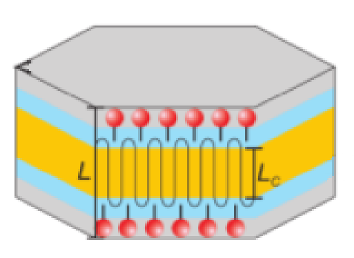
Aggregation of short polyethylene chains

Timur Shakirov

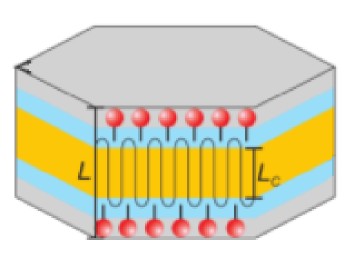
MARTIN-LUTHER-UNIVERSITÄT
HALLE-WITTENBERG

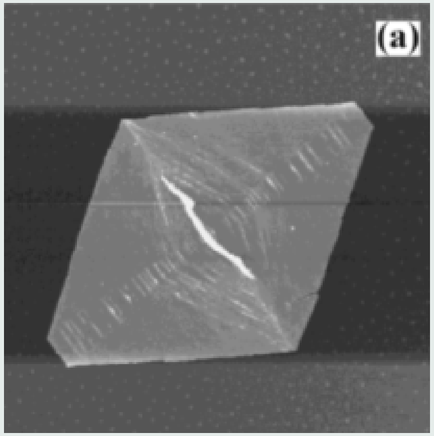
Naturwissenschaftliche
Fakultät II

Folding



Folding





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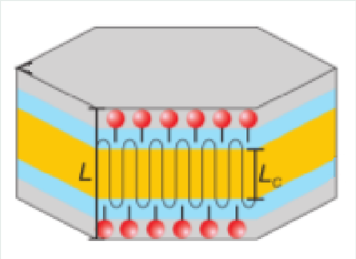
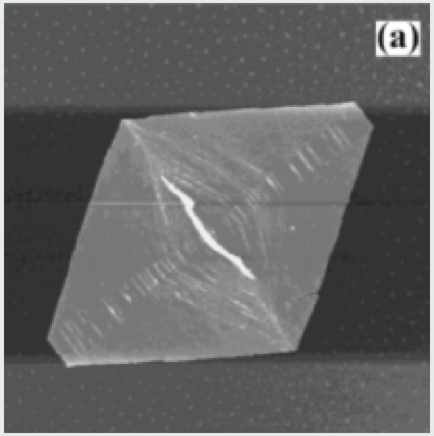
Single crystal of polyethylene
from atomic force microscopy

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

Folding of alkanes





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Single crystal of polyethylene
from atomic force microscopy

$$\rho \approx 0{,}327 \;\; \mathrm{kg/m}^{-3}$$

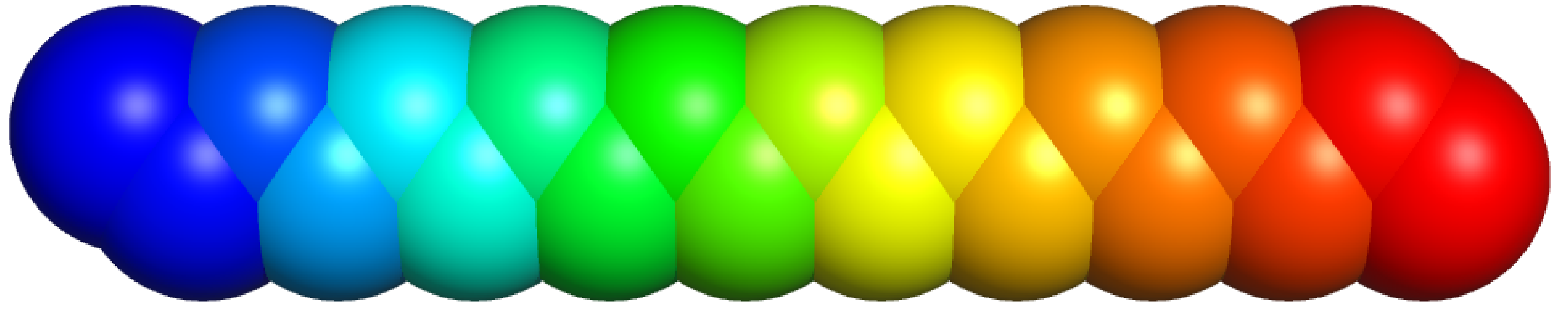
$$N_c = 2..6$$

$$N \leq 40$$

Q:
What are low temperature configurations of short-chain aggregates?

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

United atom model of polyethylene



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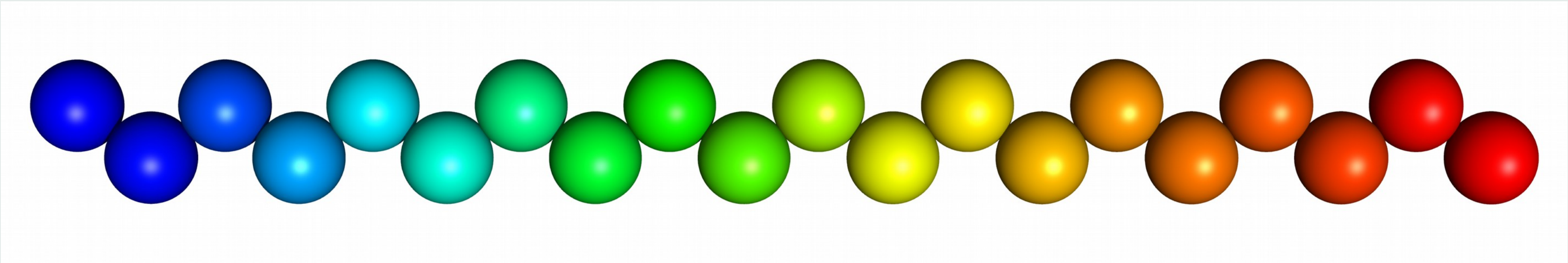

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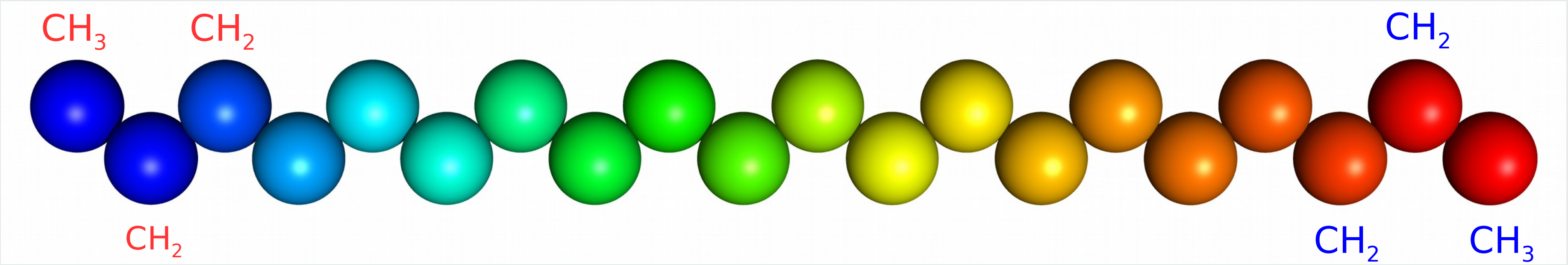

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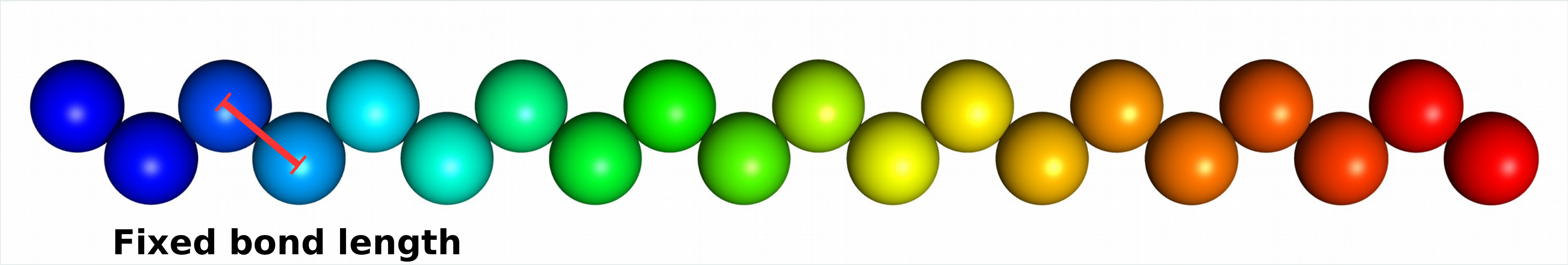

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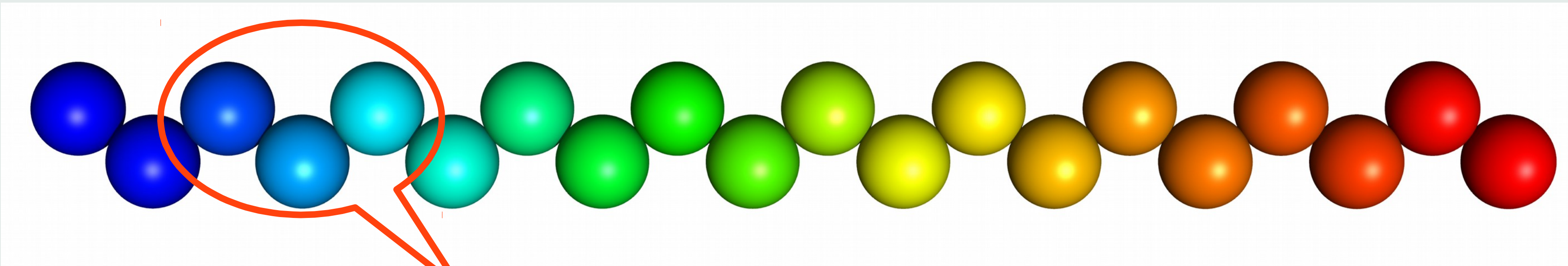
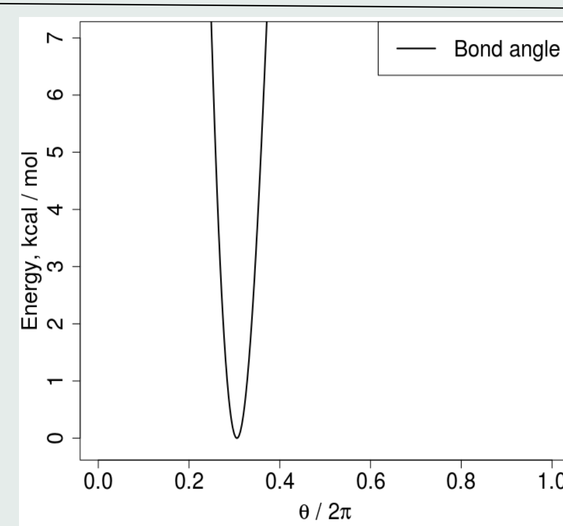


$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i)$$

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

$$k_\theta = 60\ kcal/mol$$



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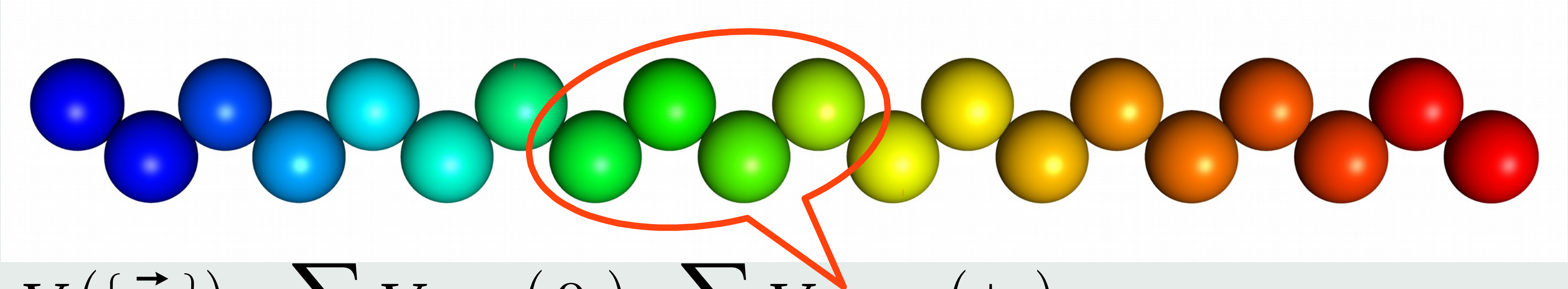


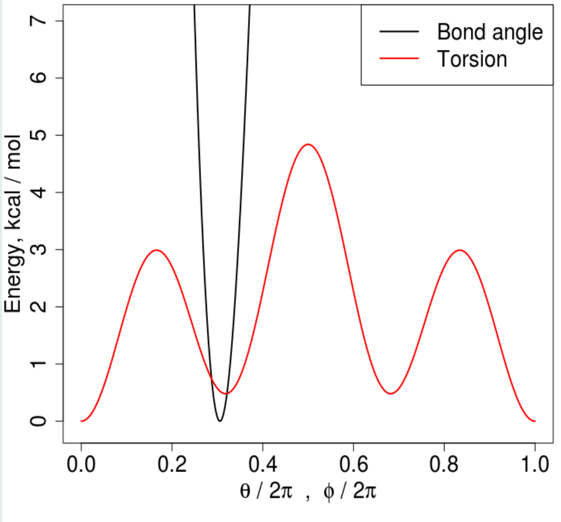
$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i)$$

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

$$k_\phi^1 = 0.8\, kcal/mol$$

$$k_\phi^2 = -0.4335\, kcal/mol$$

$$k_\phi^3 = 1.62\, kcal/mol$$



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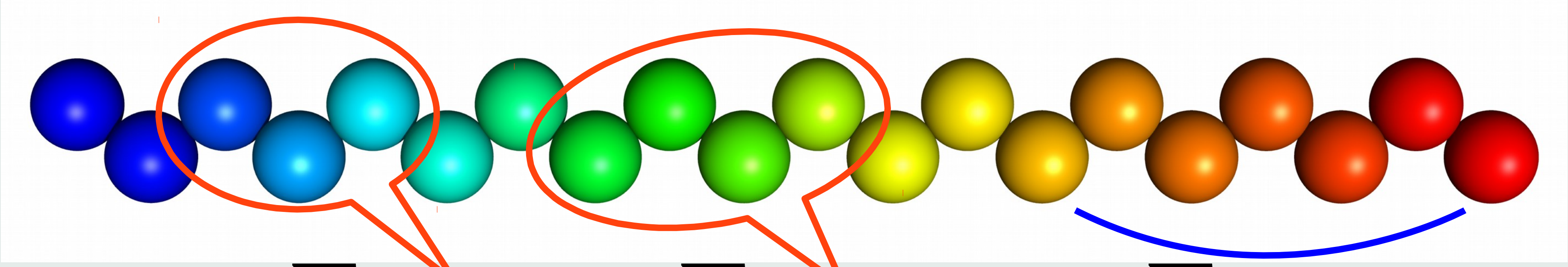


$$V(\{\vec{r}\}) = \sum_i V_{bond}(\theta_i) + \sum_i V_{torsion}(\phi_i) + \sum_{i,j \geqslant i+4} V_{LJ}(|\vec{r}_{ij}|)$$

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

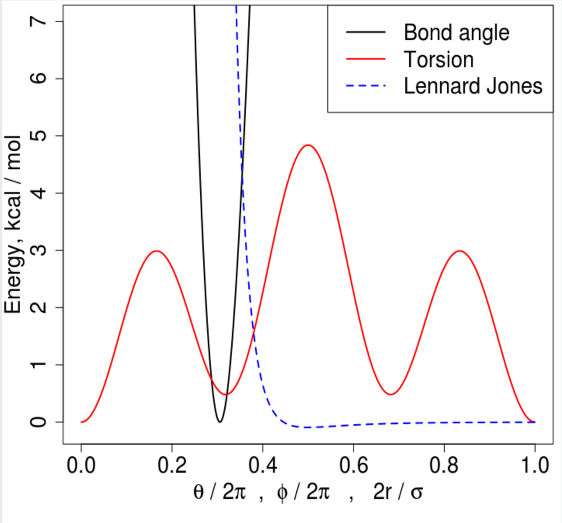
$$\varepsilon_{CH_2-CH_2} = 0.09344\, kcal/mol$$

$$\varepsilon_{CH_3-CH_3} = 0.22644\, kcal/mol$$

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

$$l_{CC} = 1.53\,\text{Å}$$

$$\sigma = 4.5\,\text{Å}$$



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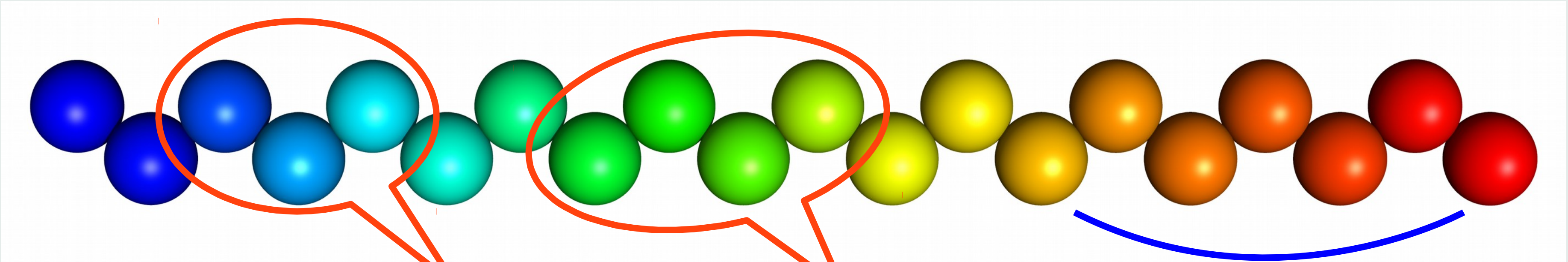

