 60 \text{ kcal/mol}$$



United atom model of polyethylene



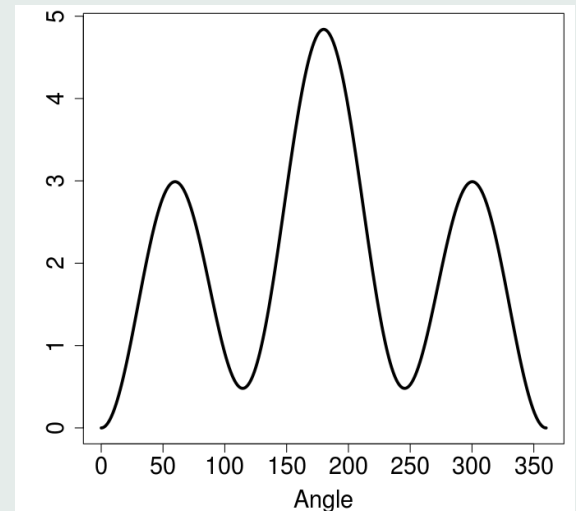
$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i)$$

$$V_{torsion}(\phi) = k_{\phi}^1 (1 - \cos \phi) + k_{\phi}^2 (1 - \cos 2\phi) + k_{\phi}^3 (1 - \cos 3\phi)$$

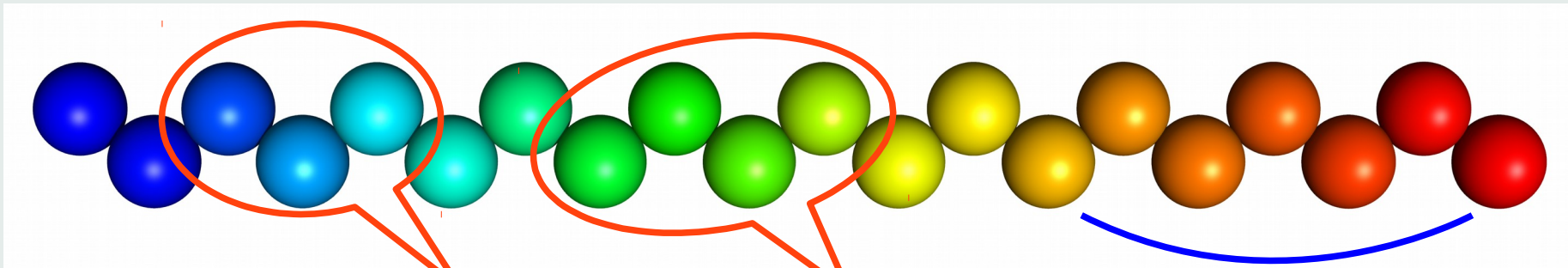
$$k_{\phi}^1 = 0.8 \text{ kcal/mol}$$

$$k_{\phi}^2 = -0.4335 \text{ kcal/mol}$$

$$k_{\phi}^3 = 1.62 \text{ kcal/mol}$$



United atom model of polyethylene



$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i) + \sum_{i,j \geq i+4} V_{LJ}(|\vec{r}_{ij}|)$$

$$V_{bond}(\theta) = k_{\theta} (\cos \theta - \cos \theta_0)^2$$

$$k_{\theta} = 60 \text{ kcal/mol}$$

$$V_{torsion}(\phi) = k_{\phi}^1 (1 - \cos \phi) + k_{\phi}^2 (1 - \cos 2\phi) + k_{\phi}^3 (1 - \cos 3\phi)$$

$$k_{\phi}^1 = 0.8 \text{ kcal/mol}$$

$$k_{\phi}^2 = -0.4335 \text{ kcal/mol}$$

$$k_{\phi}^3 = 1.62 \text{ kcal/mol}$$

$$V_{LJ}(|\vec{r}_{ab}|) = \epsilon_{ab} \left[\left(\frac{\sigma}{|\vec{r}_{ab}|} \right)^{12} - 2 \left(\frac{\sigma}{|\vec{r}_{ab}|} \right)^6 \right]$$

$$\epsilon_{CH_2-CH_2} = 0.09344 \text{ kcal/mol}$$

$$\epsilon_{CH_3-CH_3} = 0.22644 \text{ kcal/mol}$$

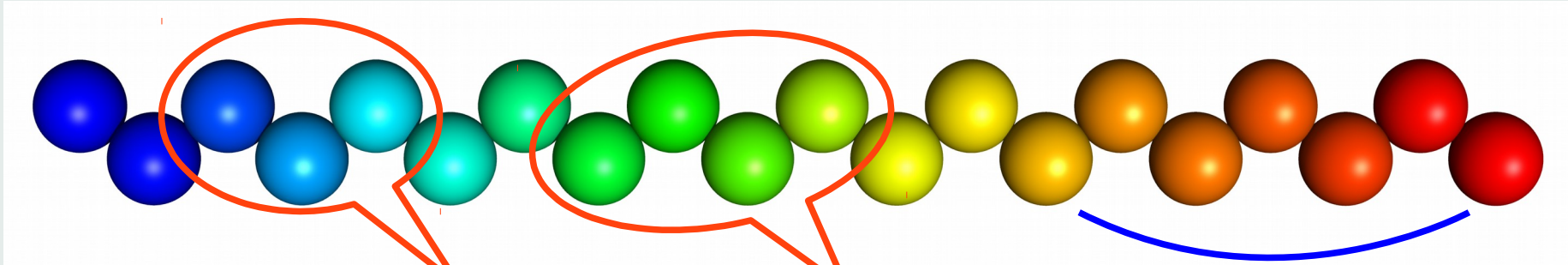
$$\epsilon_{CH_3-CH_2} = \sqrt{\epsilon_{CH_3-CH_3} \epsilon_{CH_2-CH_2}}$$

$$l_{CC} = 1.53 \text{ \AA}$$

$$\sigma = 4.5 \text{ \AA}$$



United atom model of polyethylene



$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i) + \sum_{i,j \geq i+4} V_{LJ}(|\vec{r}_{ij}|)$$

$$V_{bond}(\theta) = k_{\theta} (\cos \theta - \cos \theta_0)^2$$

$$\underline{k_{\theta} = 60 \text{ kcal/mol}}$$

$$k_{\phi}^1 = 0.8 \text{ kcal/mol}$$

$$V_{torsion}(\phi) = k_{\phi}^1 (1 - \cos \phi) + k_{\phi}^2 (1 - \cos 2\phi) + k_{\phi}^3 (1 - \cos 3\phi)$$

$$k_{\phi}^2 = -0.4335 \text{ kcal/mol}$$

$$k_{\phi}^3 = 1.62 \text{ kcal/mol}$$

$$V_{LJ}(|\vec{r}_{ab}|) = \epsilon_{ab} \left[\left(\frac{\sigma}{|\vec{r}_{ab}|} \right)^{12} - 2 \left(\frac{\sigma}{|\vec{r}_{ab}|} \right)^6 \right]$$

$$\underline{\epsilon_{CH_2-CH_2} = 0.09344 \text{ kcal/mol}}$$

$$\epsilon_{CH_3-CH_3} = 0.22644 \text{ kcal/mol}$$

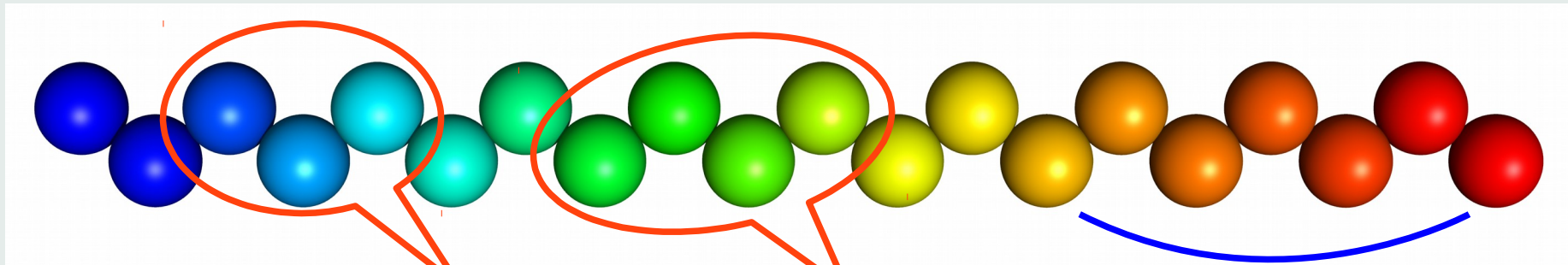
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$$l_{CC} = 1.53 \text{ \AA}$$

$$\sigma = 4.5 \text{ \AA}$$



United atom model of polyethylene



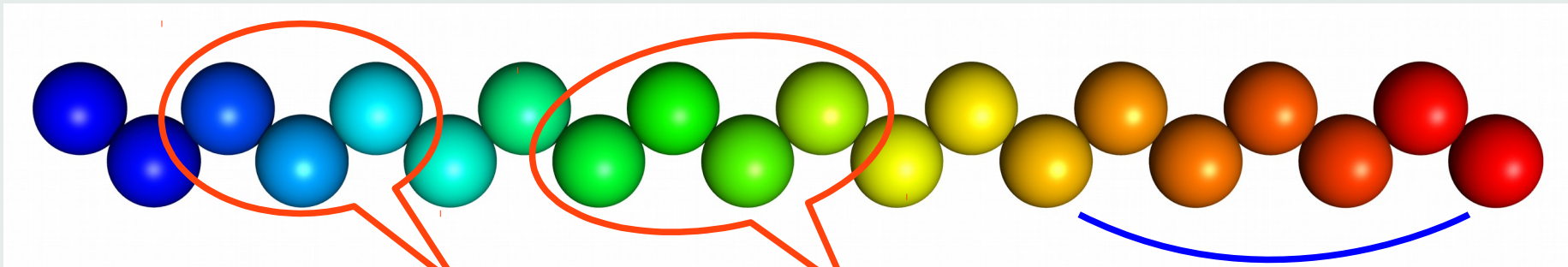
$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i) + \sum_{i, j \geq i+4} V_{LJ}(|\vec{r}_{ij}|)$$

$$N = 10..80$$

$$N_c = 1..4 \quad (7)$$



United atom model of polyethylene



$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i) + \sum_{i,j \geq i+4} V_{LJ}(|\vec{r}_{ij}|)$$

$$N = 10..80$$

$$N_c = 1..4 \quad (7)$$

Q:

How are looking intermediate ground state configurations between a stretched chain and lamella?