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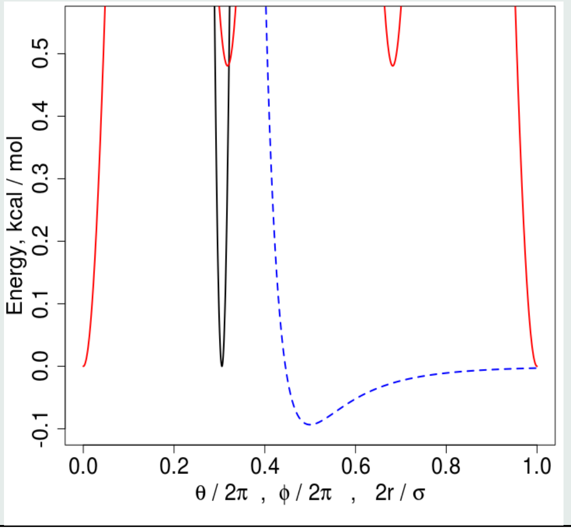


Simulation algorithm

Stochastic Approximation Monte Carlo Simulation *)

*) Liang, F. J Stat Phys (2006) 122: 511

Simulation algorithm

Stochastic Approximation Monte Carlo Simulation *)

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

+ Properties of the system in thermodynamical equilibrium

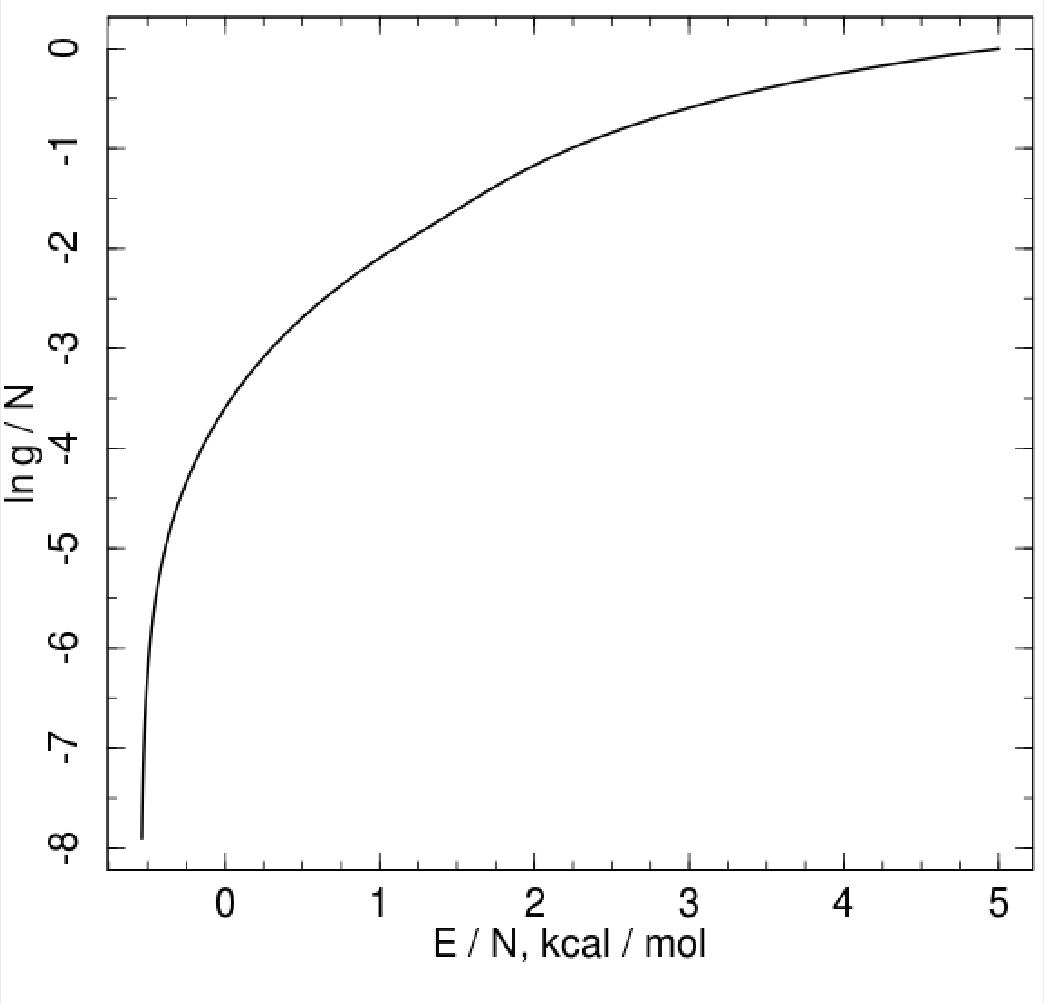
$$Z(T) = \sum_E g(E) \exp\left(-\frac{E}{k_B T}\right)$$

$$\langle O \rangle (T) = \frac{1}{Z(T)} \sum_E \overline{O}(E) g(E) \exp\left(-\frac{E}{k_B T}\right)$$

- No information about dynamics

*) Liang, F. J Stat Phys (2006) 122: 511

Density of states



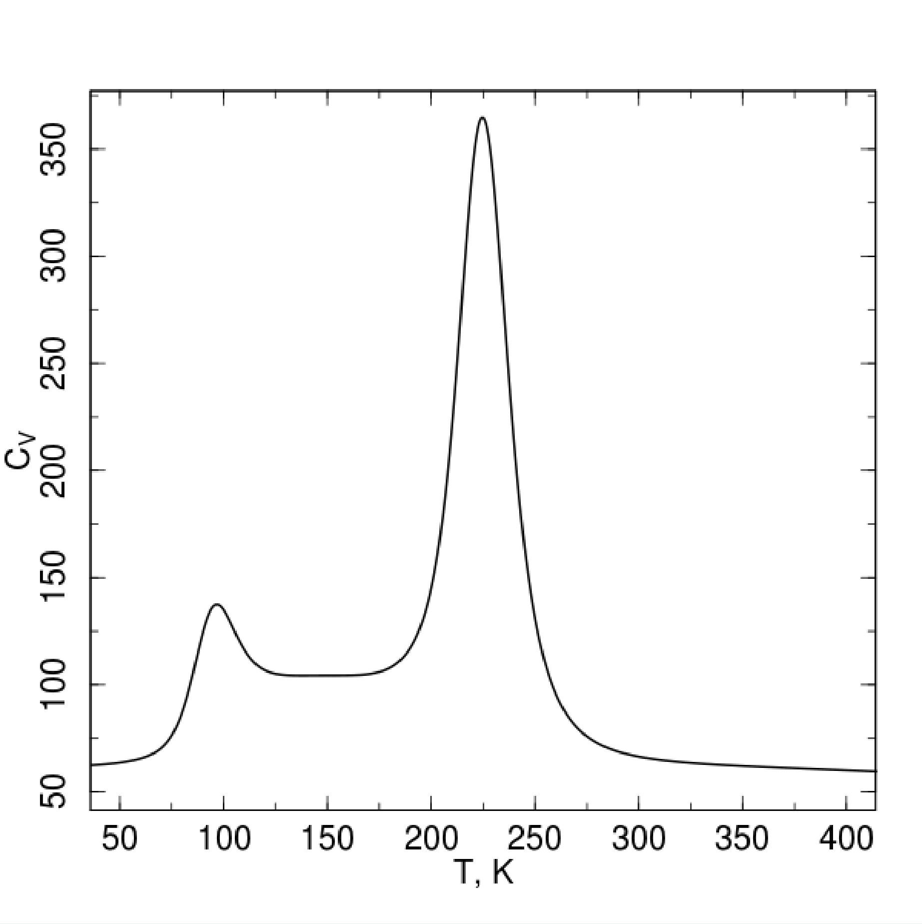
$$S_{\text{Norm}}(E) = \frac{\ln g(E) - \max(\ln g(E))}{N}$$

Heat capacity

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

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

Heat capacity



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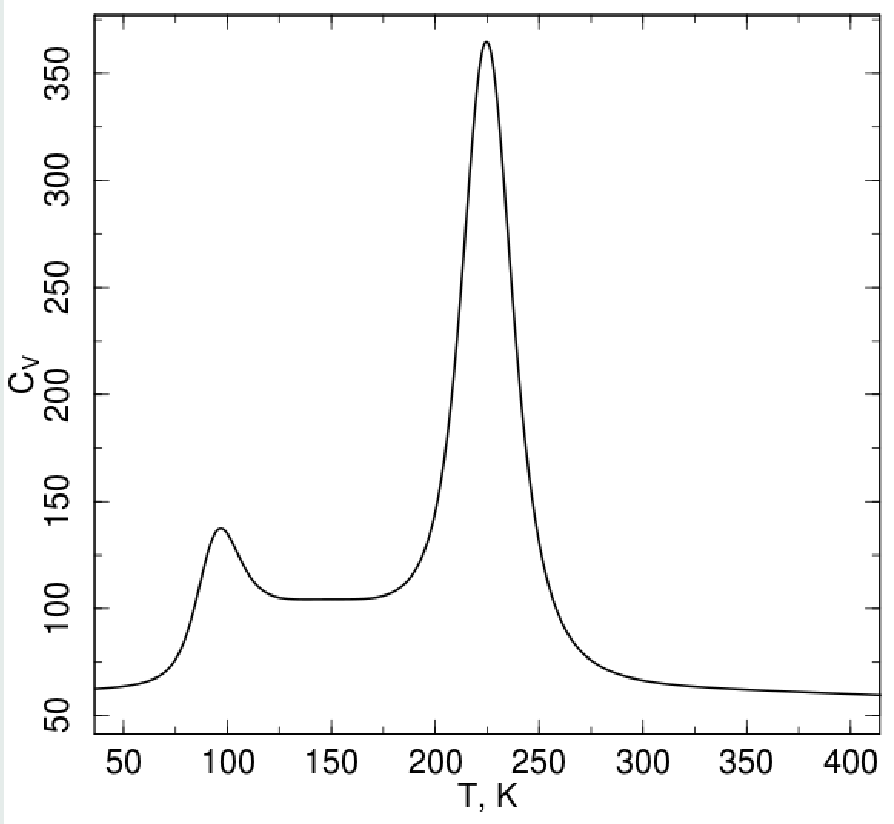
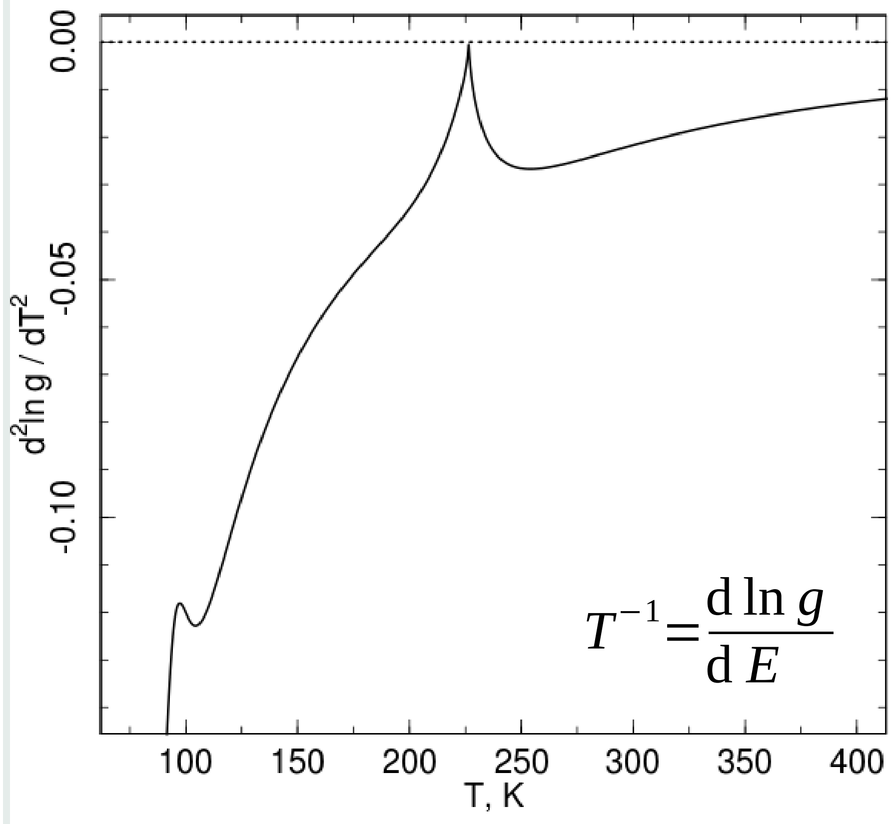
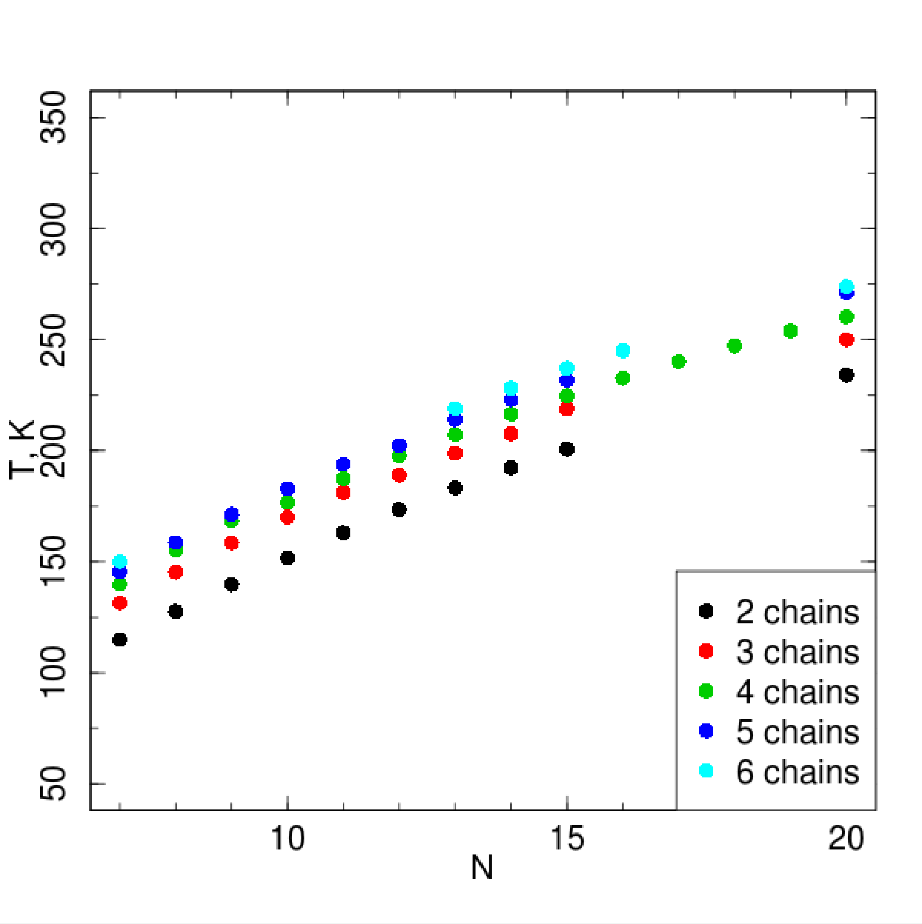
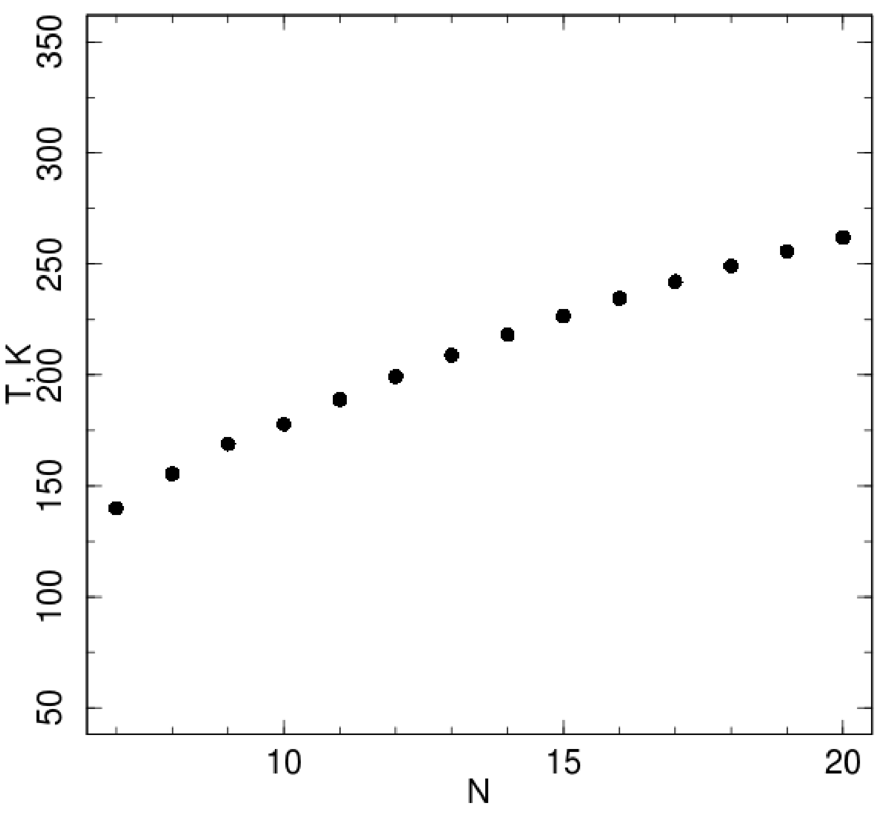