Simulation

Stochastic Approximation Monte Carlo Simulation



Simulation

Stochastic Approximation Monte Carlo Simulation

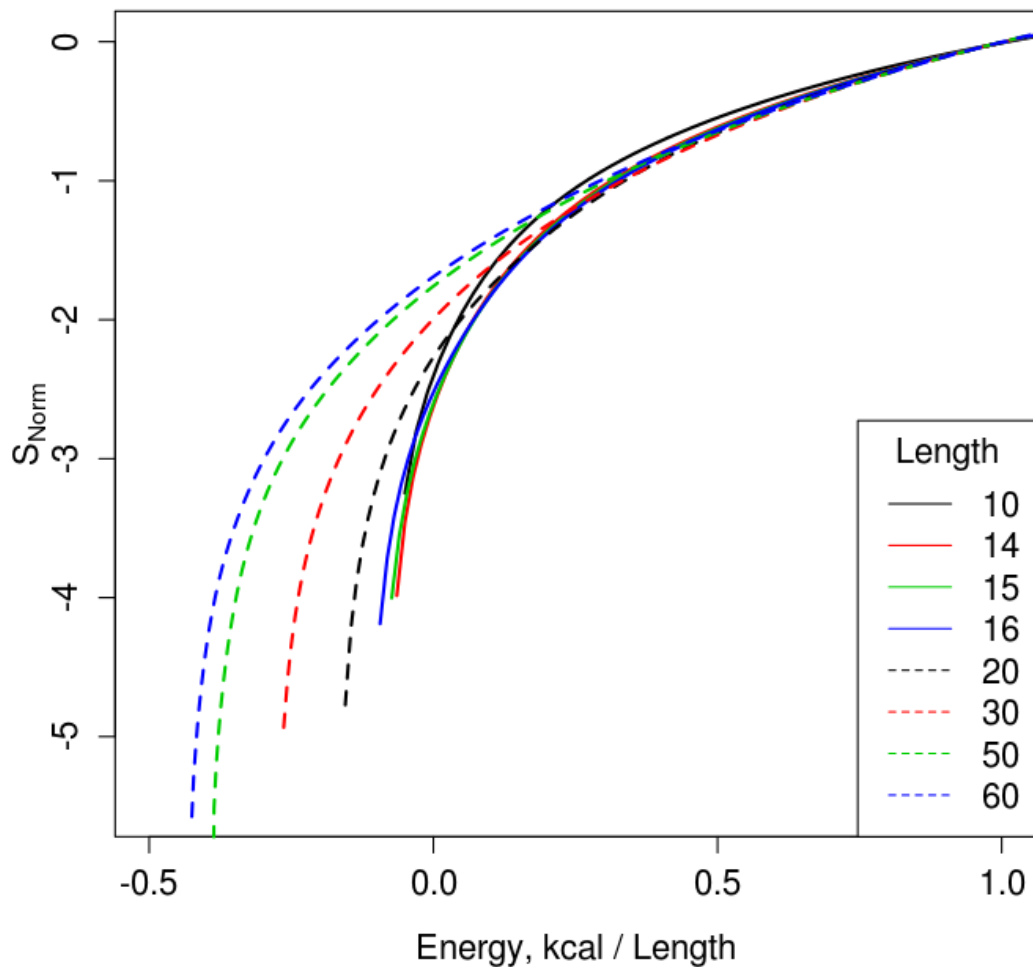
Estimation of configurational density of states
(or microcanonical configurational entropy)

+ Properties of the system in thermodynamical equilibrium

- No information about dynamics



Density of states



$$S_{\text{Norm}}(E) = \frac{\ln g(E) - \max(\ln g(E))}{N}$$

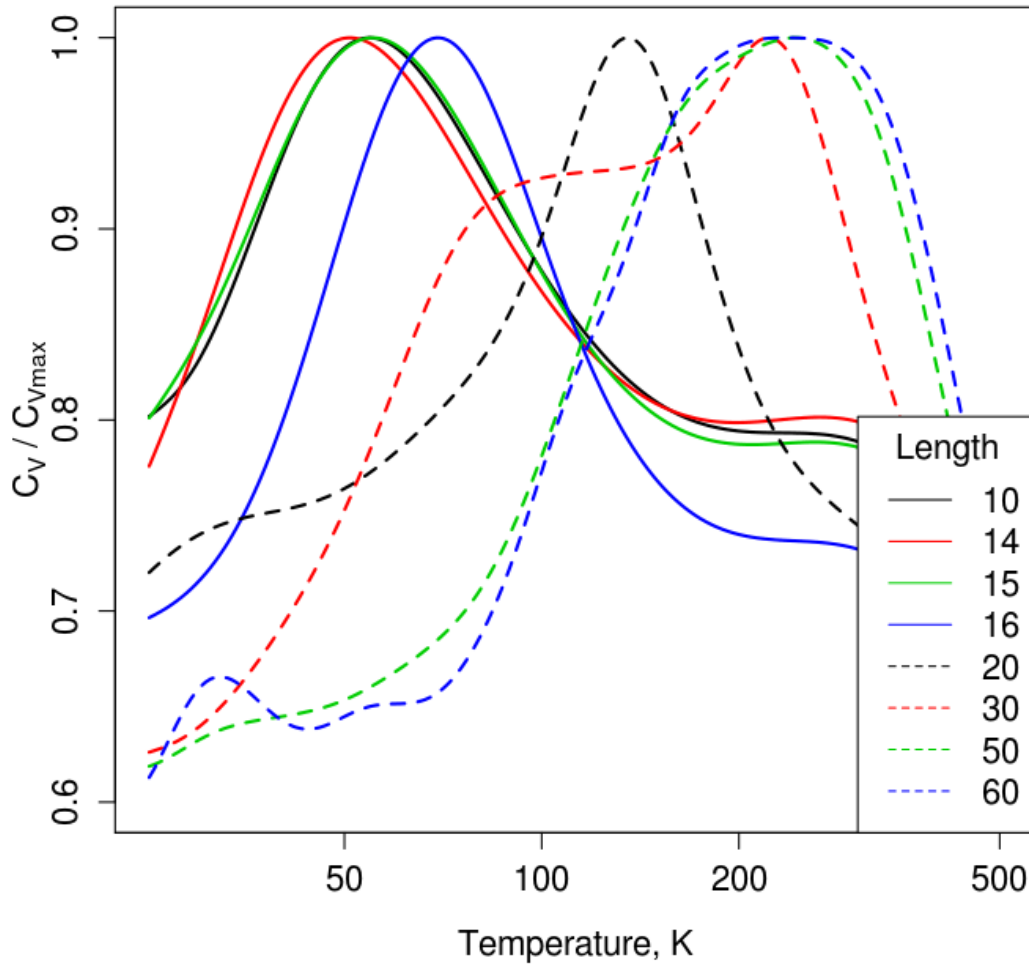


Heat capacity

$$C_V(T) = \frac{\langle E^2 \rangle(T) - \langle E \rangle^2(T)}{T^2}$$
$$\langle E^n \rangle(T) = \frac{\sum_E E^n g(E) \exp\left(-\frac{E}{k_B T}\right)}{\sum_E g(E) \exp\left(-\frac{E}{k_B T}\right)}$$