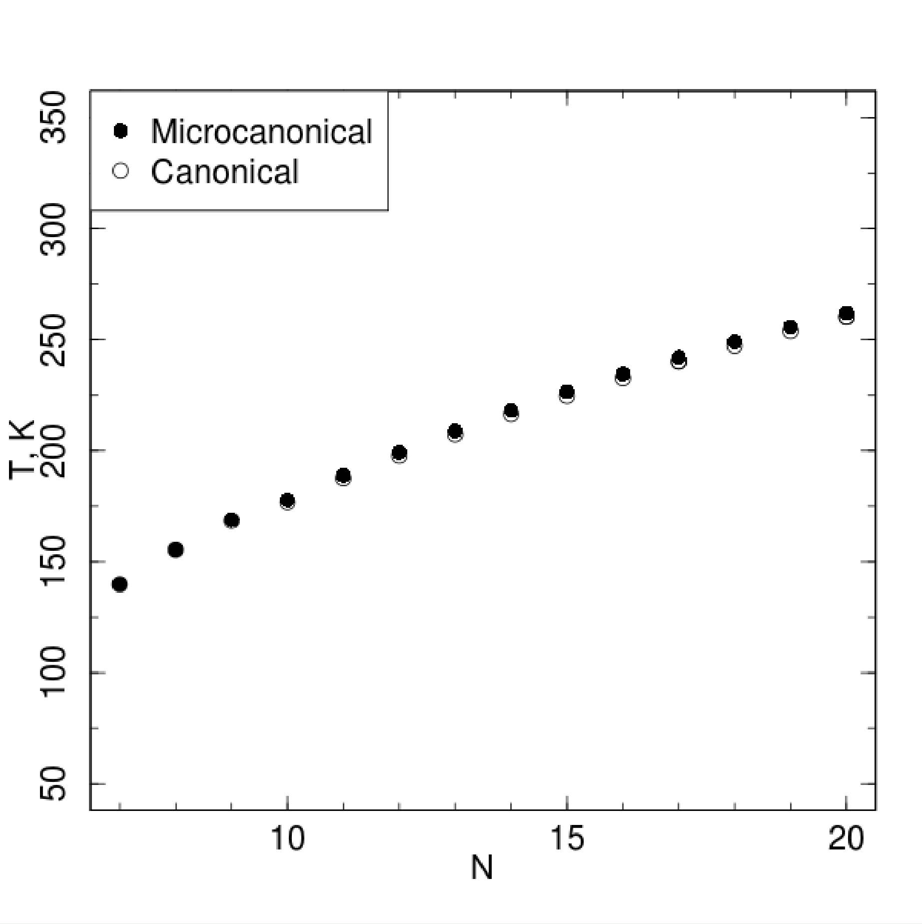
Aggregation transition



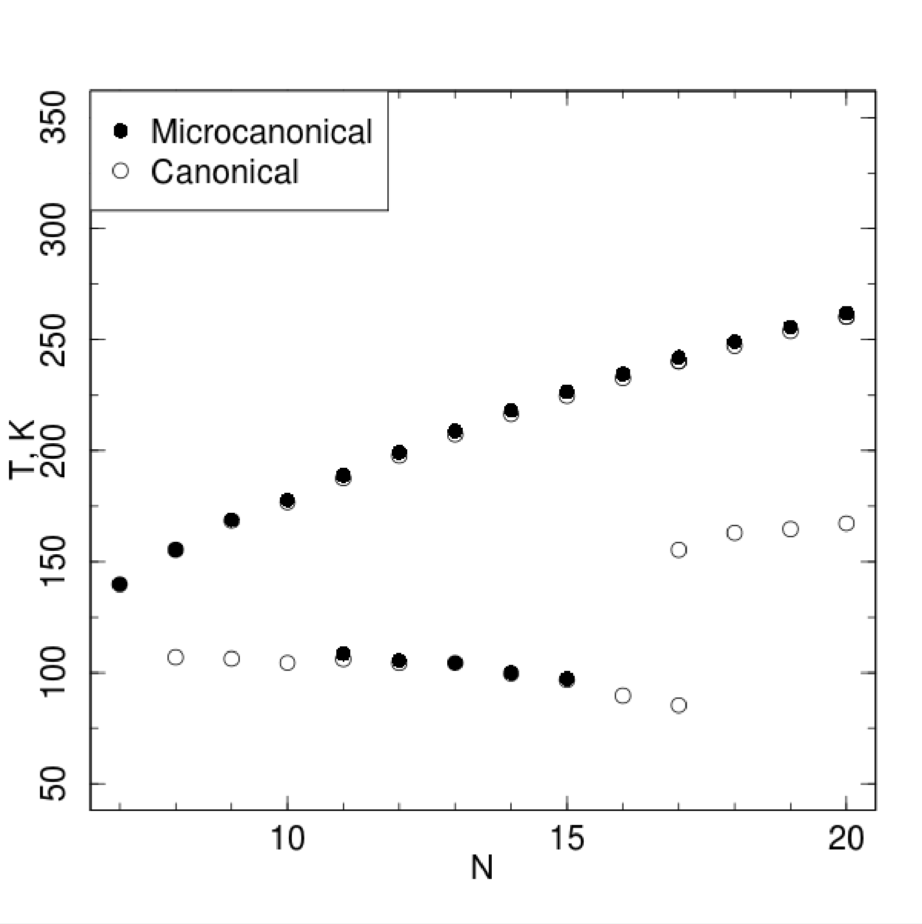
Aggregation of 4-chain systems



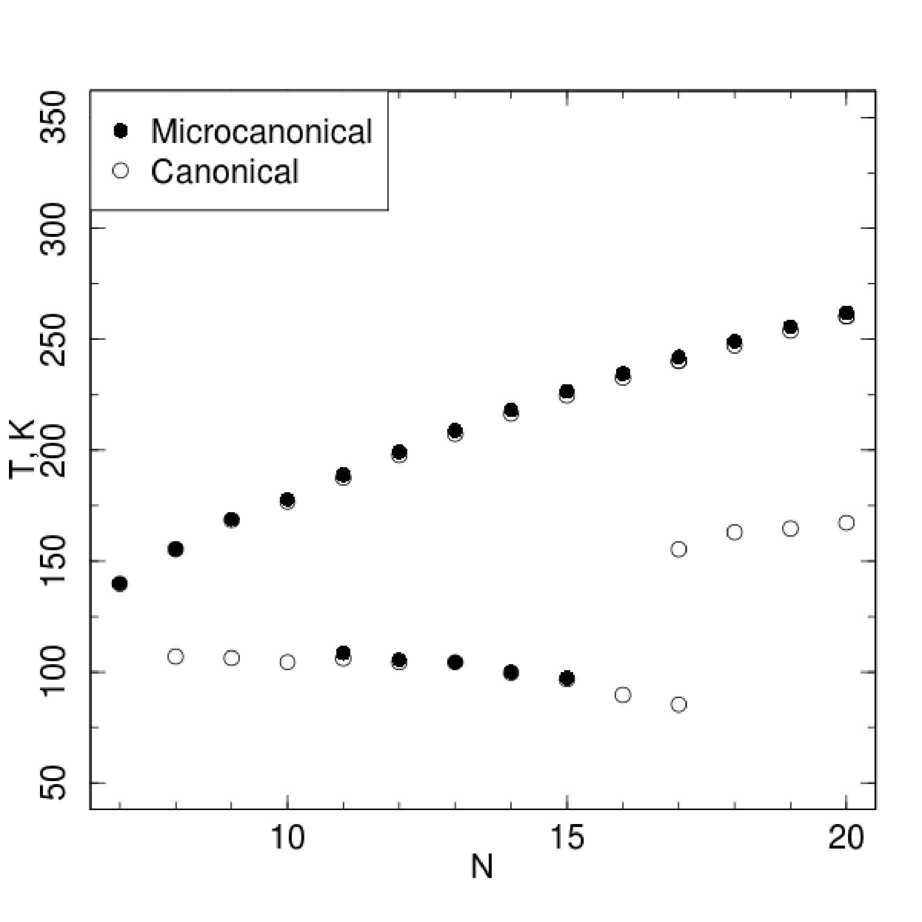
Aggregation of 4-chain systems



Aggregation of 4-chain systems



Aggregation of 4-chain systems



$$Z(T) = \int \mathrm{d}E\, g(E)\, e^{-\beta E}$$

Partition function zeros

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Partition function zeros

$$Z(T) = \int \mathrm{d}E\, g(E)\, e^{-\beta E} \approx \sum_n g(E_n)\, e^{-\beta E_n} = \sum_n g(E_n)\, e^{-\beta (E_{\min} + n \Delta E)}$$

Partition function zeros

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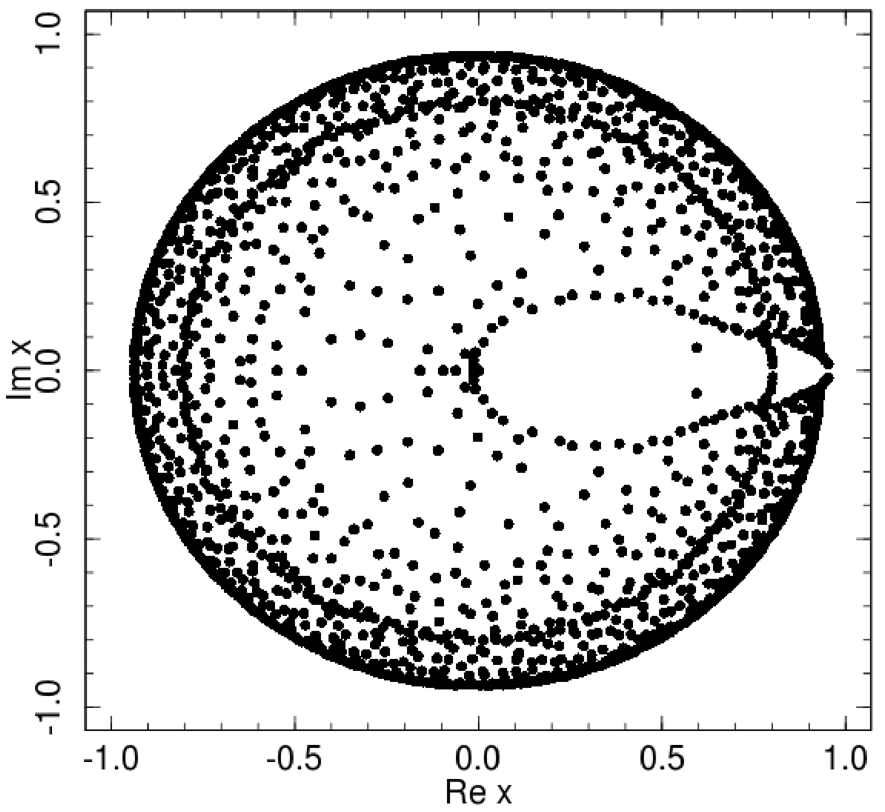
$$Z(T) \approx e^{-\beta E_{\min}} \sum_n g_n\, e^{-n \beta \Delta E} = e^{-\beta E_{\min}} \sum_n g_n \left(e^{-\beta \Delta E}\right)^n$$

$$Z(T) \approx e^{-\beta E_{\min}} \sum_n g_n x^n$$

$$x = e^{-\beta \Delta E}$$

$$g_n = g(E_n)$$

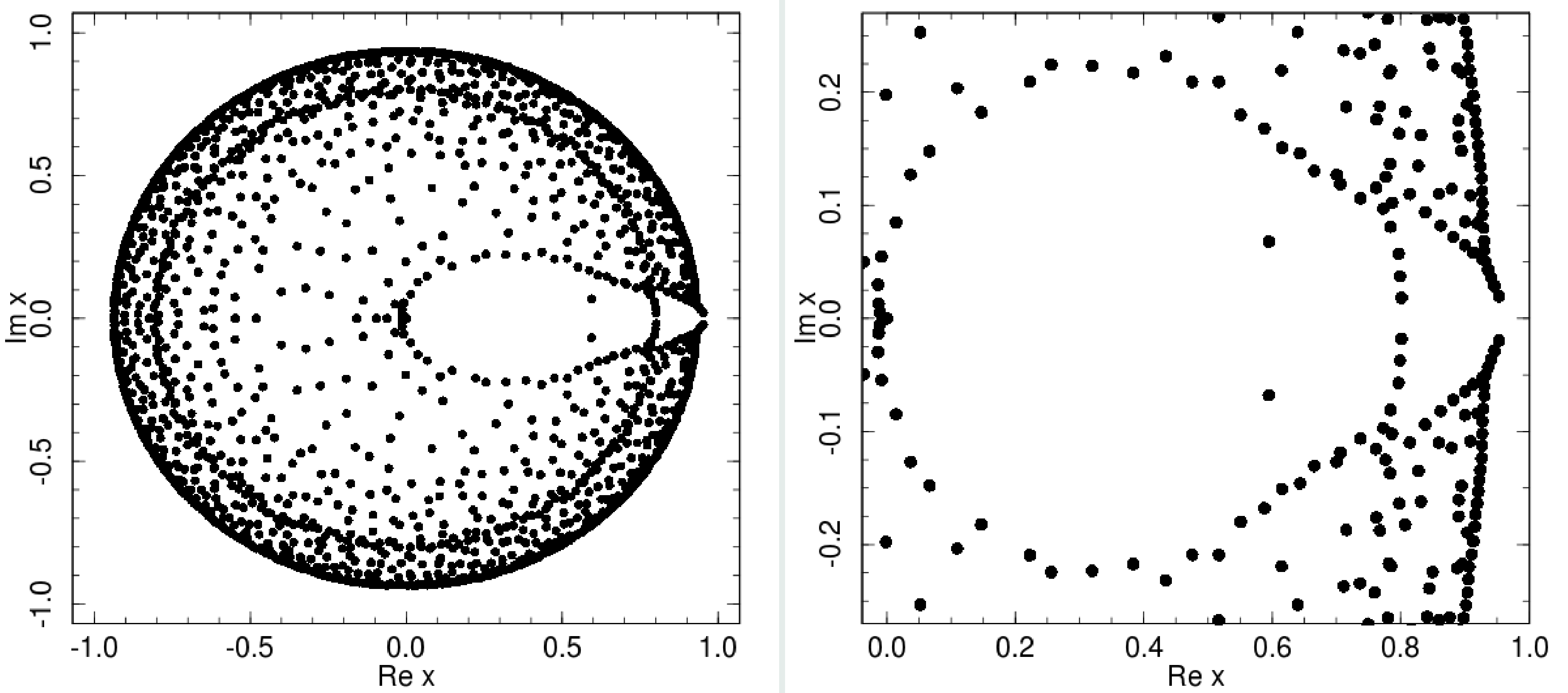
Partition function zeros. 4 C_{15}-aggregates



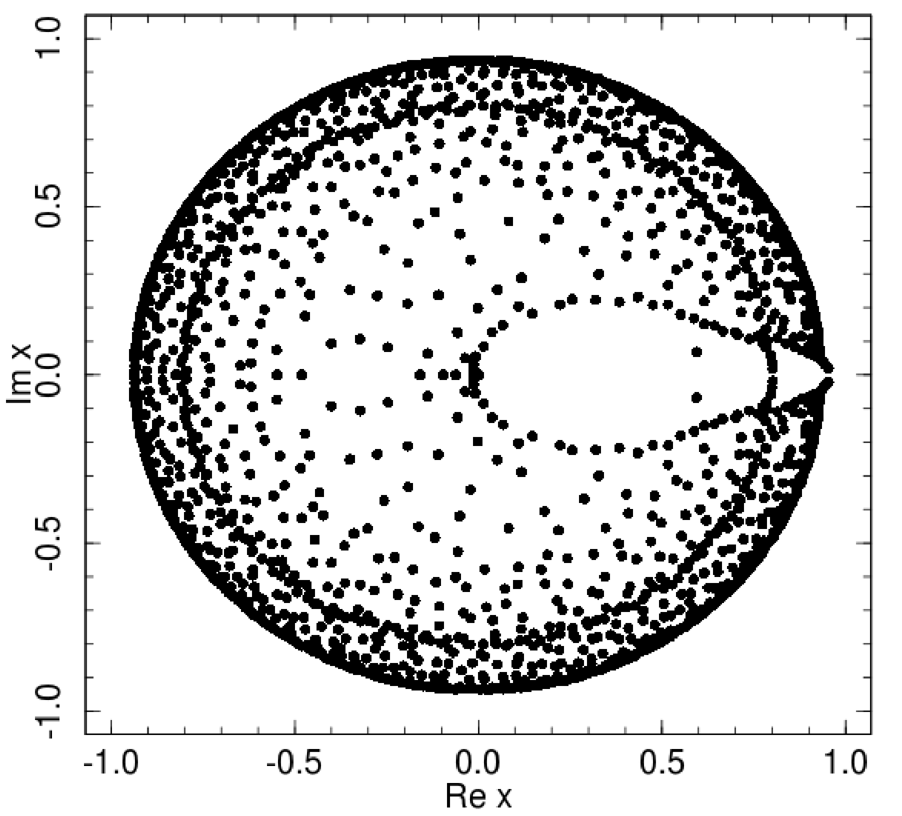
$$\sum_n g_n x^{n-1} = 0$$

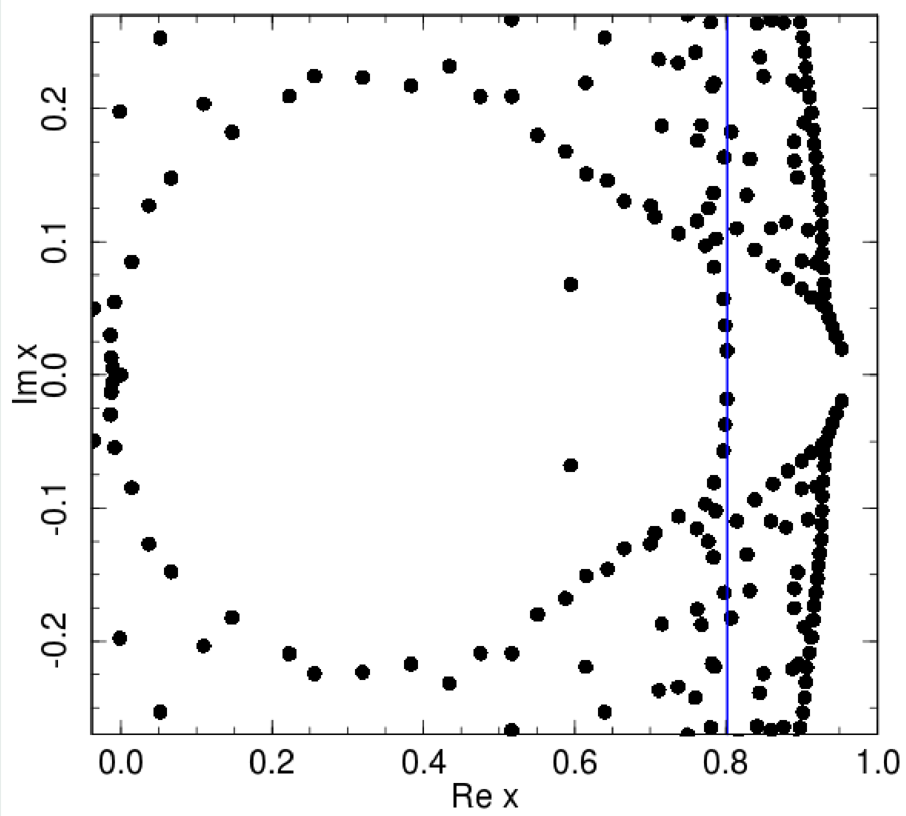
$$x = e^{-\beta \Delta E}$$

Partition function zeros. 4 C_{15}-aggregates

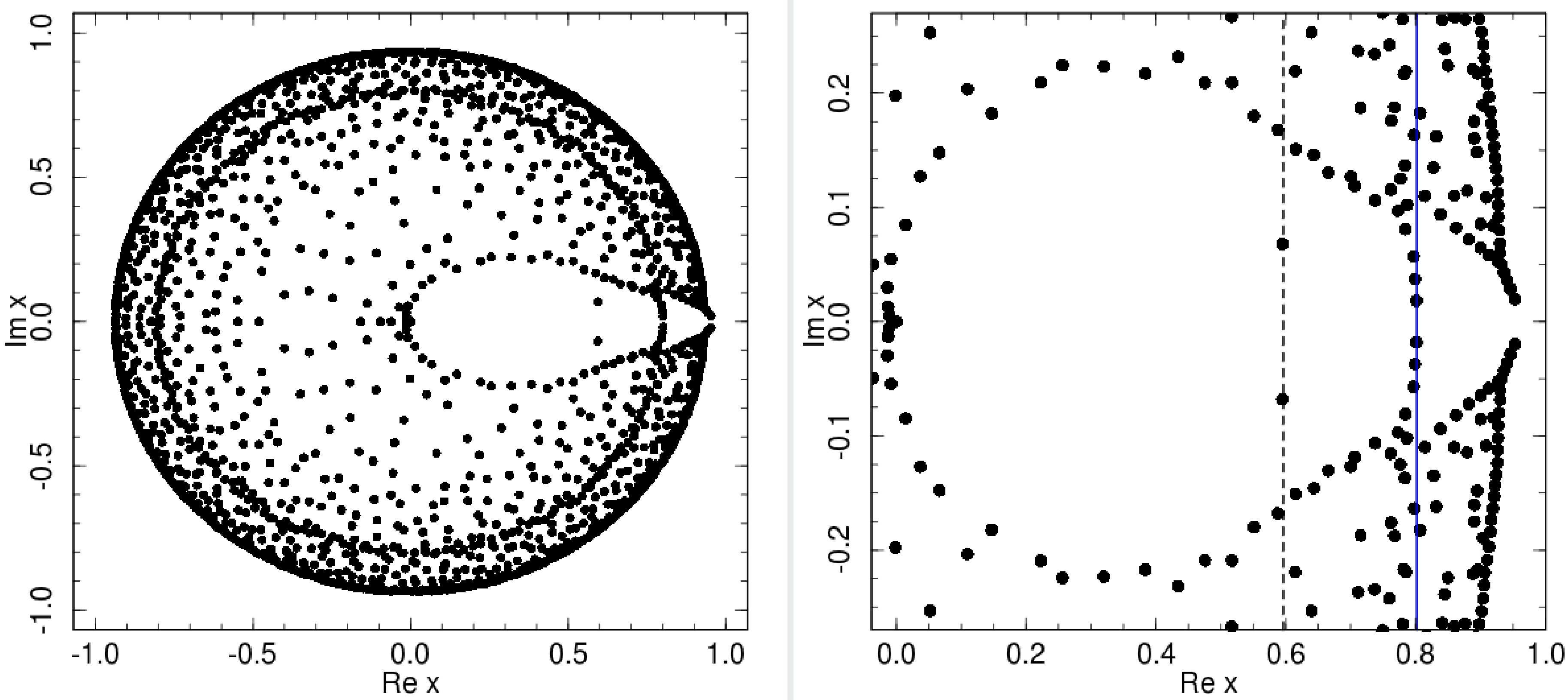


Partition function zeros. 4 C_{15}-aggregates





Partition function zeros. 4 C_{15}-aggregates



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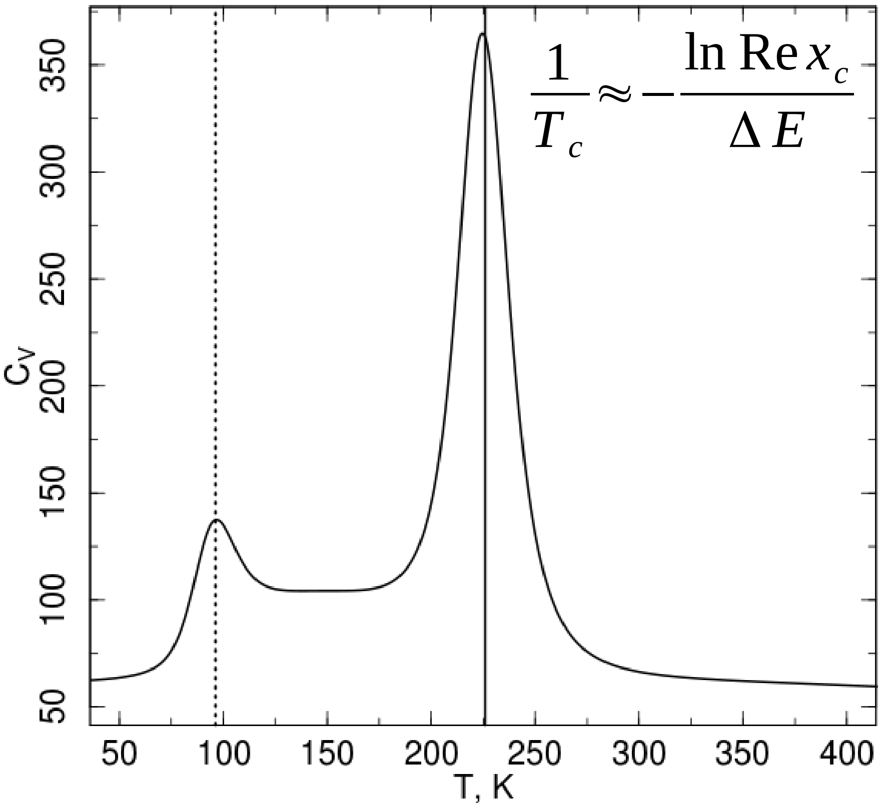
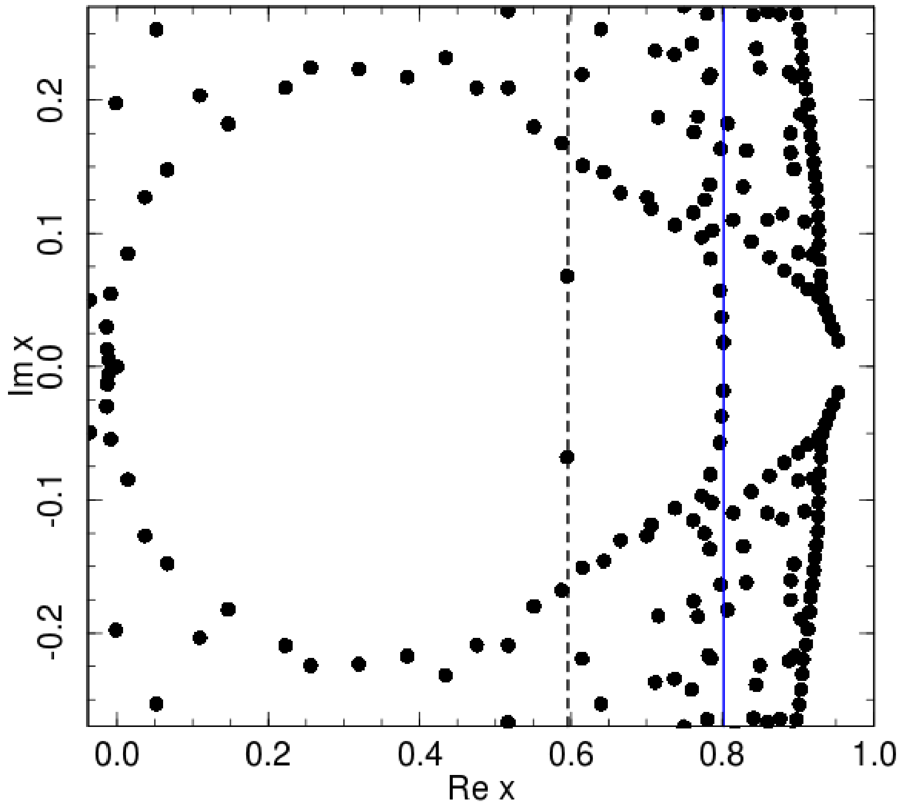
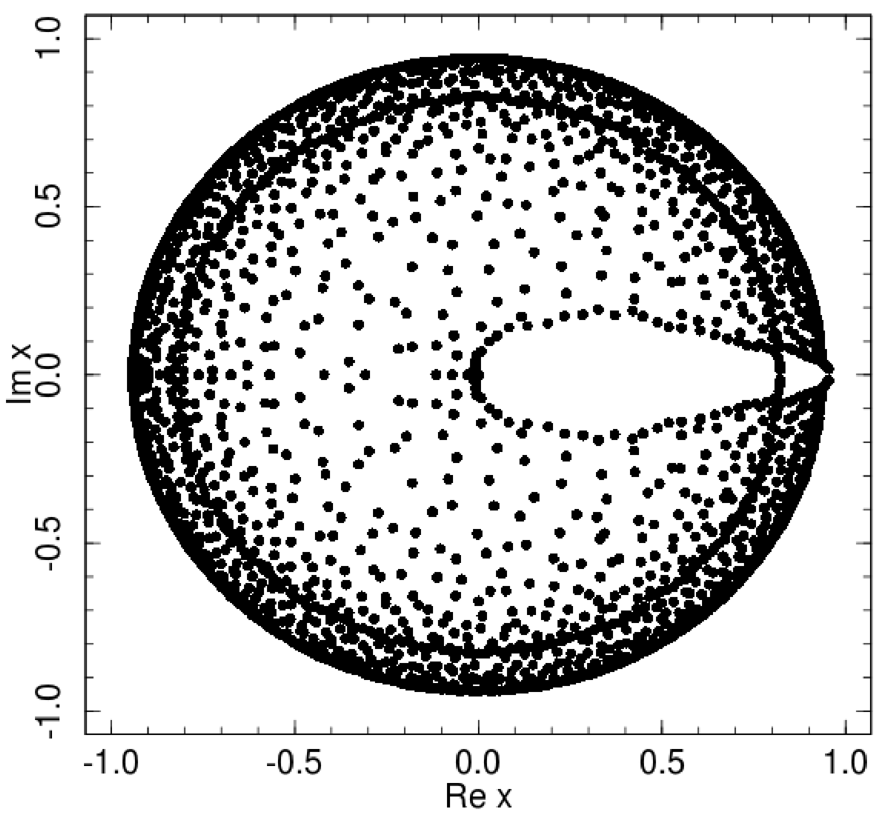


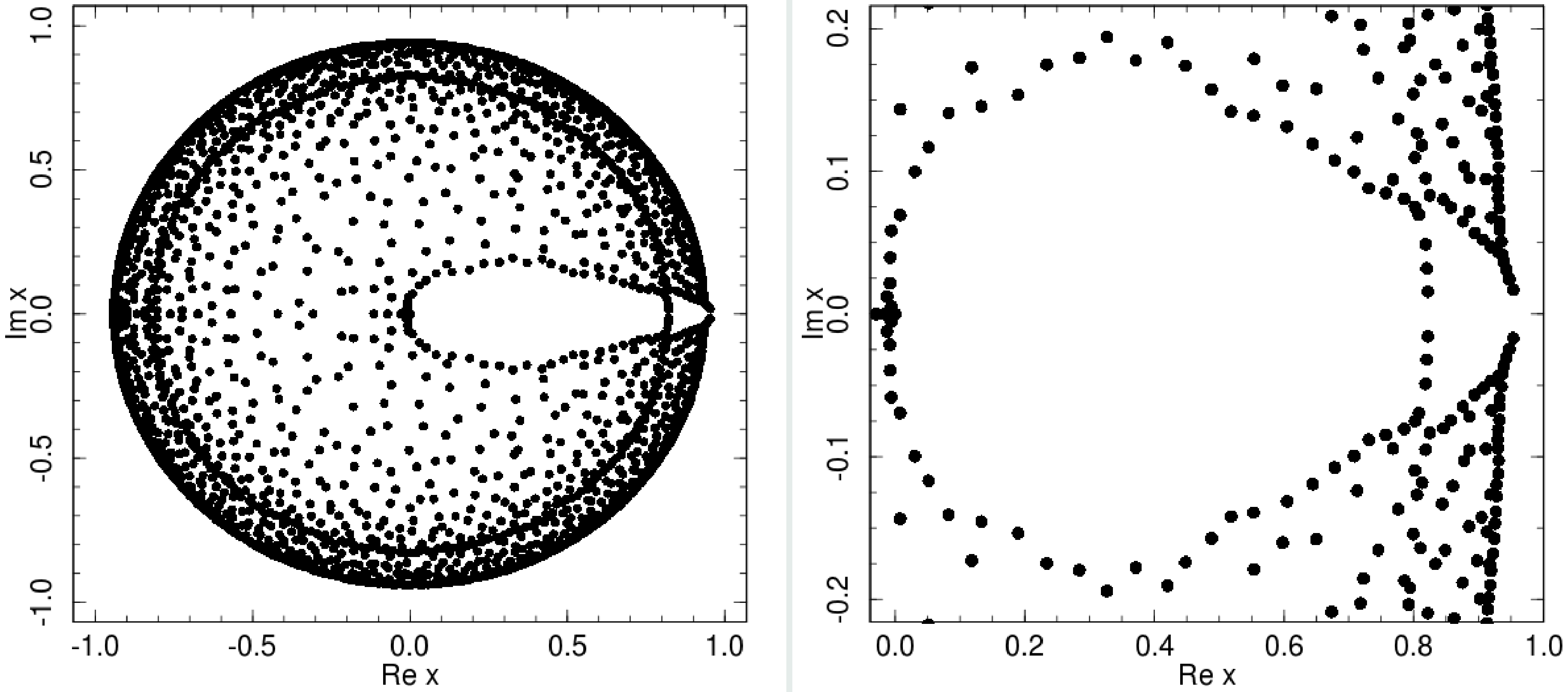
$$\frac{1}{T_c} \approx -\frac{\ln \mathrm{Re}\, x_c}{\Delta E}$$