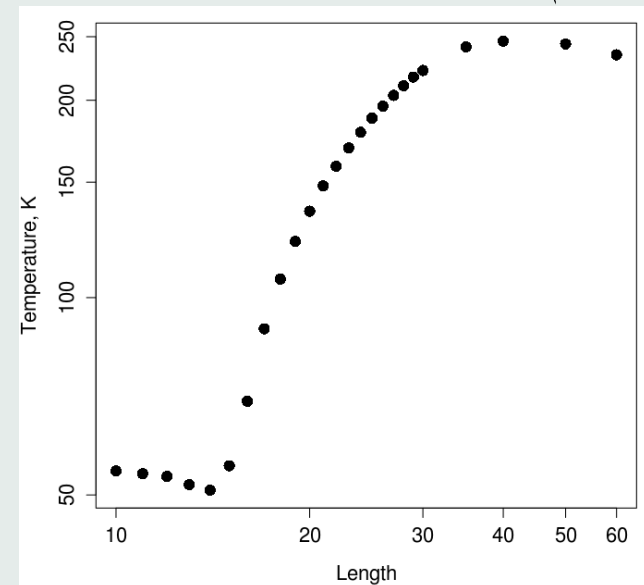


Heat capacity

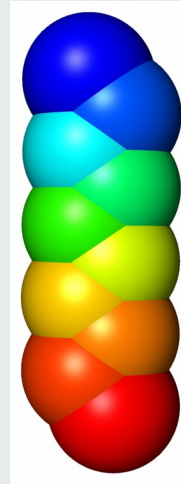
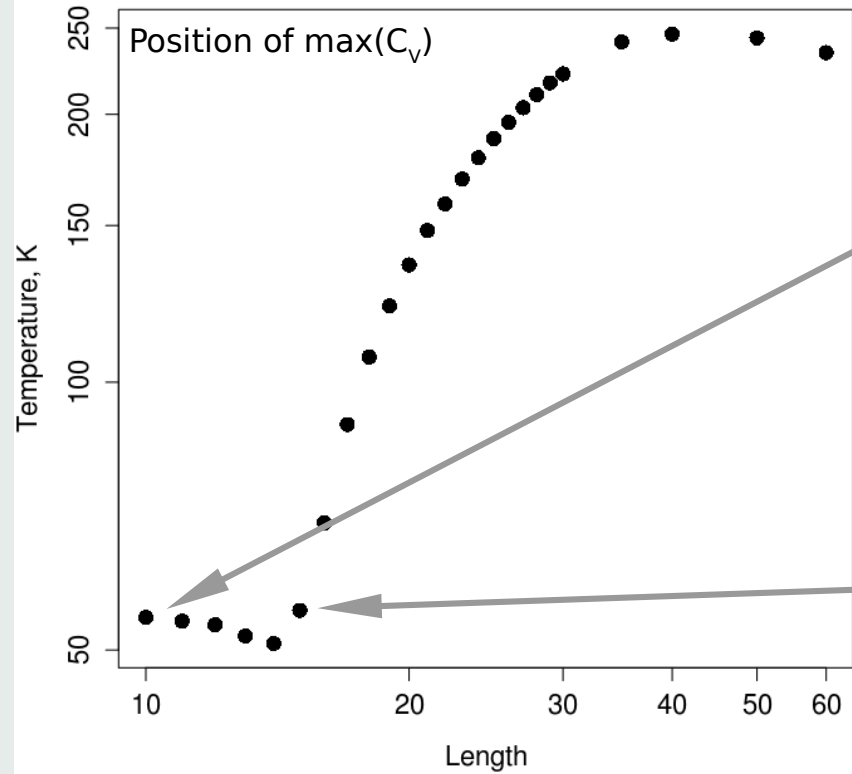


$$C_V(T) = \frac{\langle E^2 \rangle(T) - \langle E \rangle^2(T)}{T^2}$$

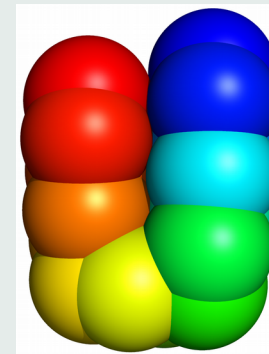
$$\langle E^n \rangle(T) = \frac{\sum_E E^n g(E) \exp\left(-\frac{E}{k_B T}\right)}{\sum_E g(E) \exp\left(-\frac{E}{k_B T}\right)}$$



Ground States



N = 10



N = 15



Ground States. Comparison

What is «critical» length?



Ground States. Comparison

VIP Alkanes

The Last Globally Stable Extended Alkane**

N.O.B. Lüttschwager et al, Angew. Chem. Int. Ed. 2013, 52, 463-466



MARTIN-LUTHER-UNIVERSITÄT
HALLE-WITTENBERG

Timur Shakirov and Wolfgang Paul
**Folding in small polyethylene systems:
Single chains and few chains**

Naturwissenschaftliche
Fakultät II

Ground States. Comparison

VIP Alkanfaltung

DOI: 10.1002/ange.201202894



Das letzte Alkan mit gestreckter Grundzustandskonformation**

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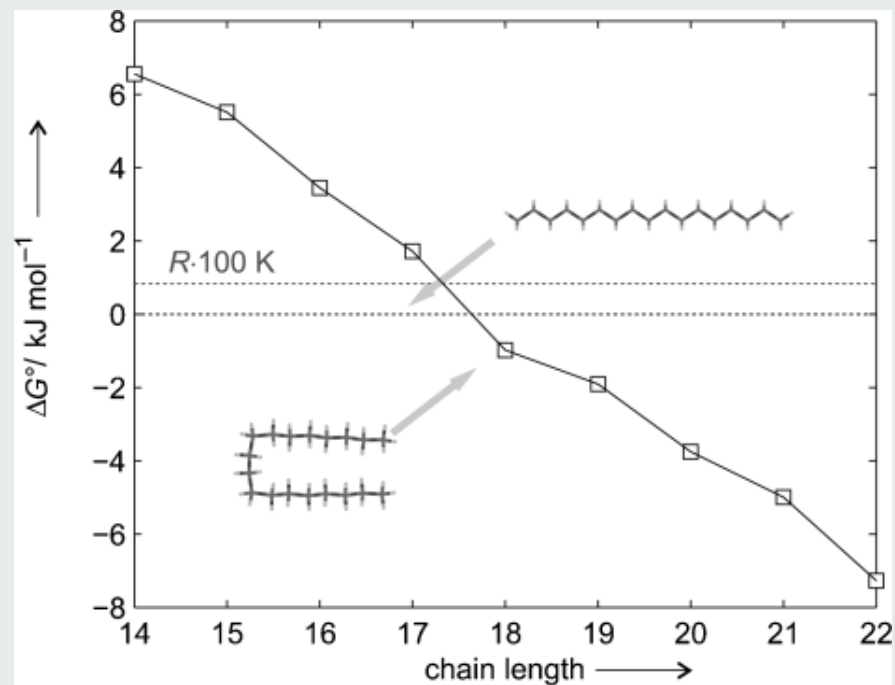
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T = 100 K



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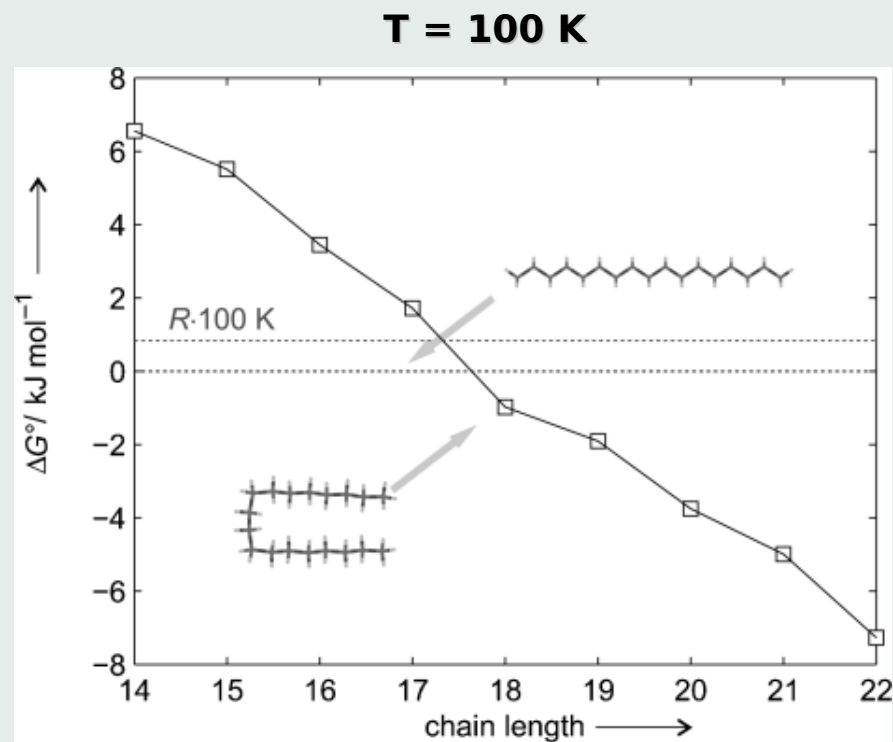
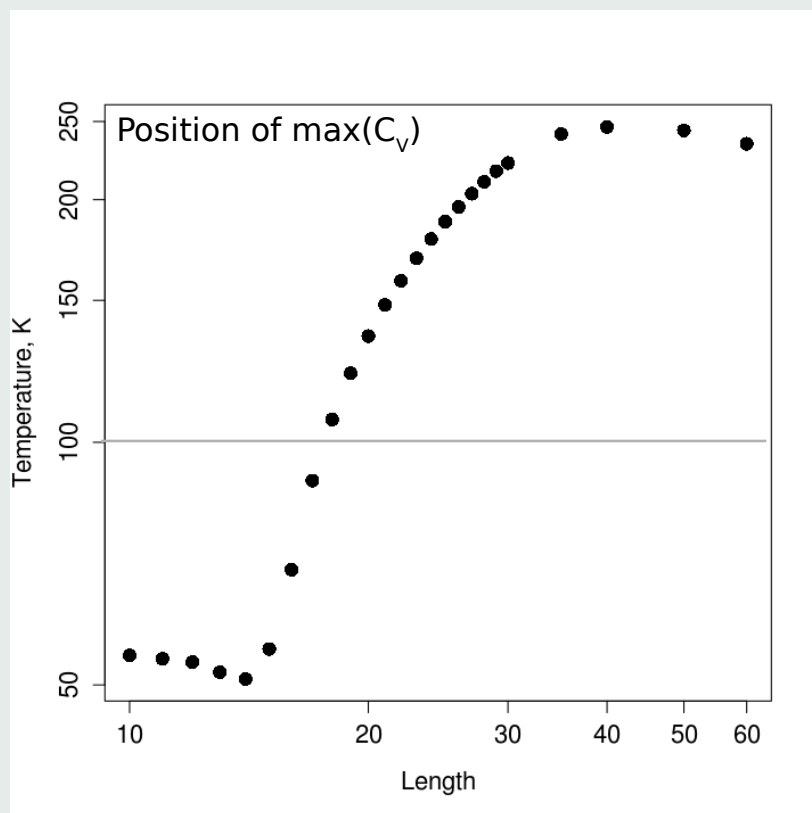
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Fakultät II