Partition function zeros. 4 C_{19}-aggregates



Partition function zeros. 4 C_{19}-aggregates



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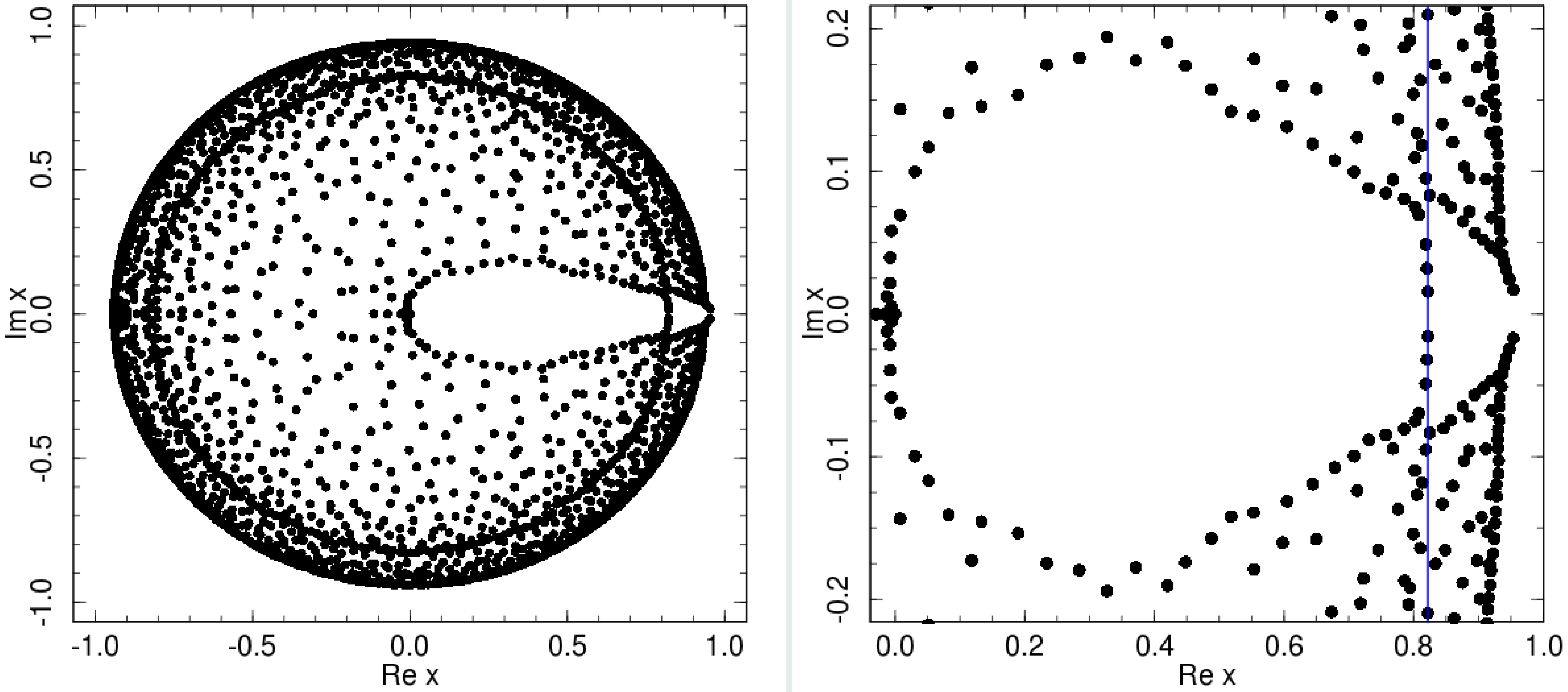
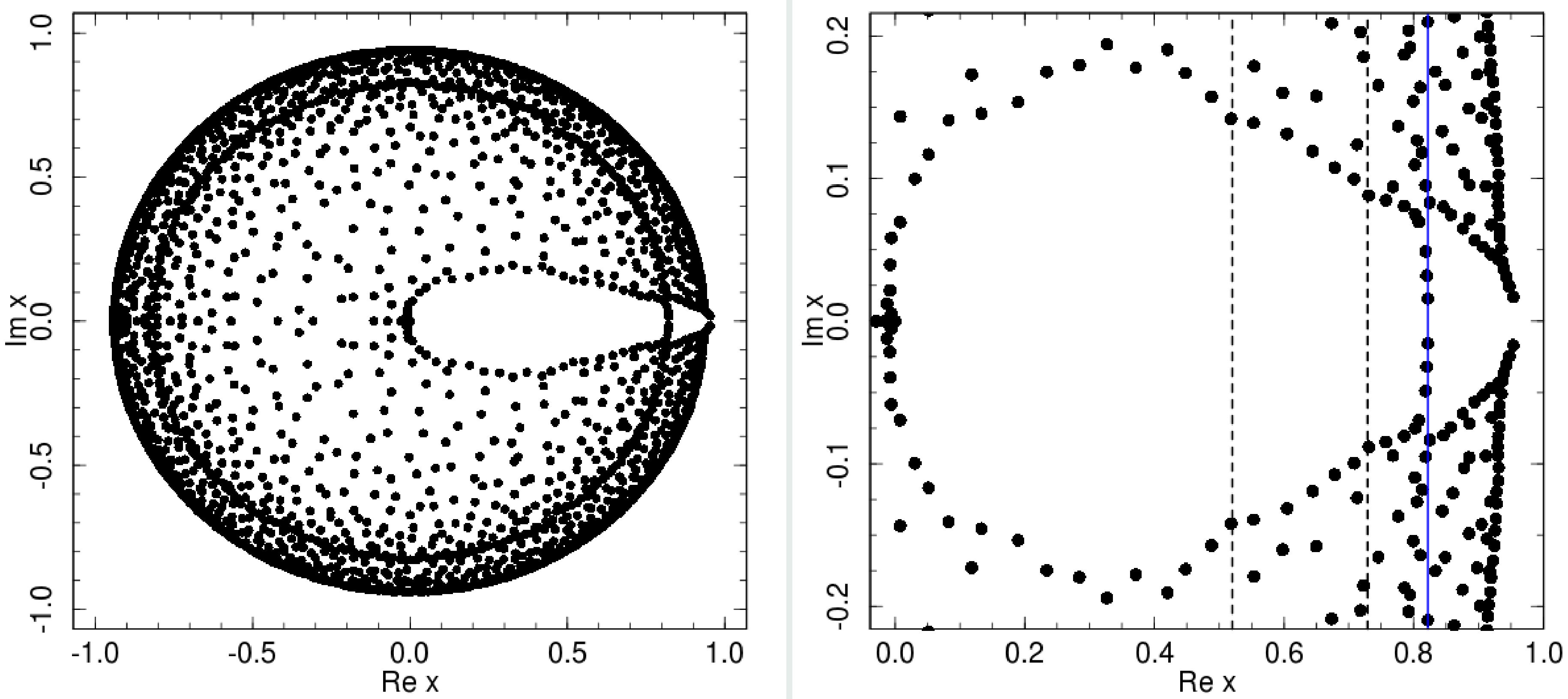
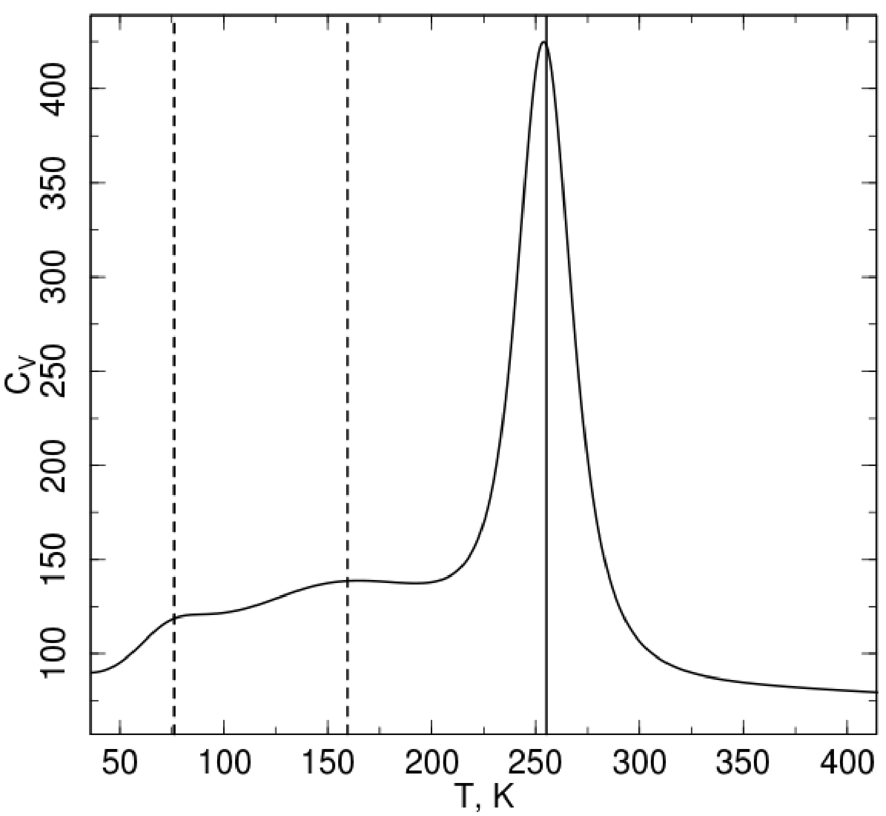
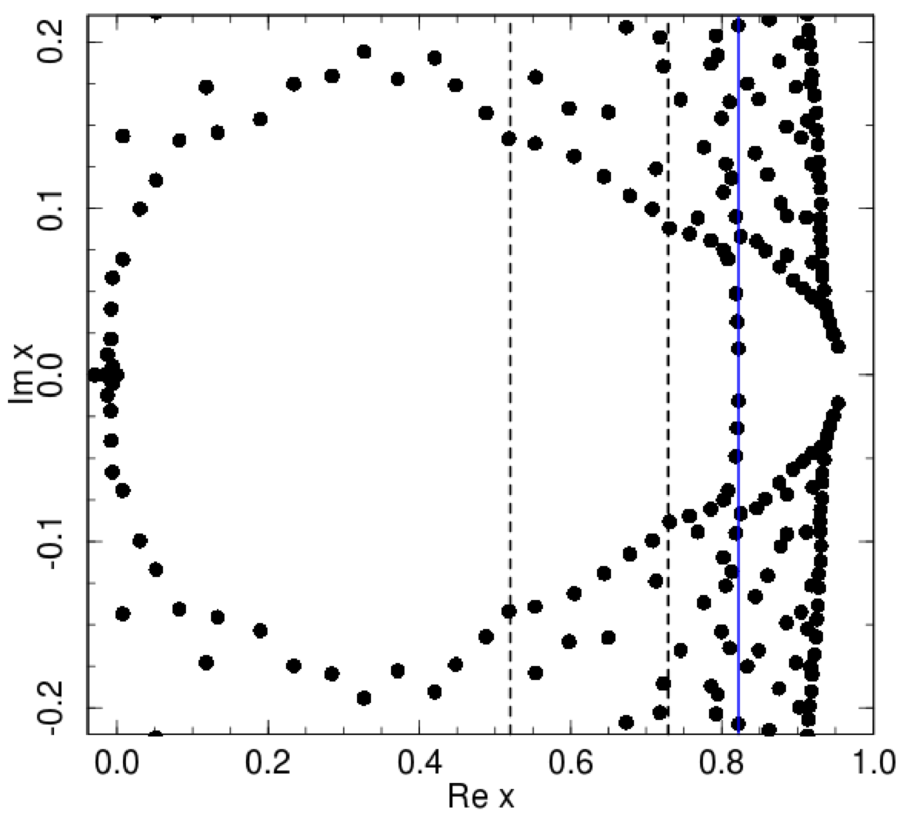


Partition function zeros. 4 C_{19}-aggregates



Partition function zeros. 4 C_{19}-aggregates





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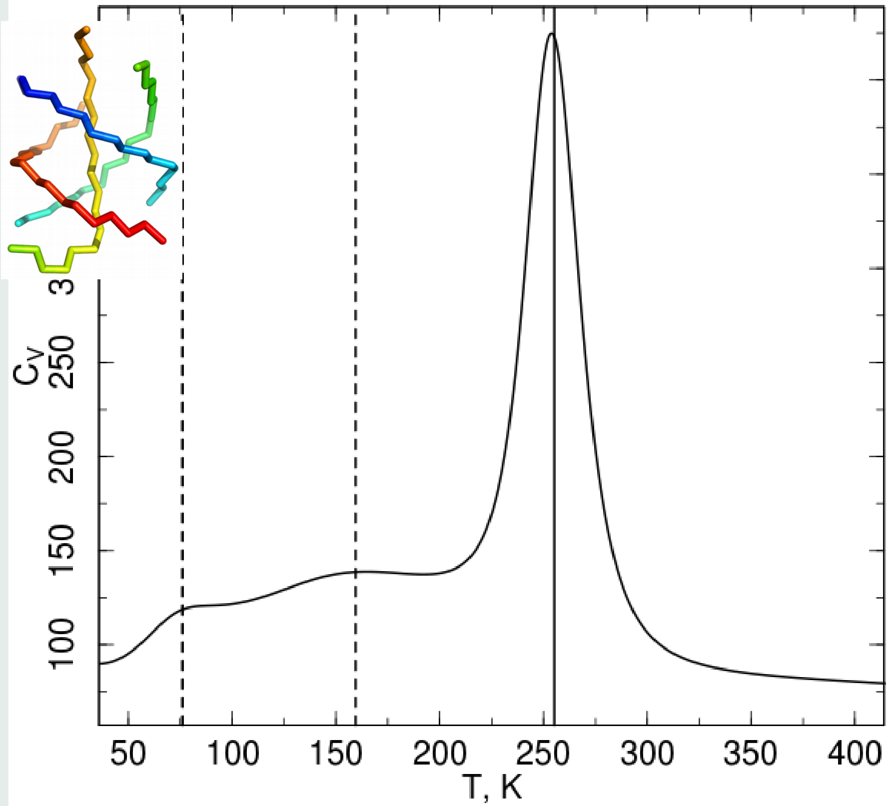

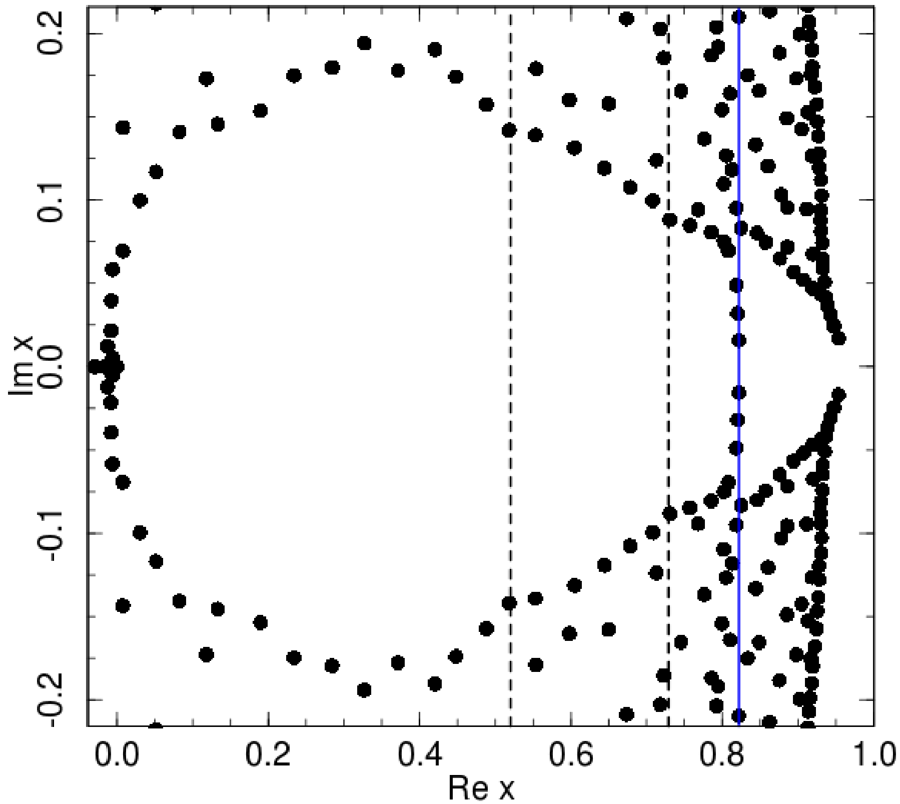

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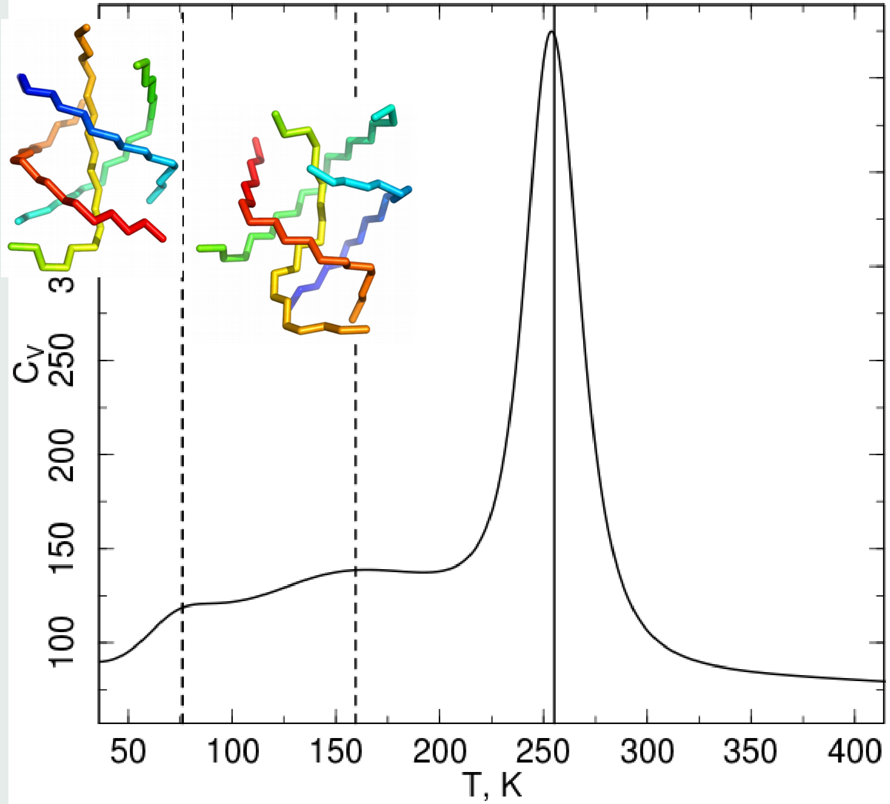

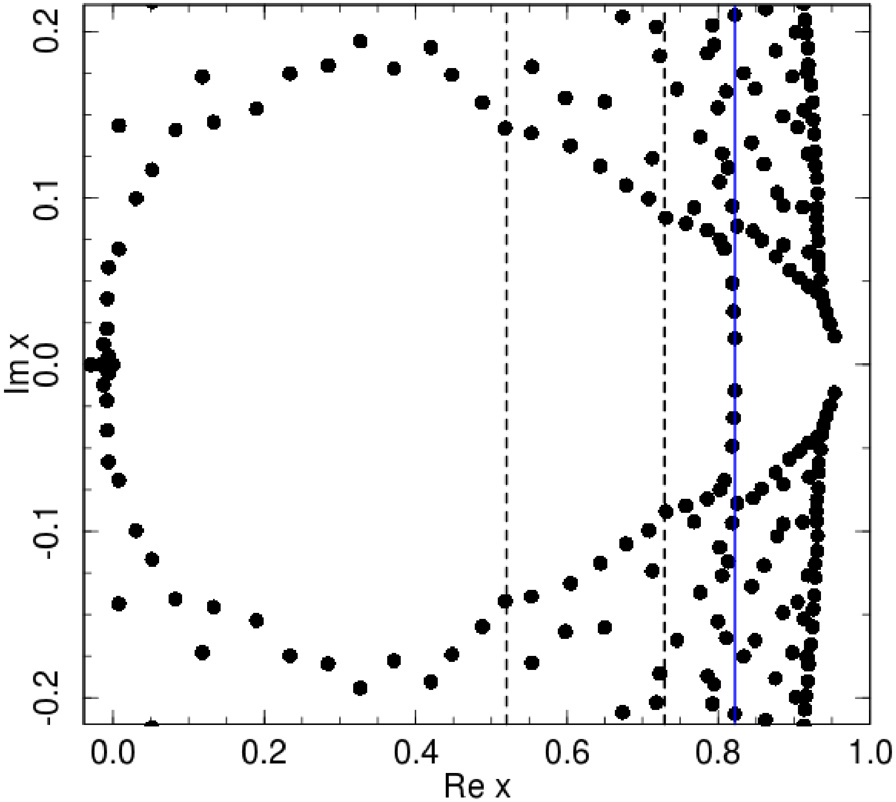

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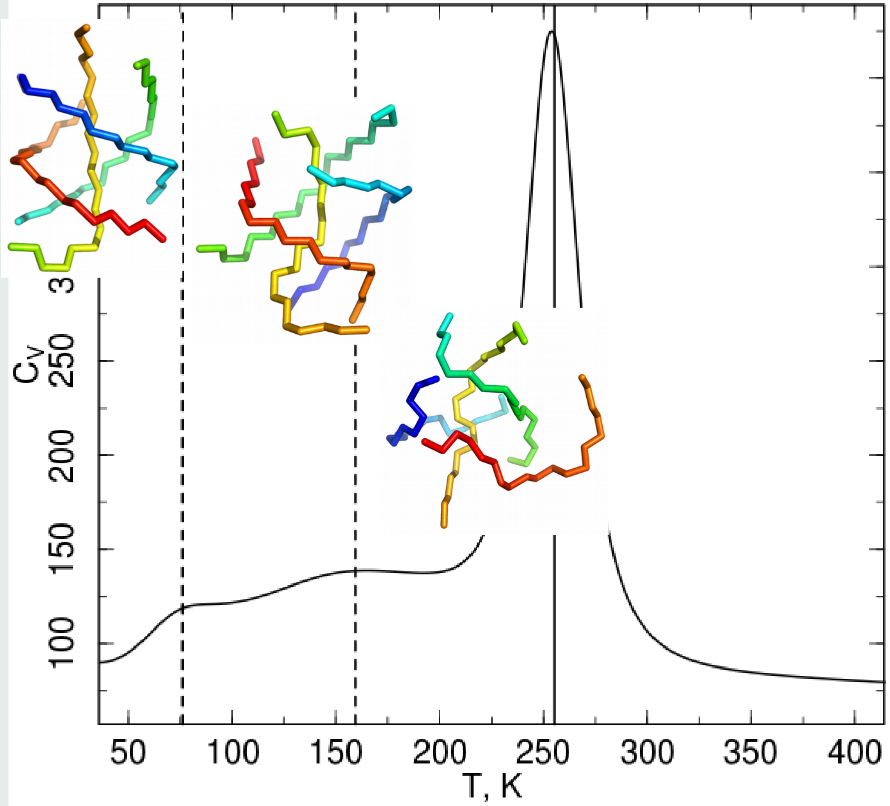
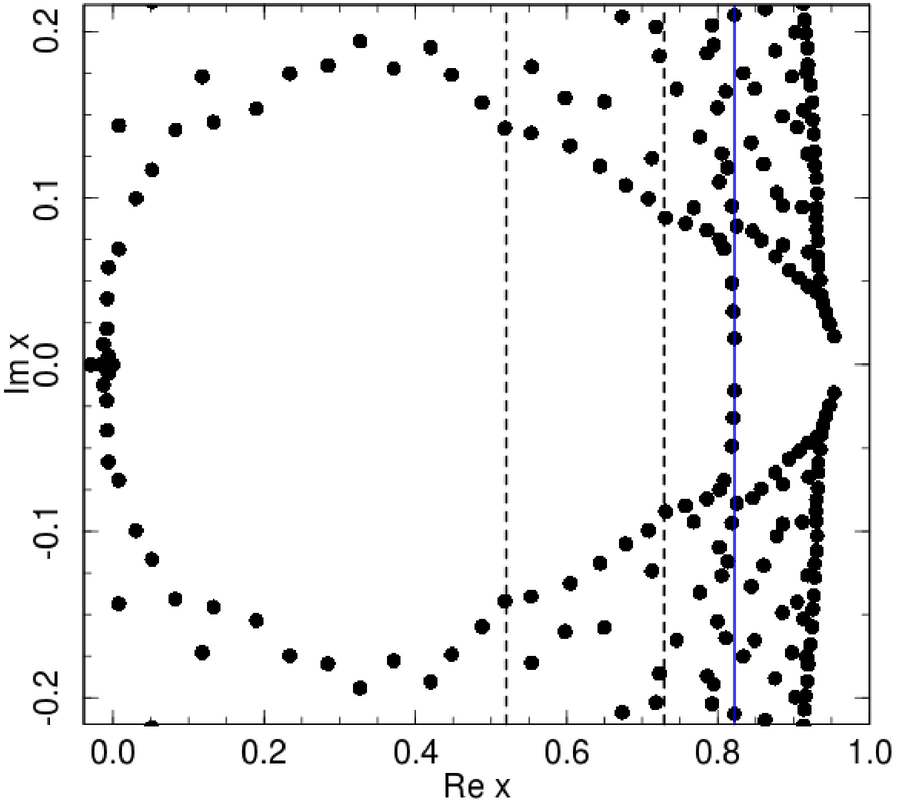
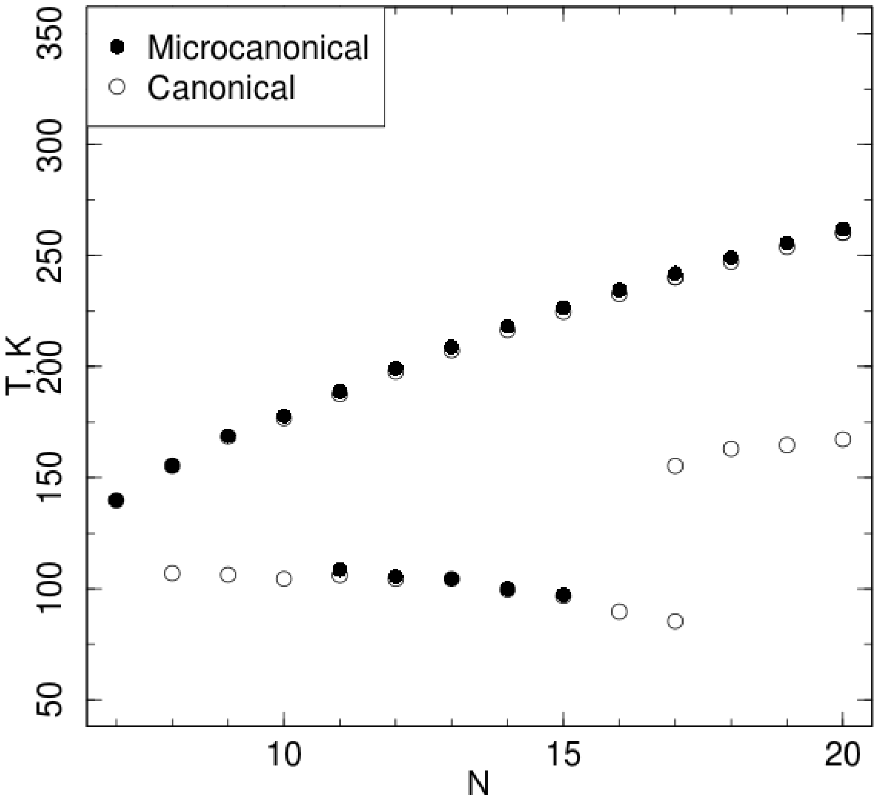
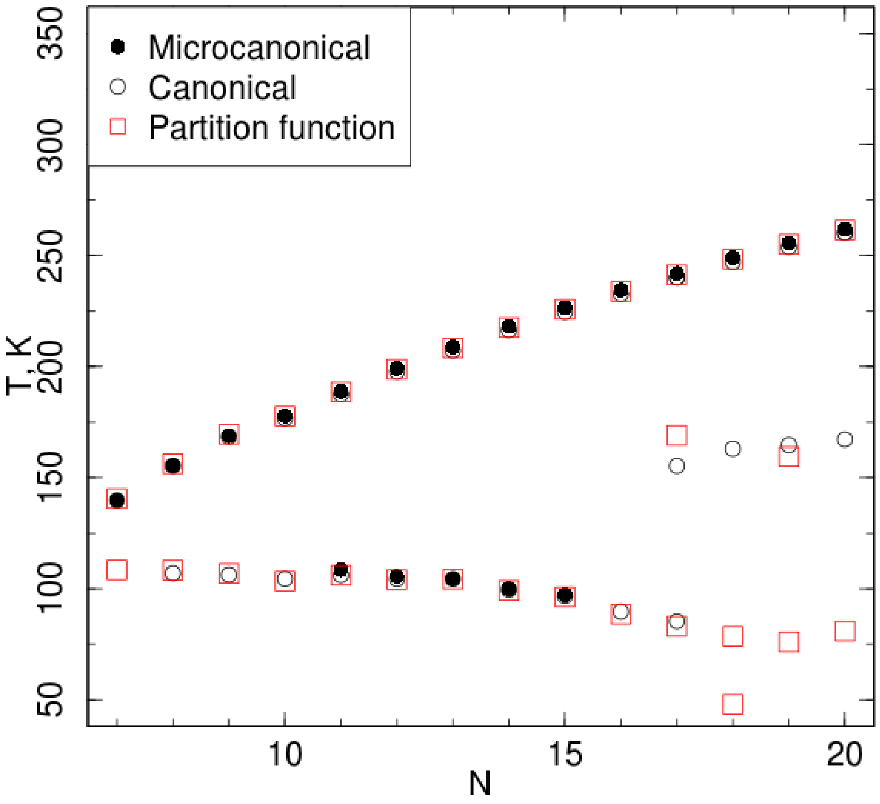


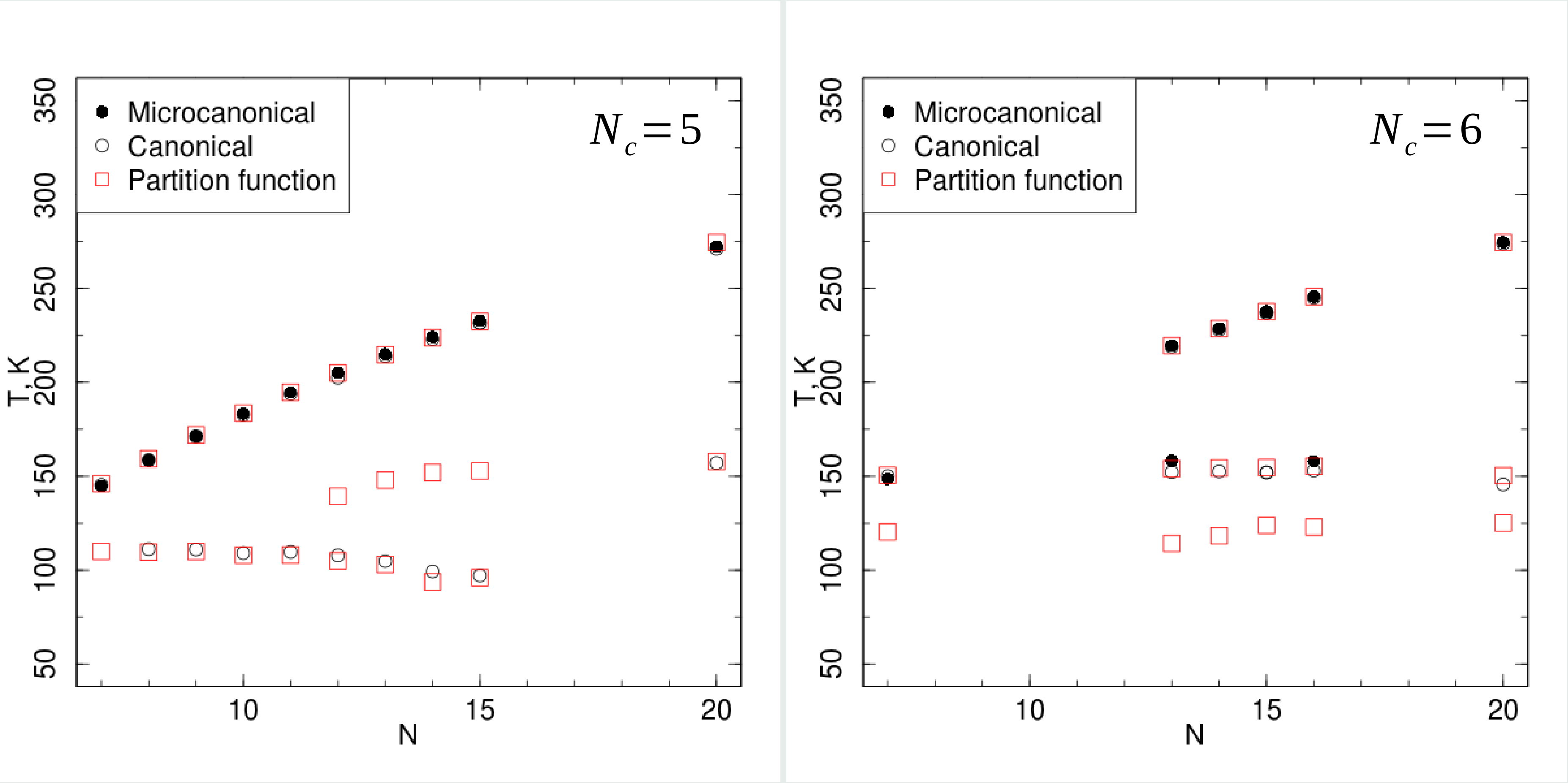


Partition function zeros of 4-chain aggregates





Partition function zeros of 5- and 6-chain systems



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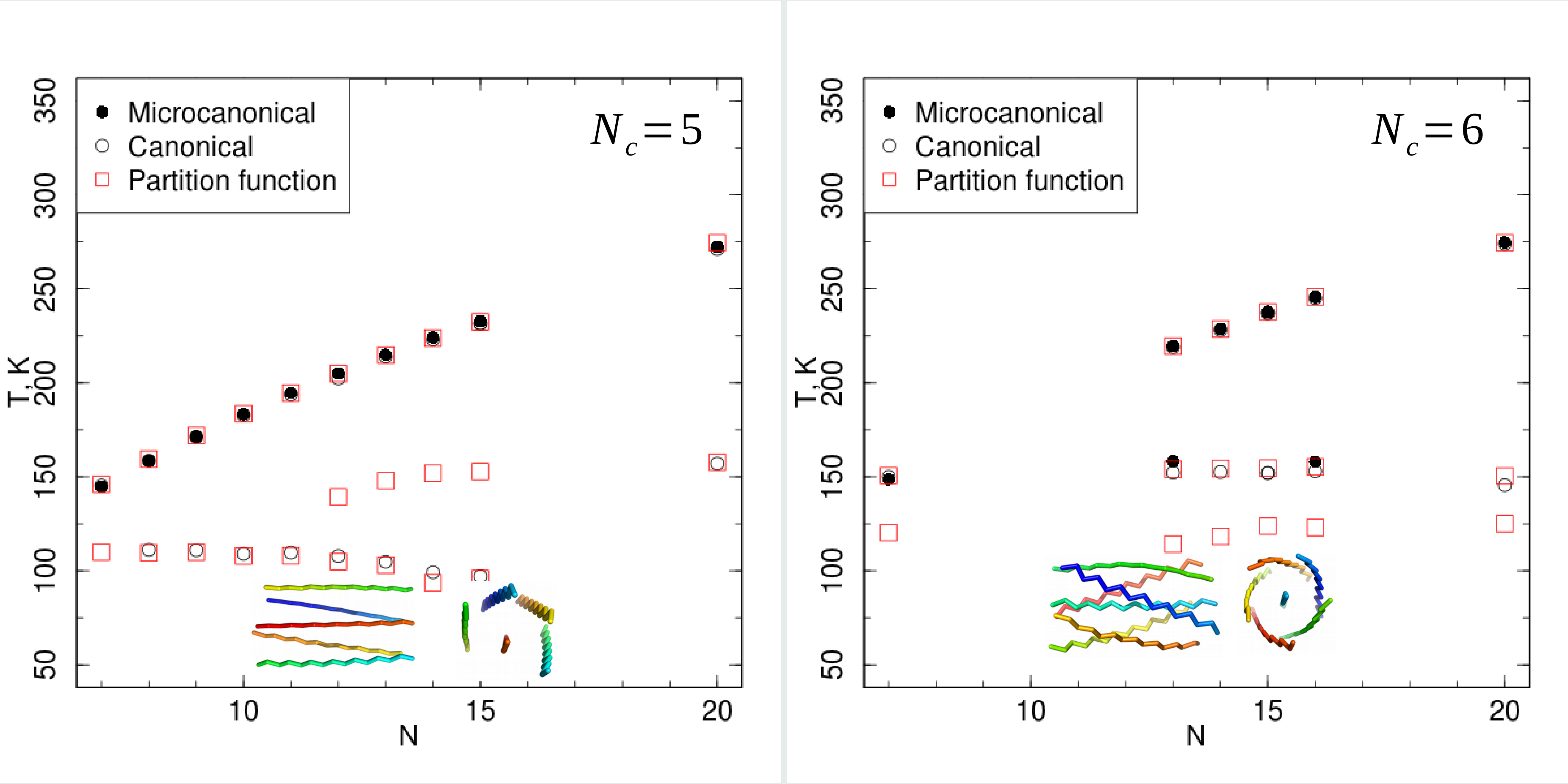