Diagram of states

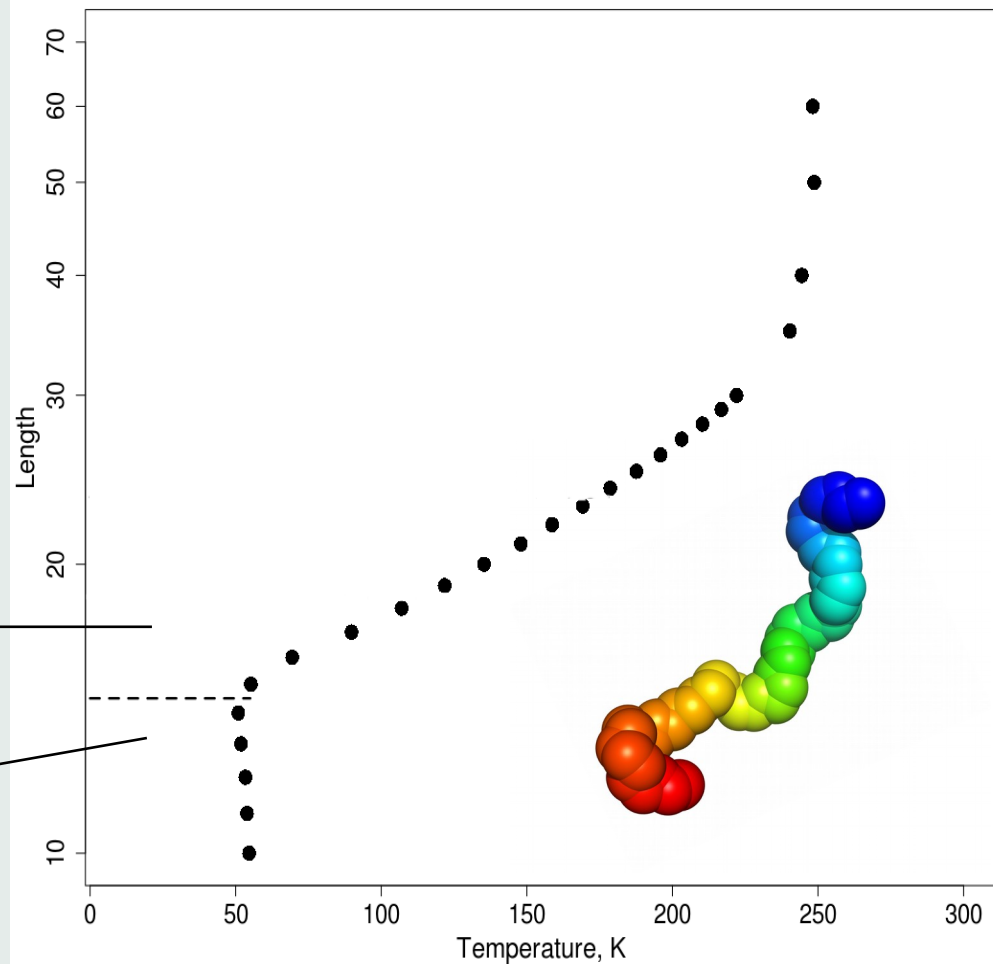


Diagram of states

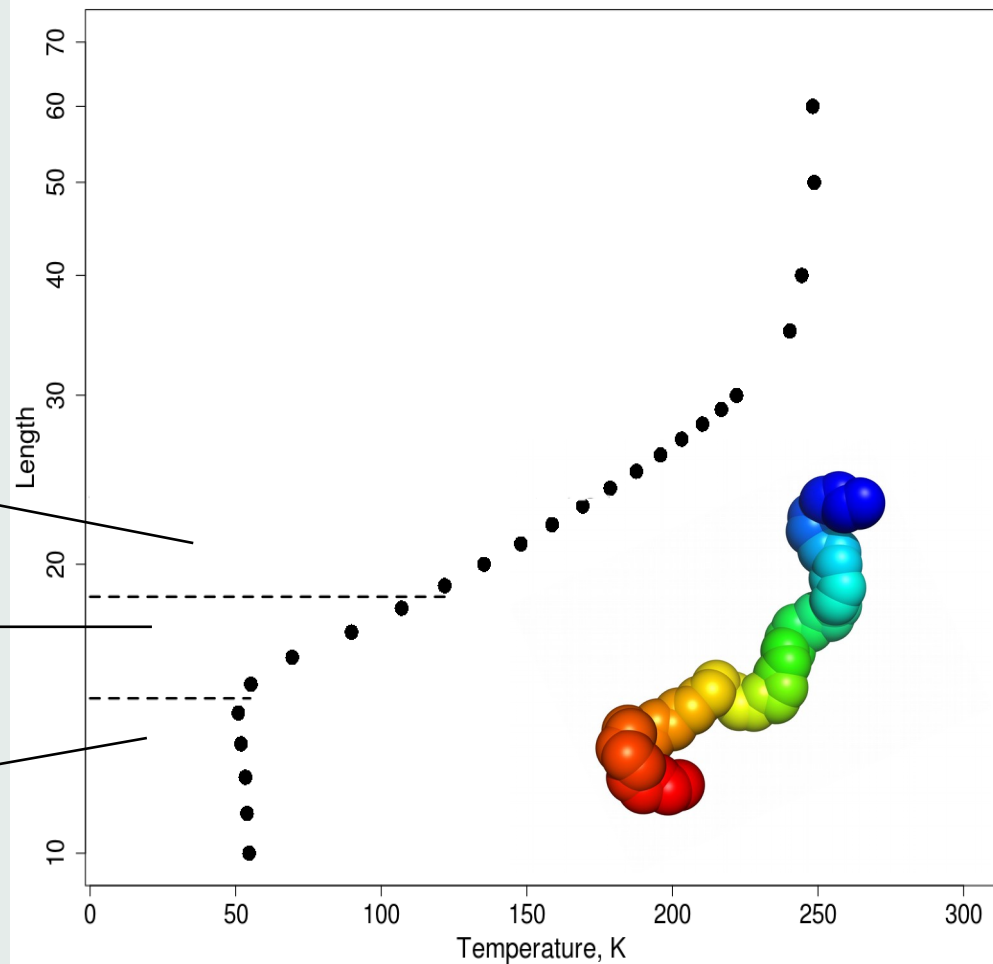
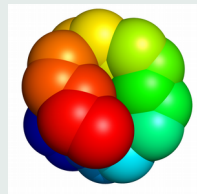


Diagram of states

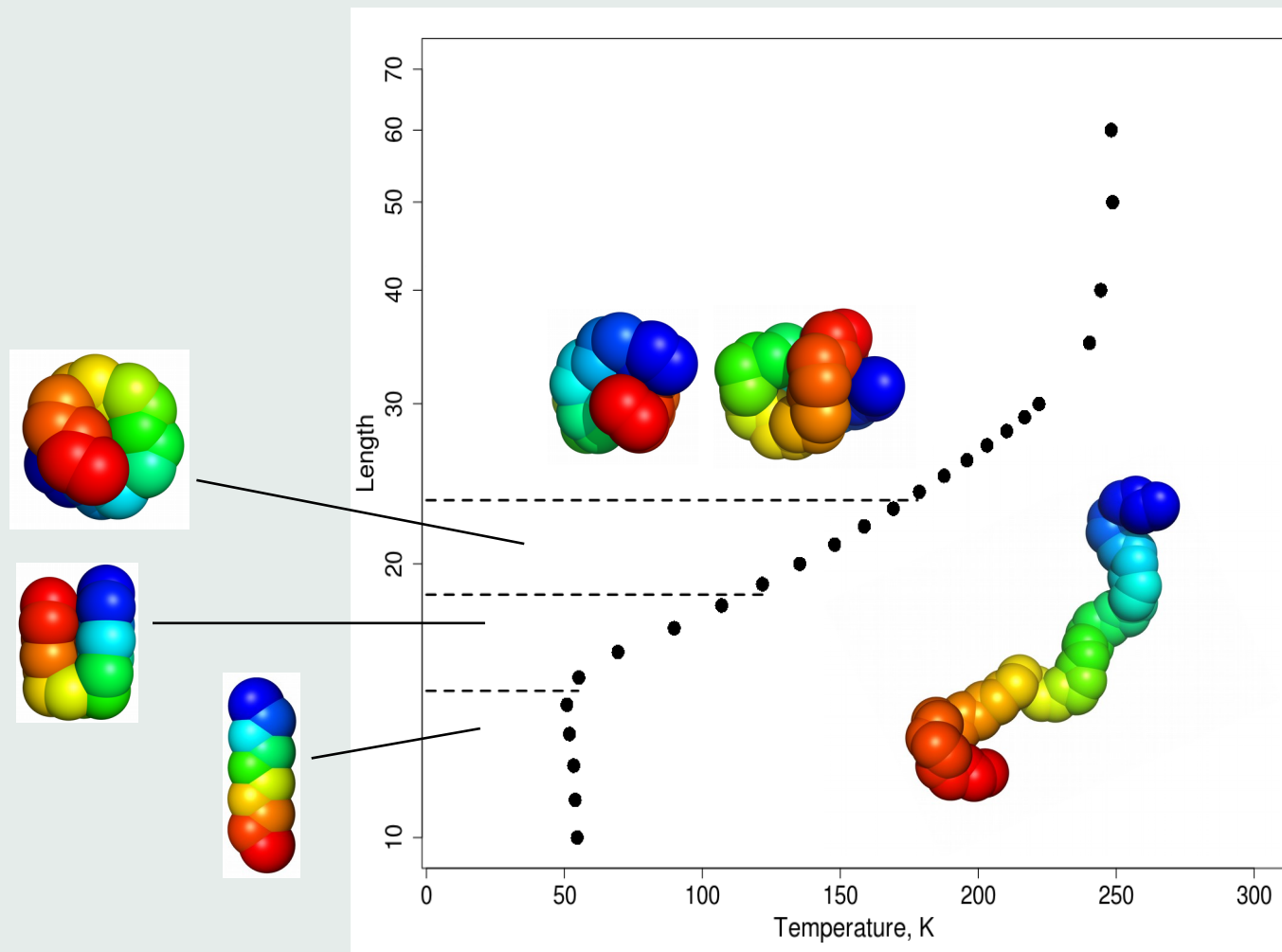
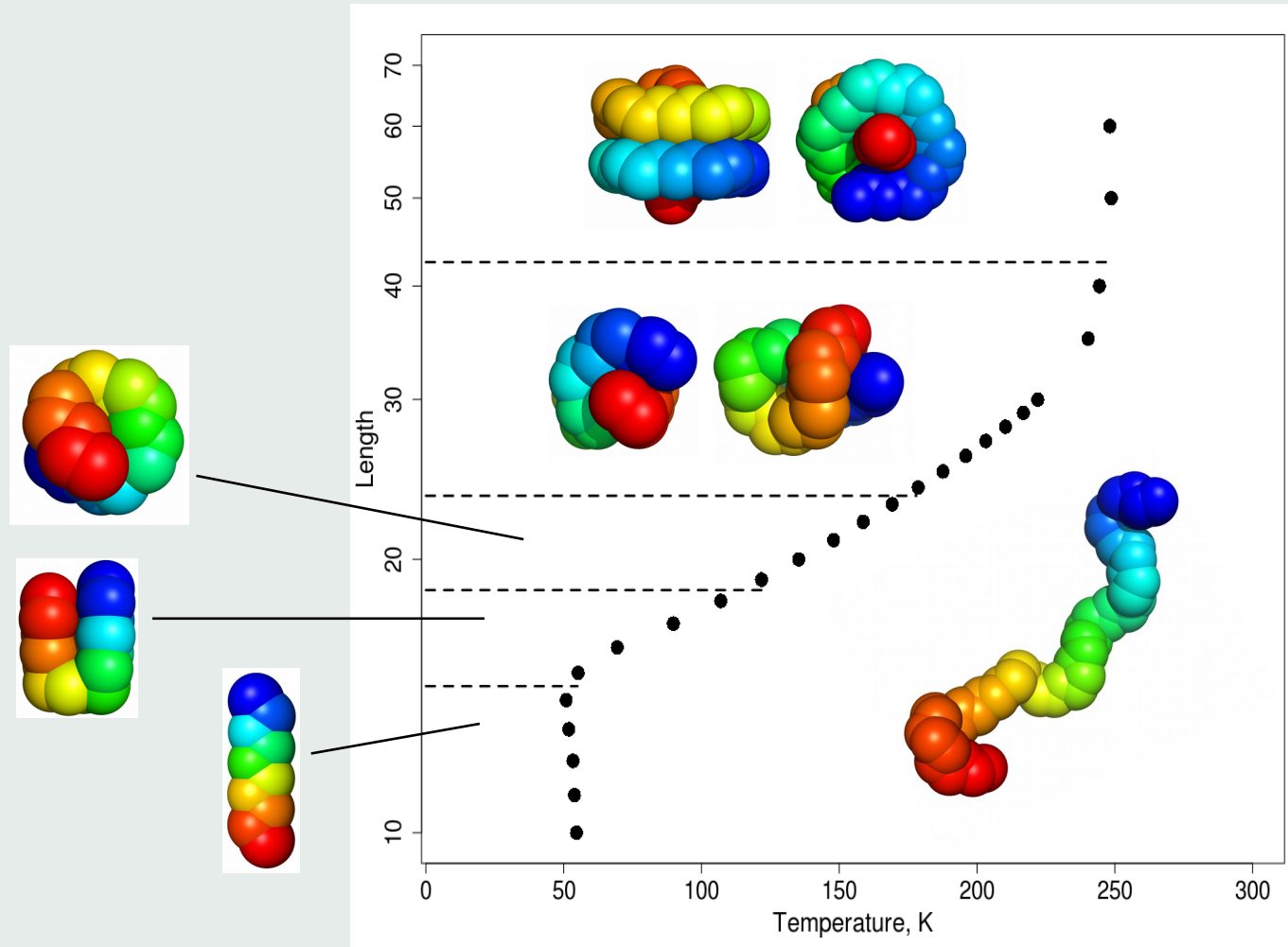
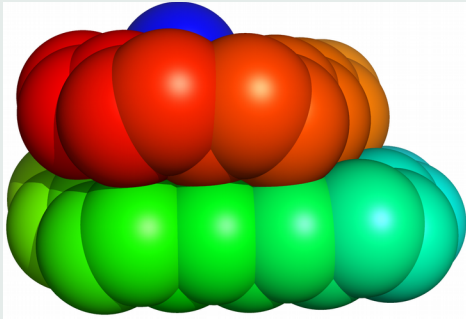


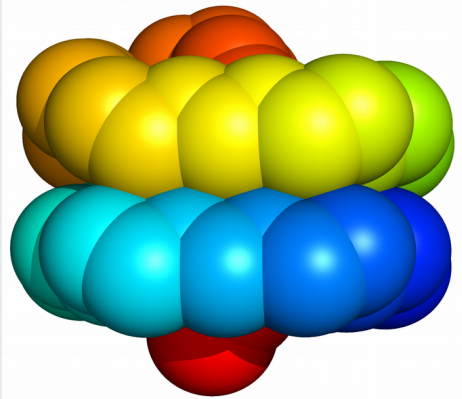
Diagram of states



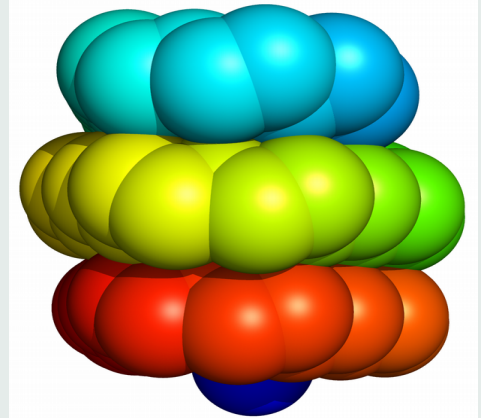
Low energy configurations of longest chains



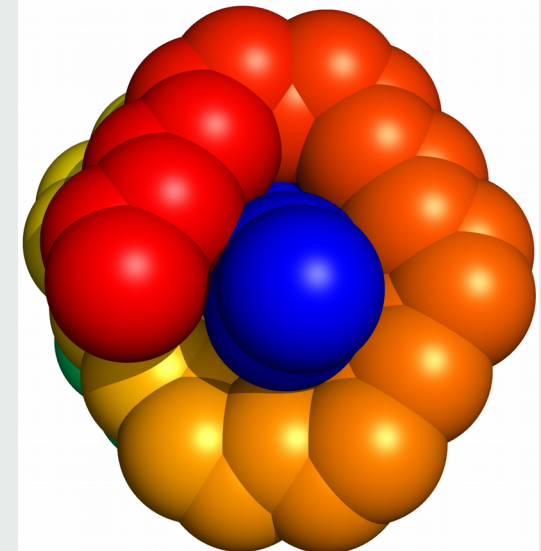
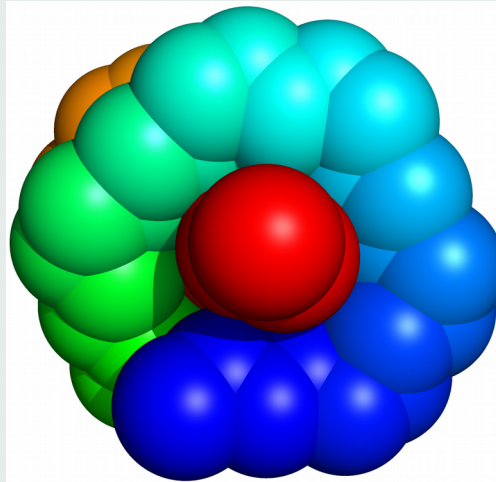
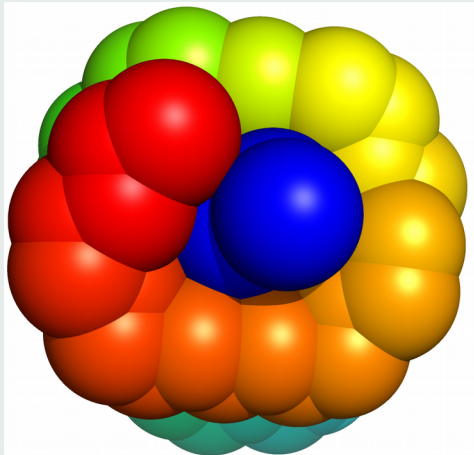
N=50