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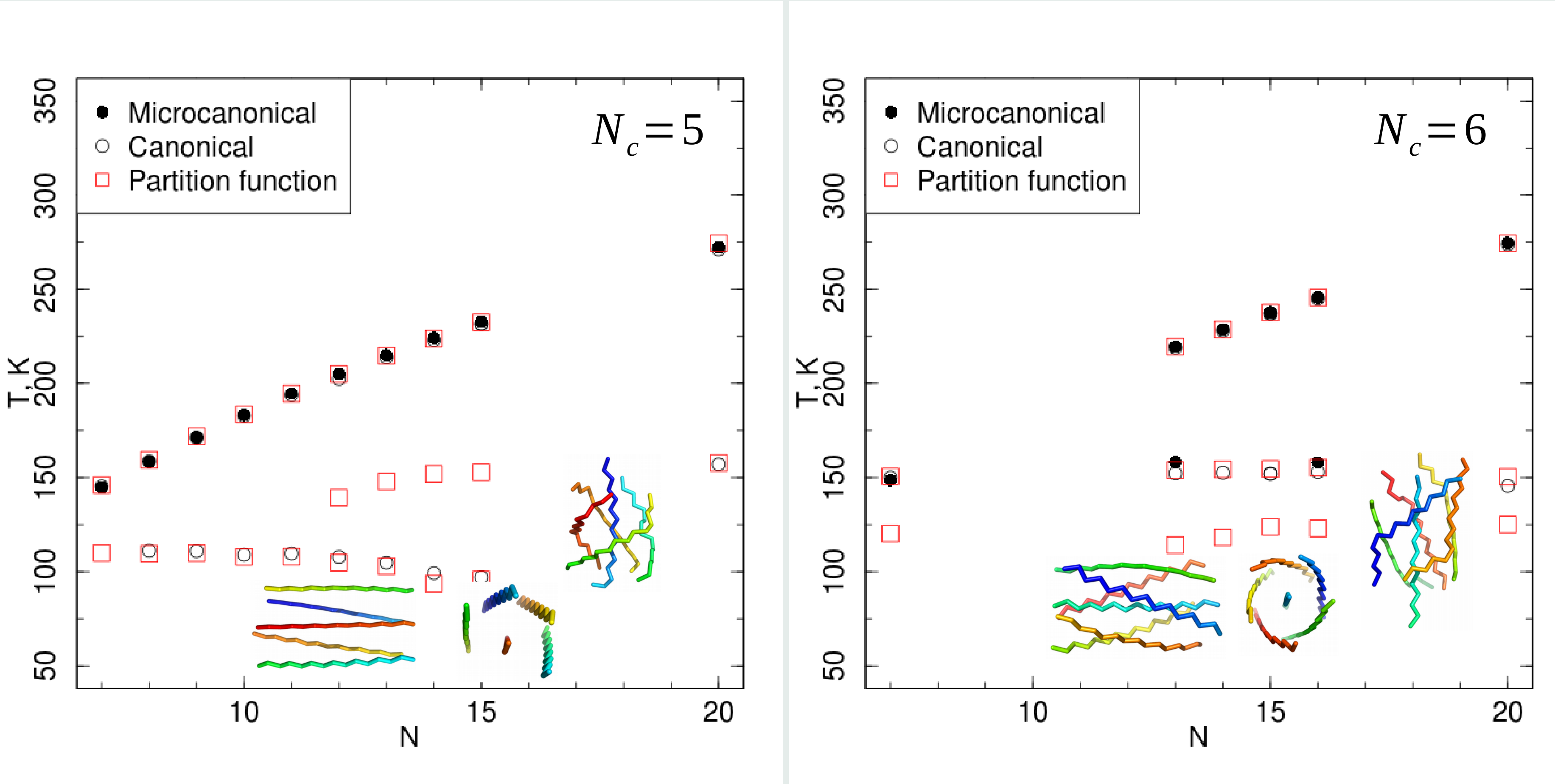
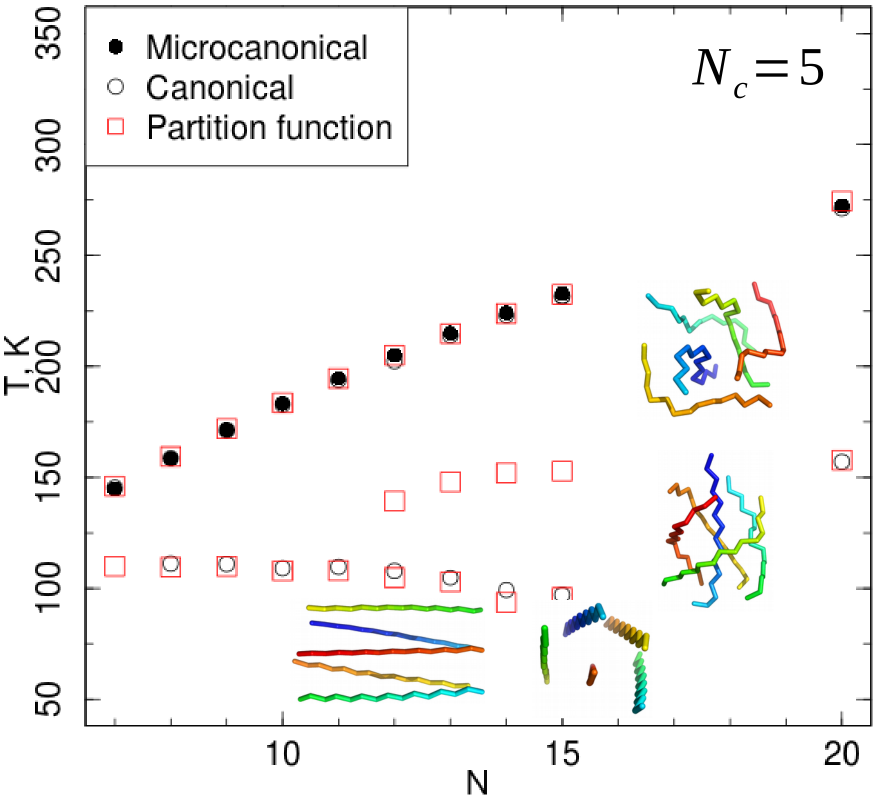