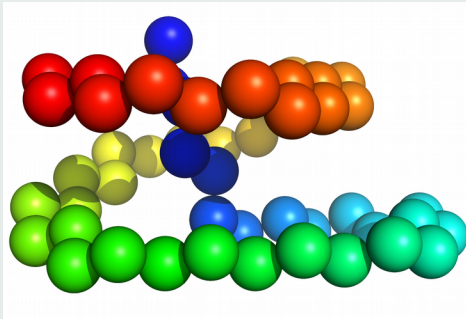
N=60



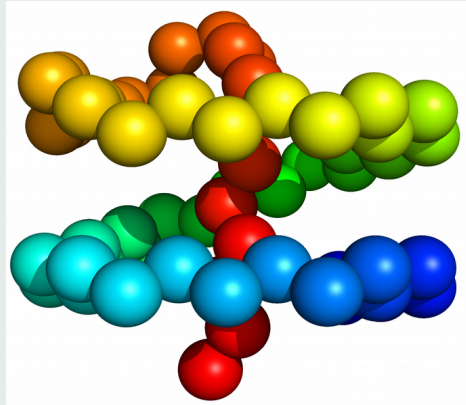
N=80



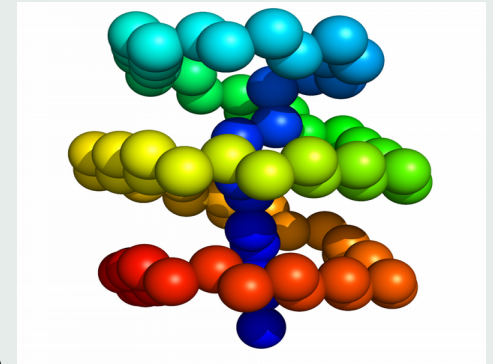
Low energy configurations of longest chains



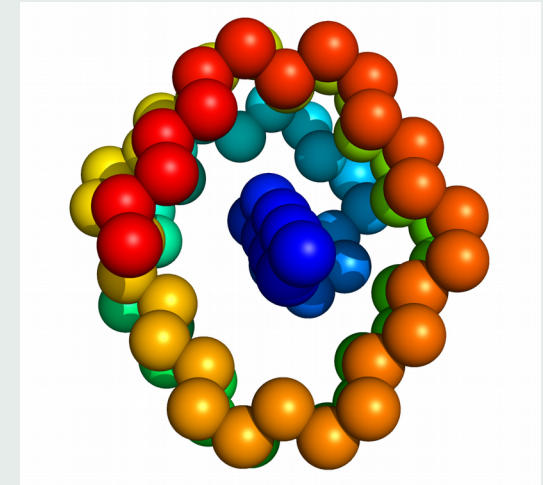
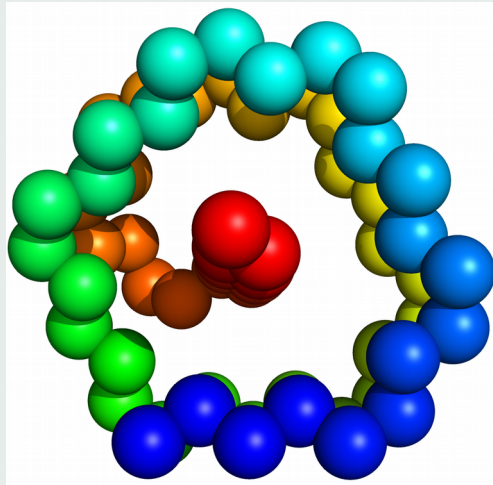
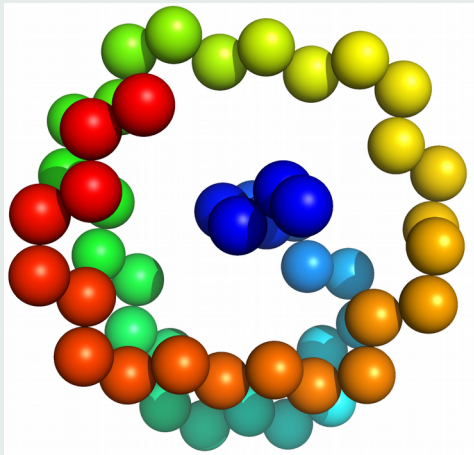
N=50



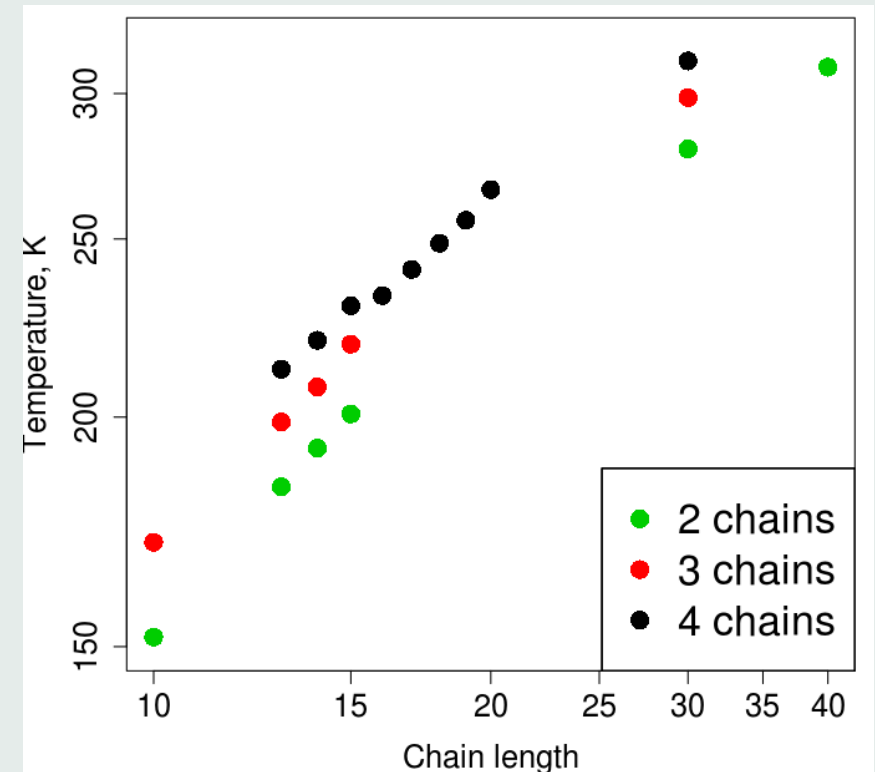
N=60



N=80



Aggregation of few chains



Aggregation of few chains

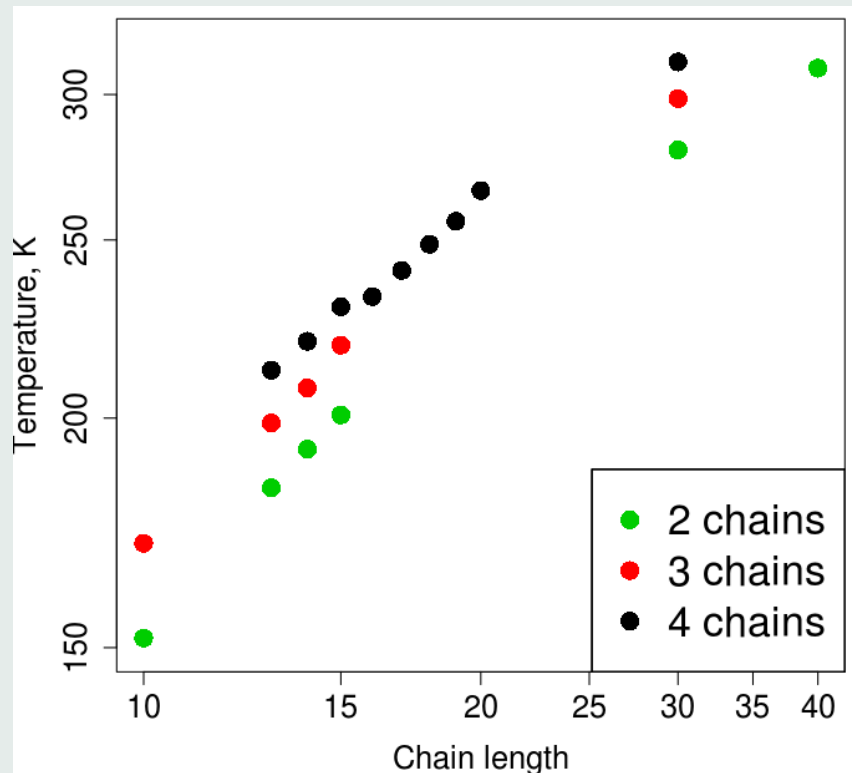
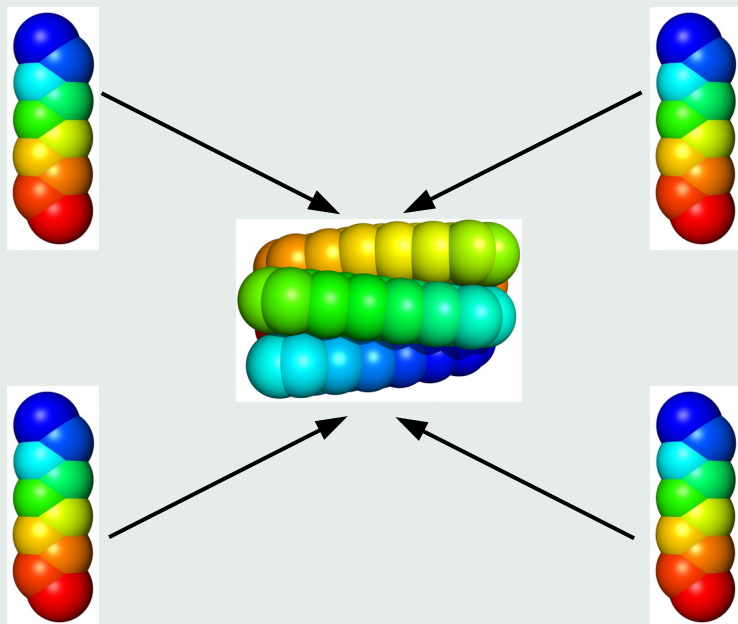


Diagram of states of chain`s aggregates

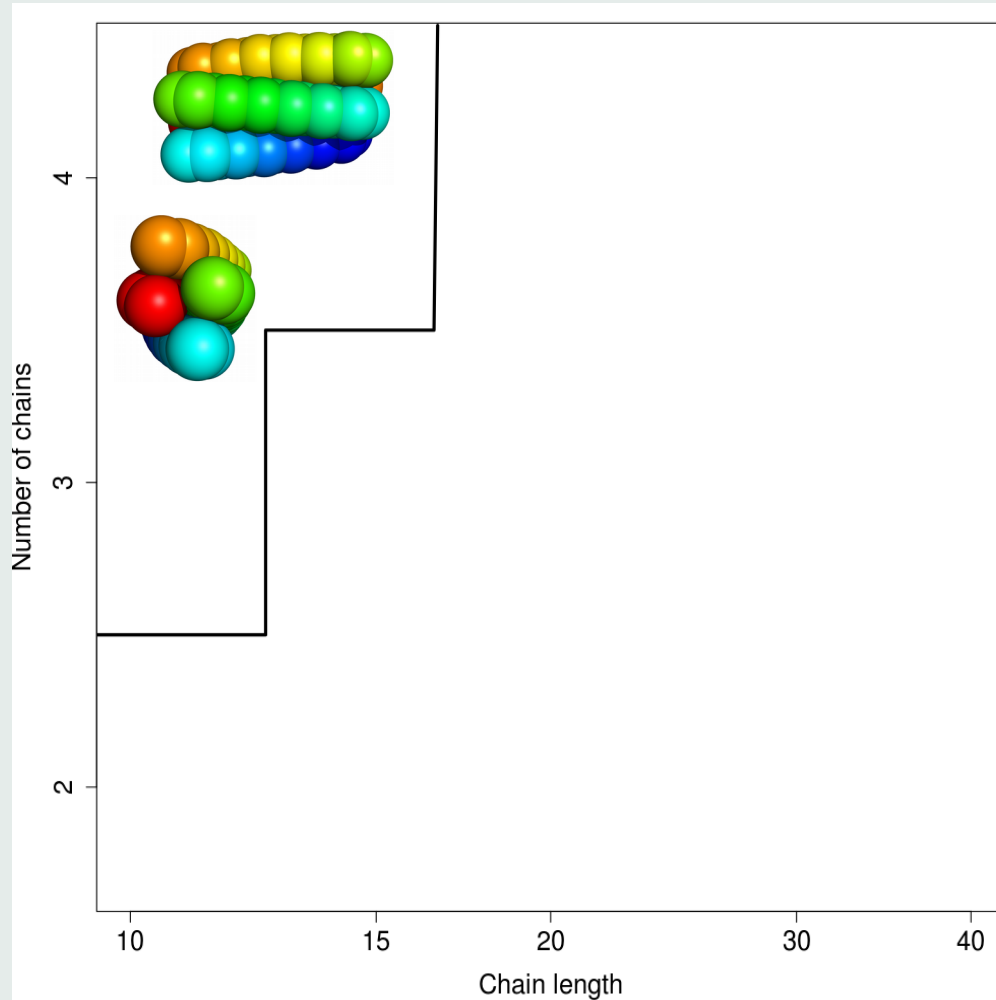


Diagram of states of chain`s aggregates

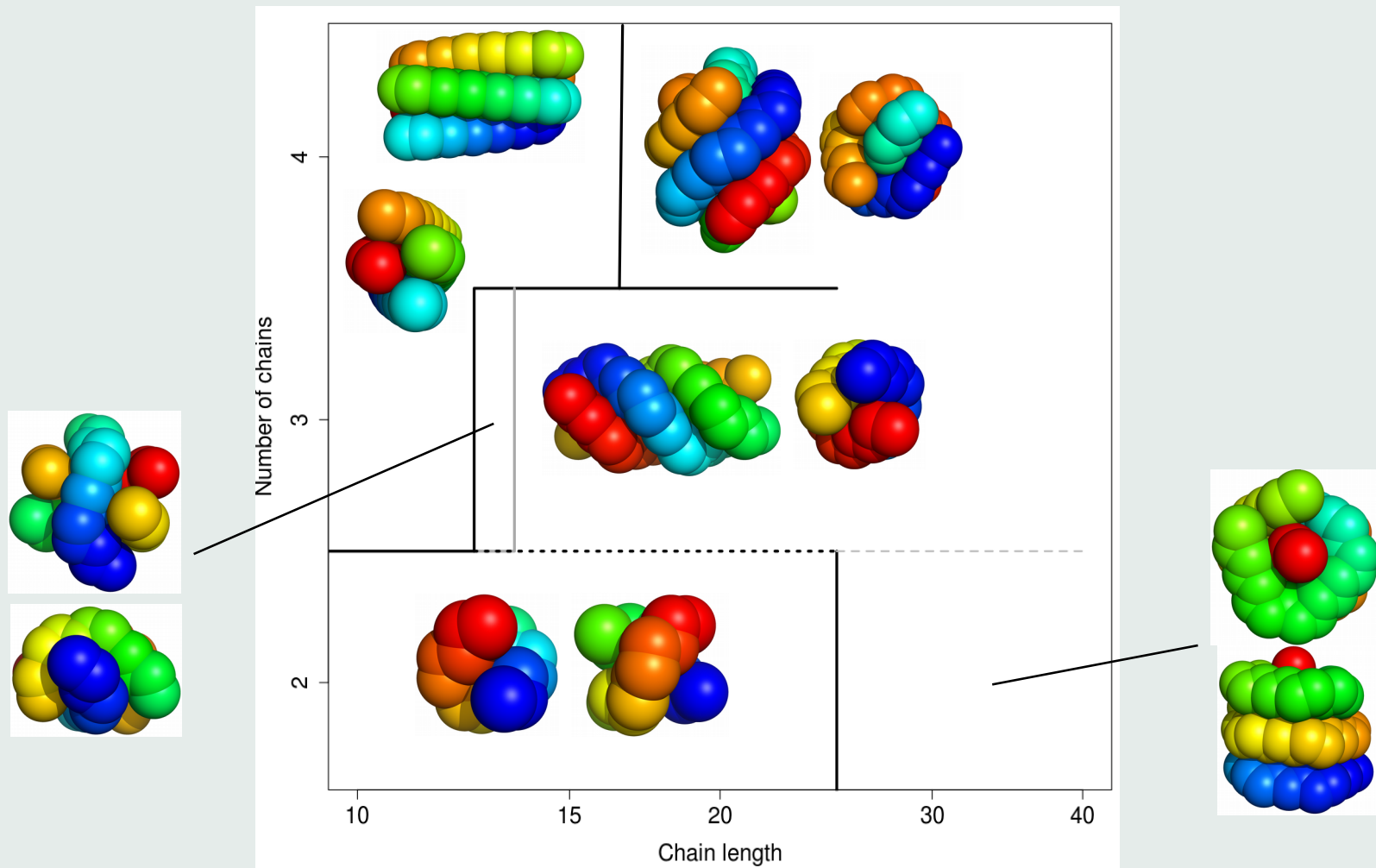
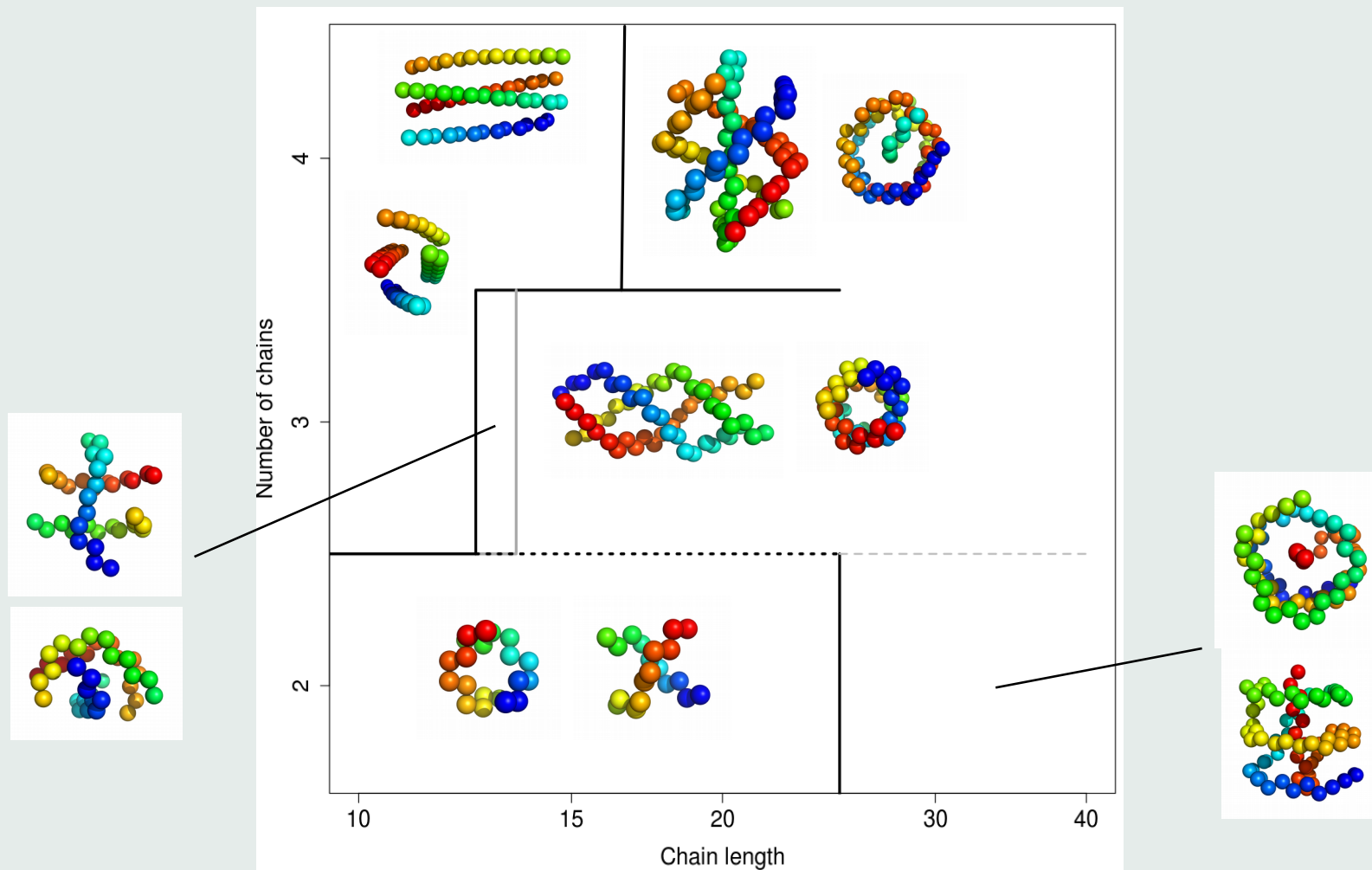
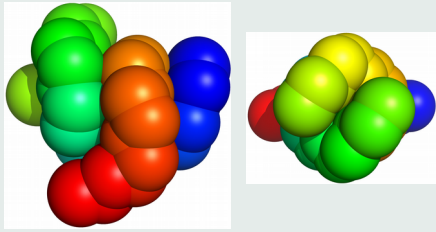