Partition function zeros of 5- and 6-chain systems



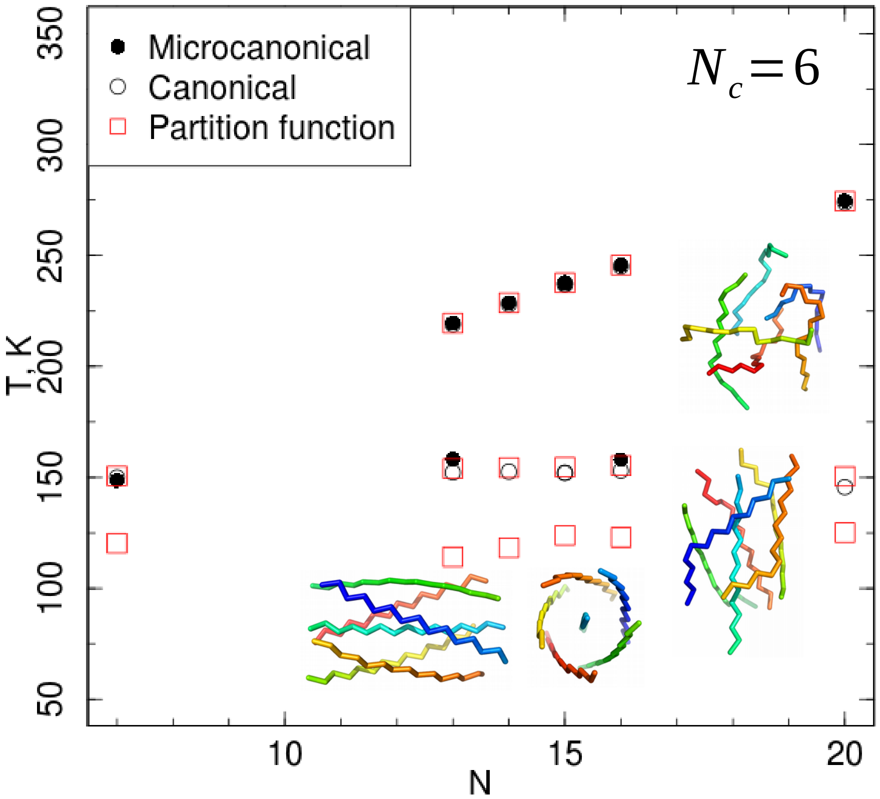


Diagram of low-temperature states of single chains

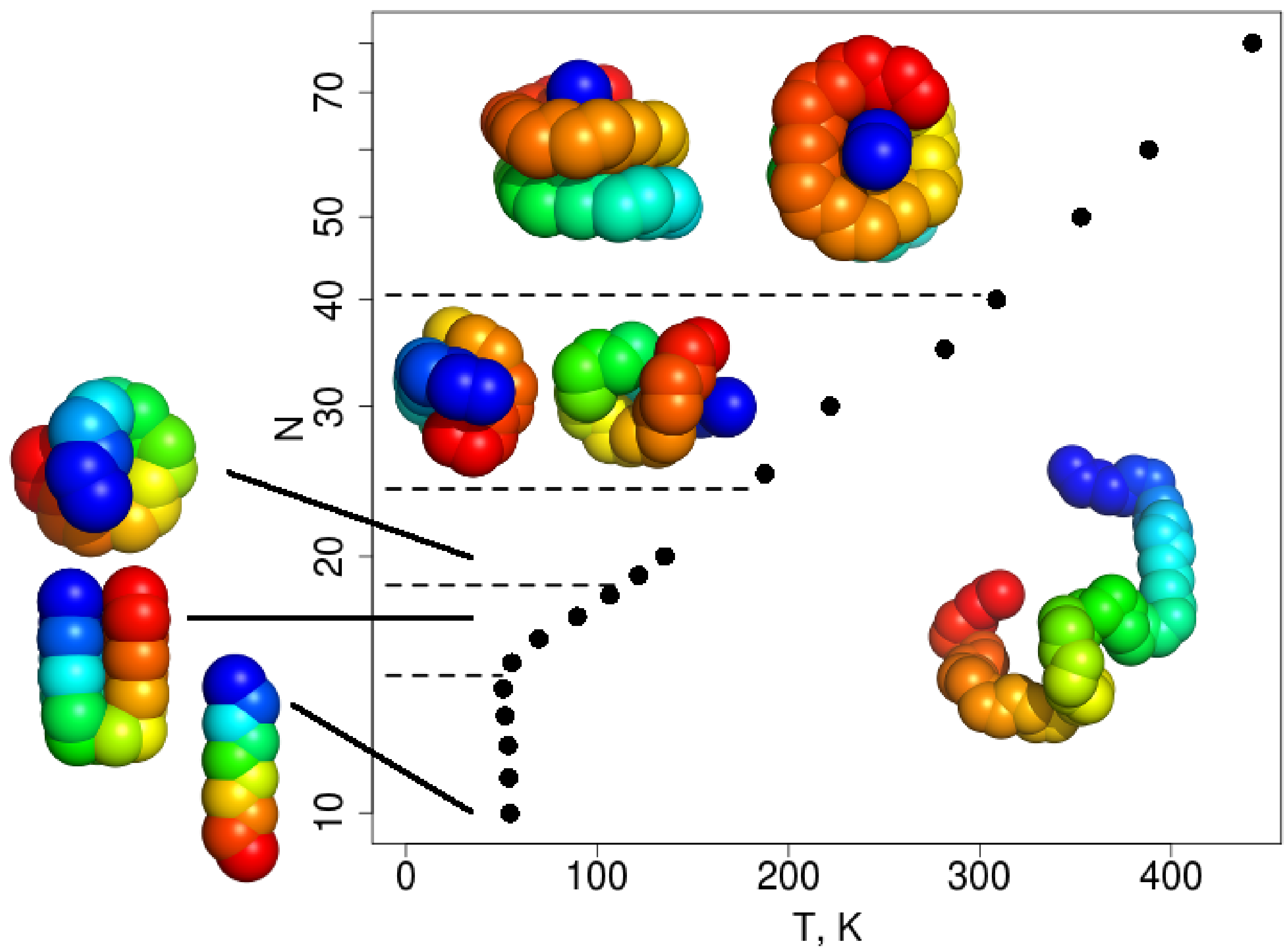


Diagram of low-temperature states of small aggregates

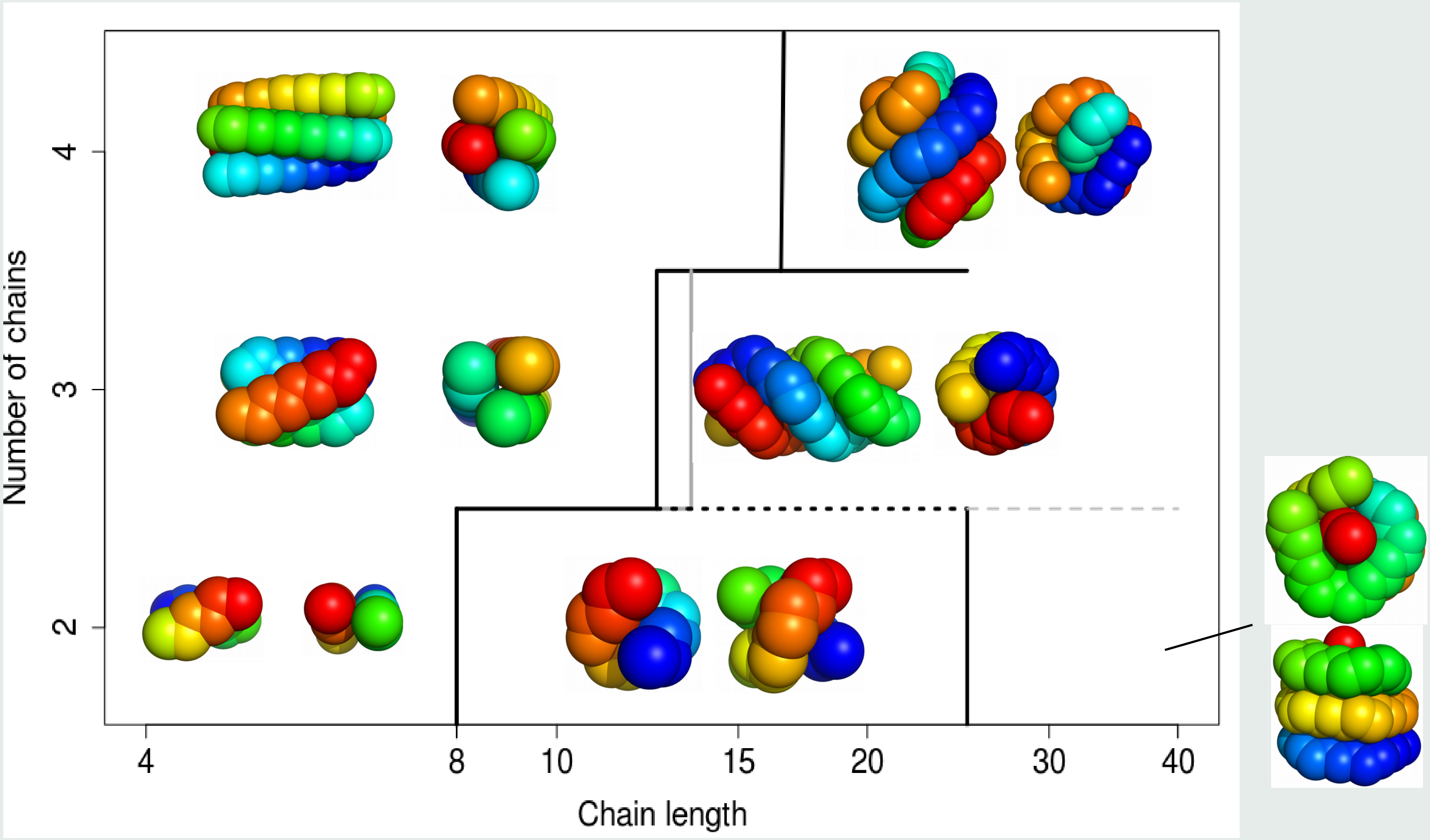
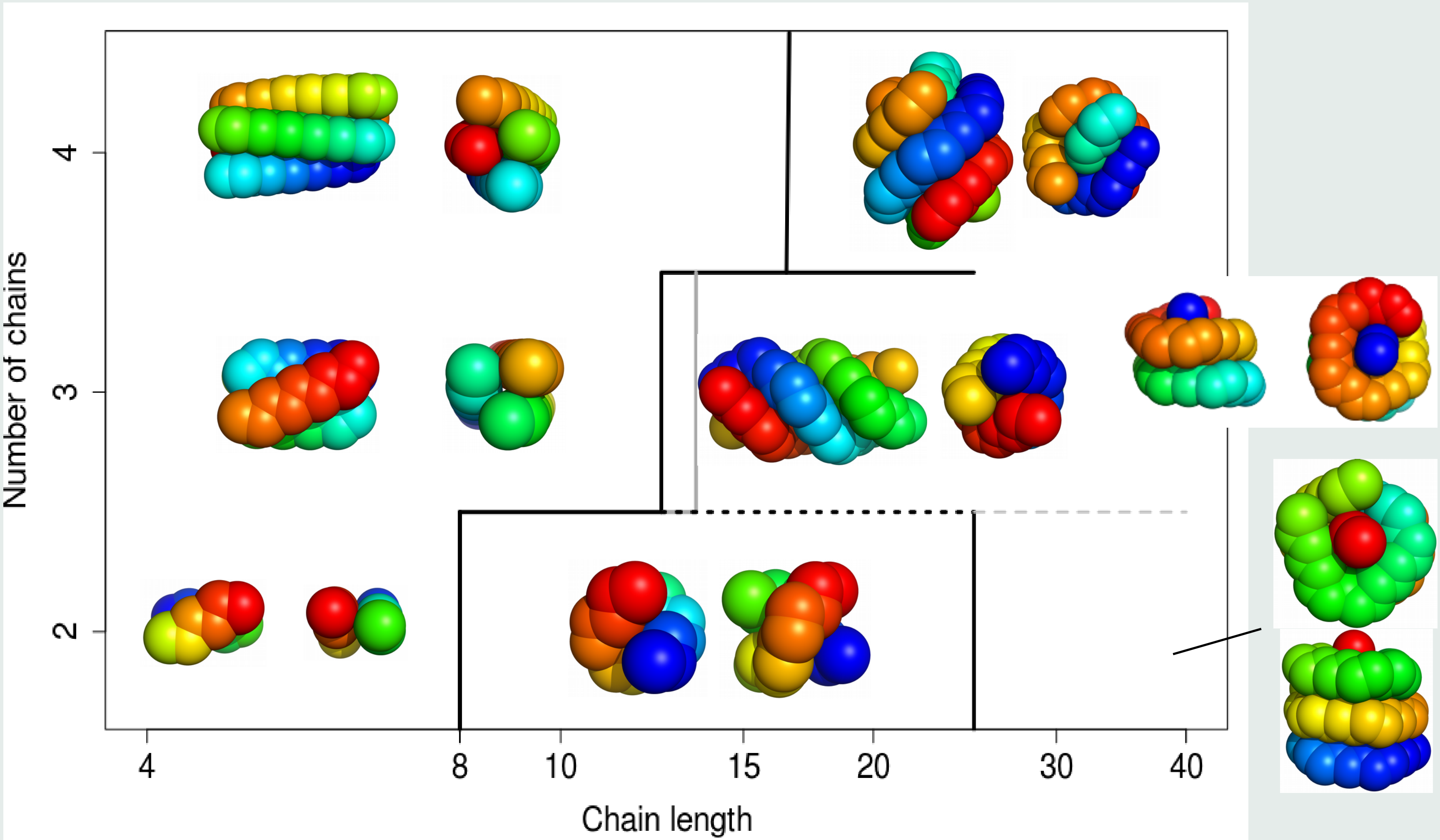


Diagram of low-temperature states of small aggregates



Conclusion

Simple syntetic homopolymers can have non-trivial series of ground states

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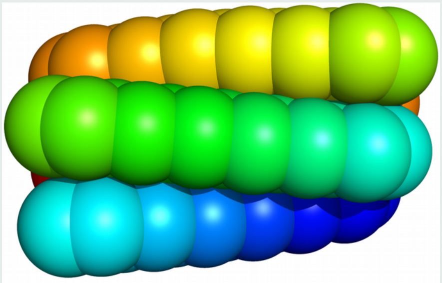
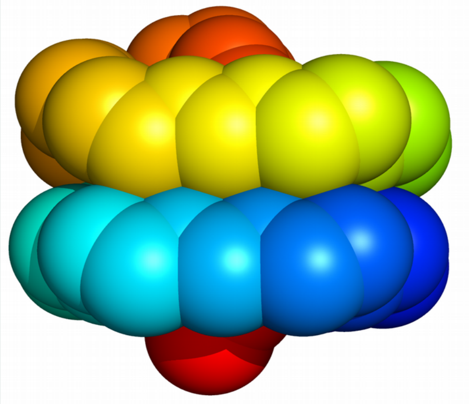
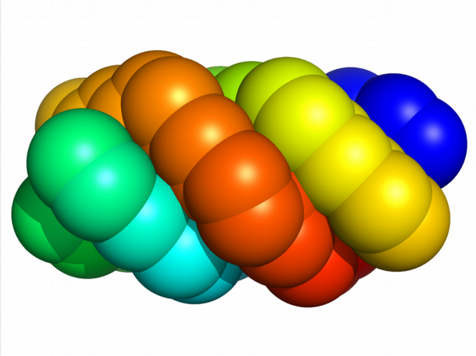
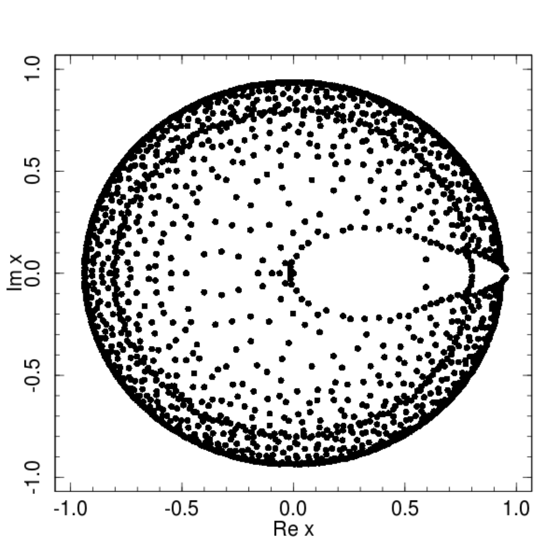
Partition function zeros can (may be) give information related not only phase transitions, but also structural changes

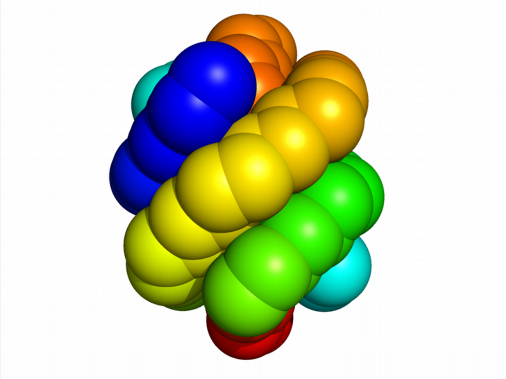
Thank you for your attention!

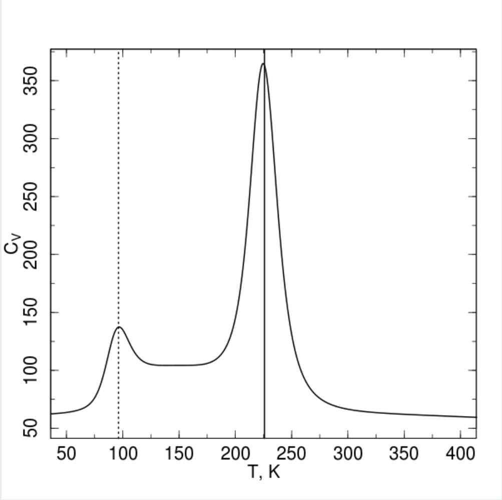




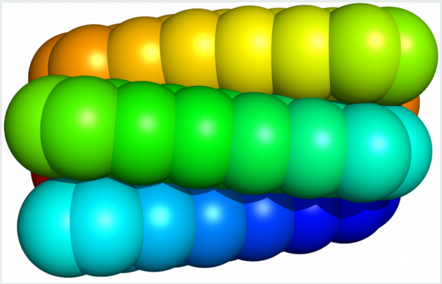


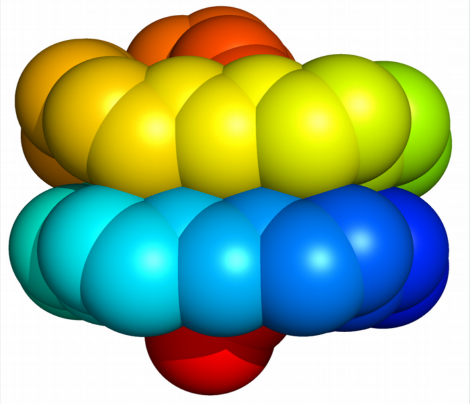


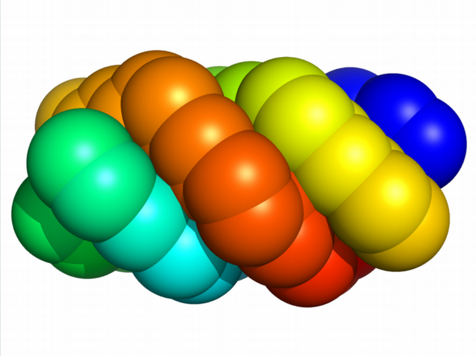


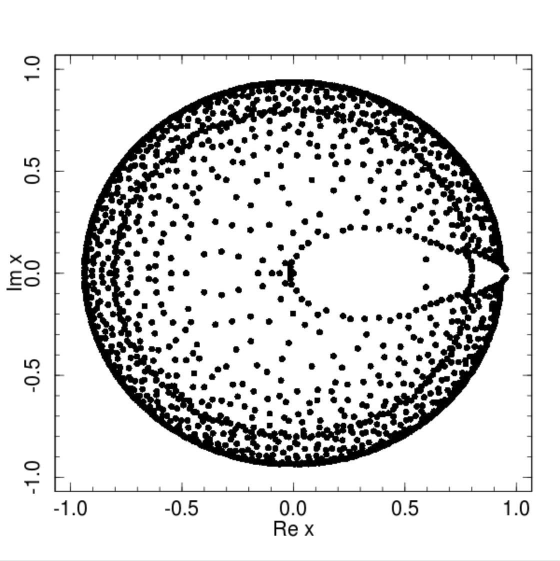


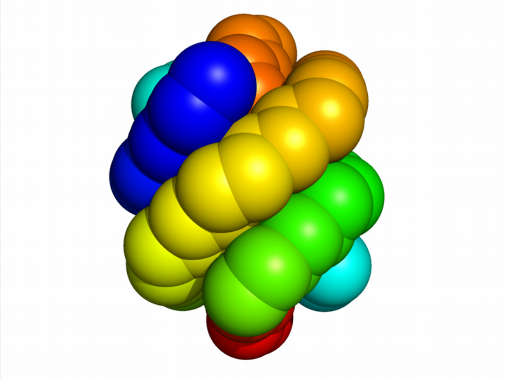
Thank you for your attention!

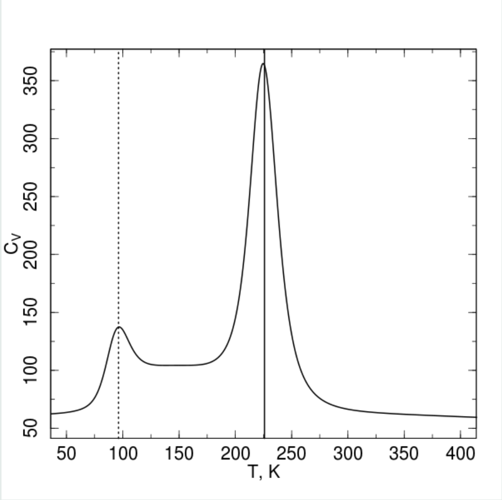




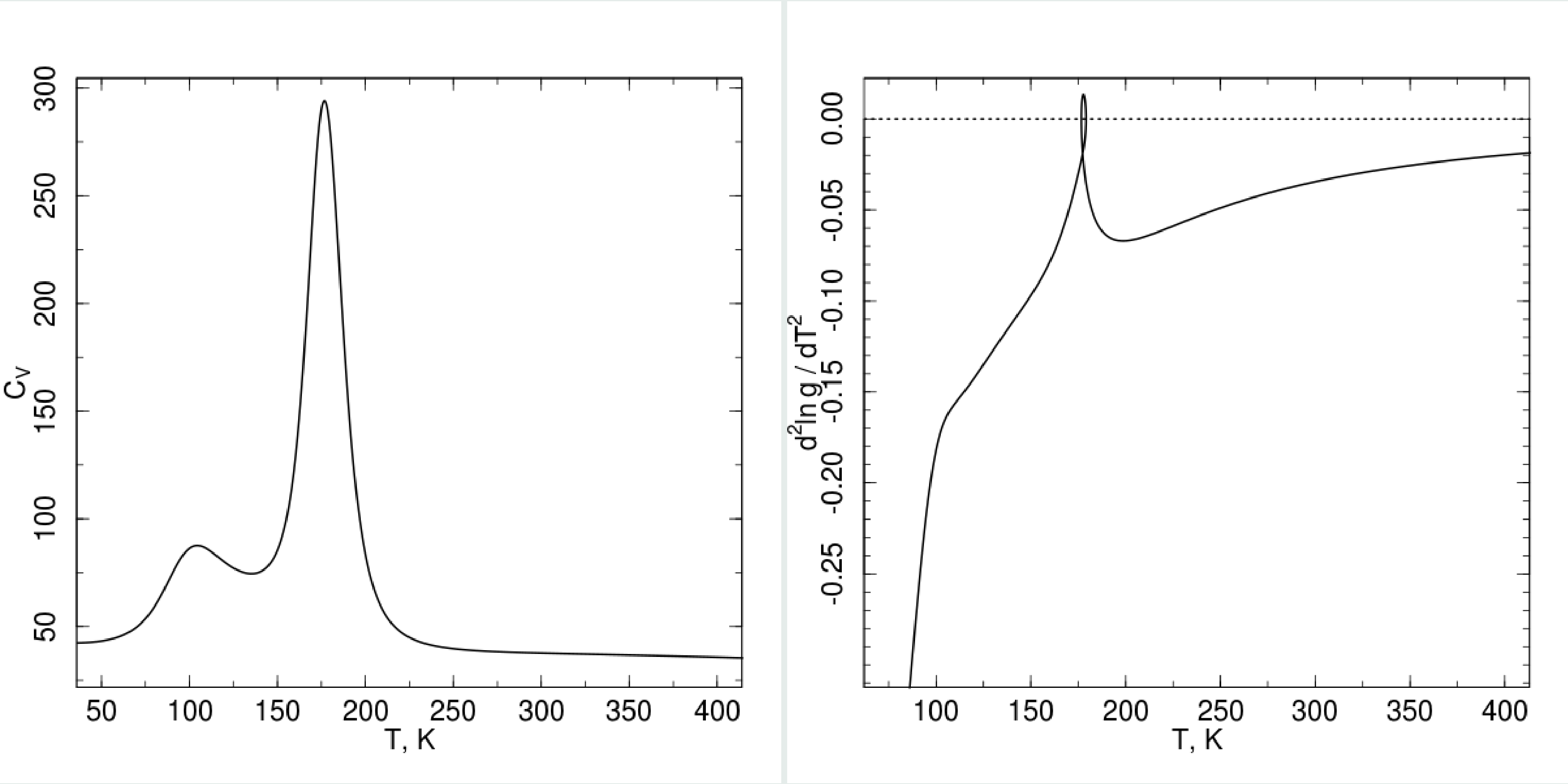








Heat capacity of 4 C_{10} system



Heat capacity of 5 C_{10} system