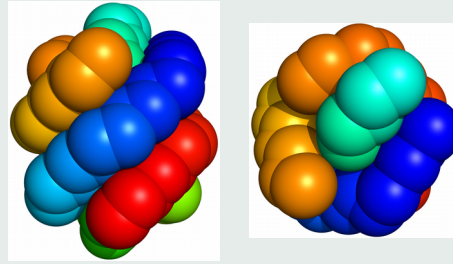
Diagram of states of chain`s aggregates



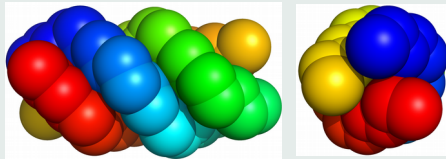
States of bigger chain`s aggregates



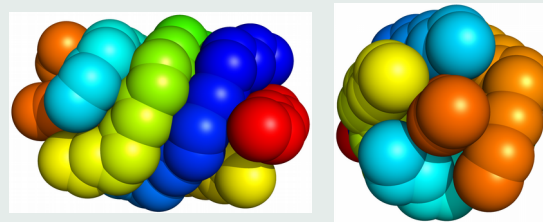
2 chains



4 chains



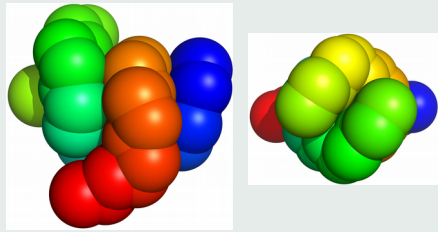
3 chains



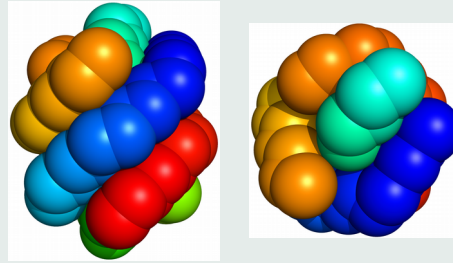
5 chains



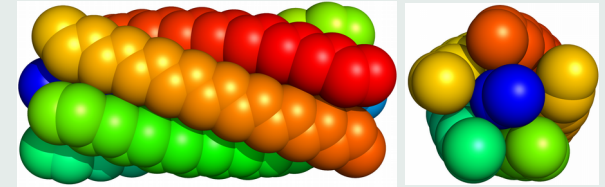
States of bigger chain`s aggregates



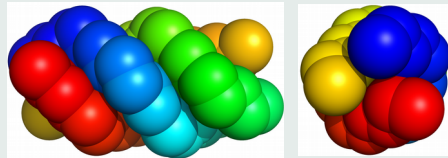
2 chains



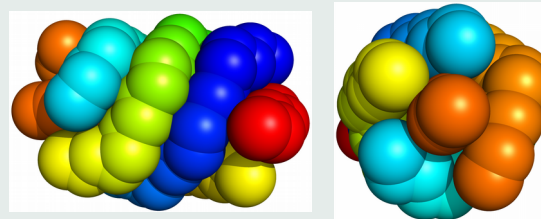
4 chains



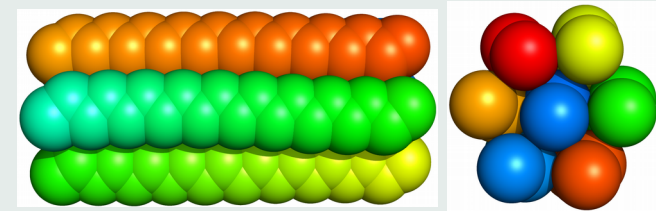
6 chains



3 chains



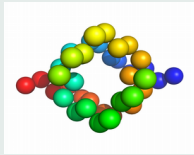
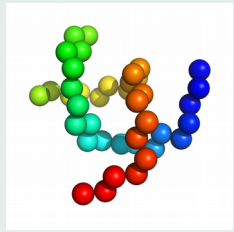
5 chains



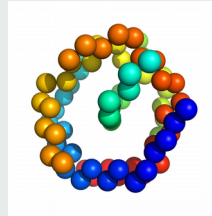
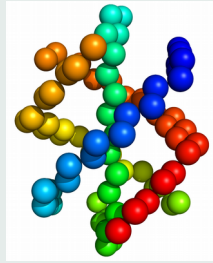
7 chains



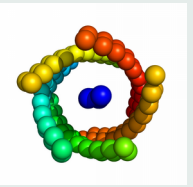
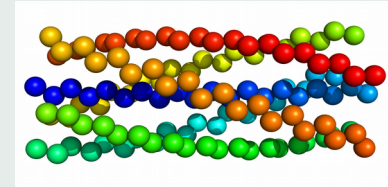
States of bigger chain`s aggregates



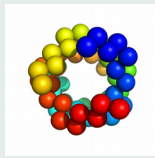
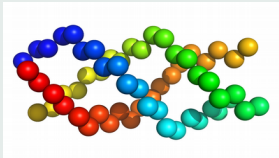
2 chains



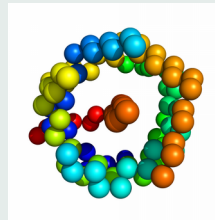
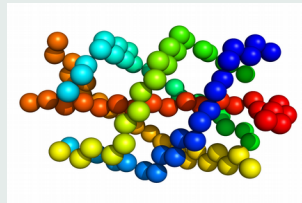
4 chains



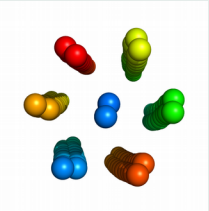
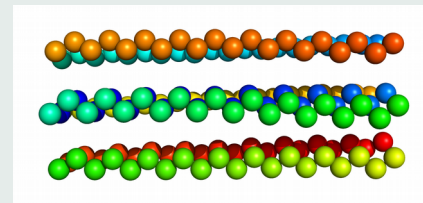
6 chains



3 chains



5 chains



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Conclusion

Analysis of polyethylene model shows that even simple syntetic homopolymers can have non-trivial ground states



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Thank you for your attention!



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