

## Overview

Although Flory theory provides a robust basis for the description of the collapse transition of polymers the predicted scaling behavior has not been confirmed in MC simulations due to the small size of the systems under investigation. A large degree of polymerization was only reached with simulations of lattice-polymers with short-range interactions [1]. We simulate large polymers with continuous degrees of freedom and long-range interaction using tree-based approach [2] combined with a novel modification to the well known Metropolis algorithm [3]. We employ two different strategies to obtain finite-size transition temperatures. One uses geometrical properties of the polymer, namely, its resemblance to a Gaussian random walk, while the other, the so-called Boyle temperature, is based on the second virial coefficient, i.e., the free energy of two interacting chains [4].

## Model and Method

### Polymer Model:

A bead-stick model with 12-6 Lennard-Jones interaction:

$$U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

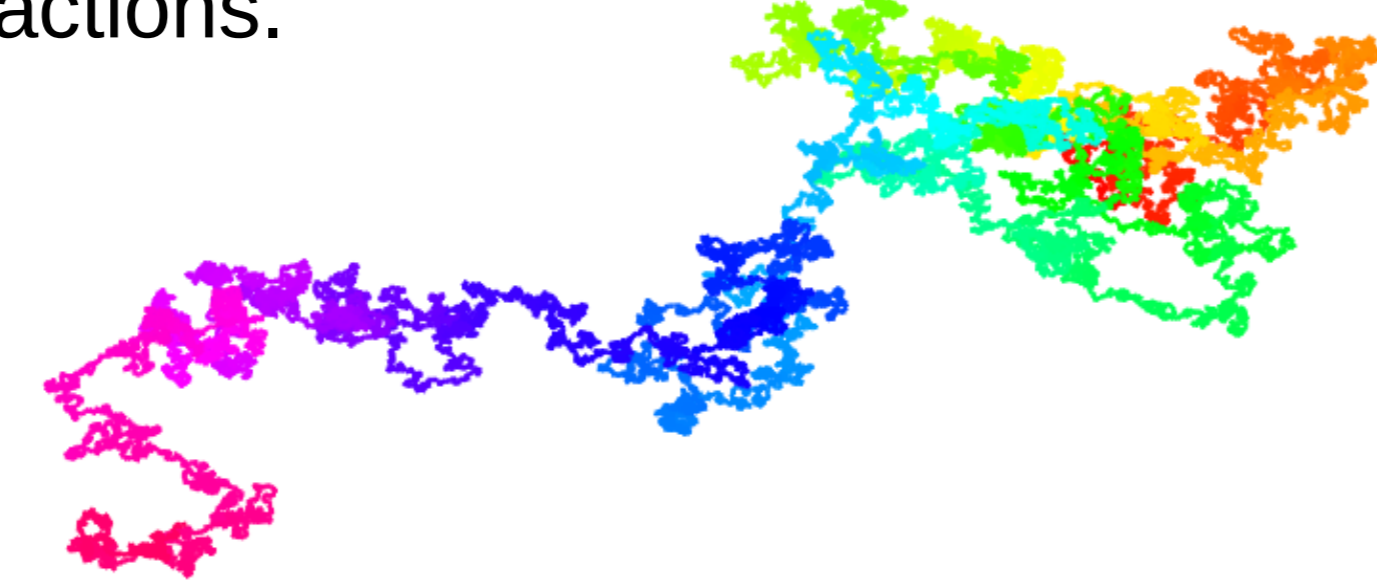
The fixed bond length matches the equilibrium distance of the potential:

$$|\mathbf{x}_{i+1} - \mathbf{x}_i| = 2^{1/6} \sigma$$

The Hamiltonian thus reads

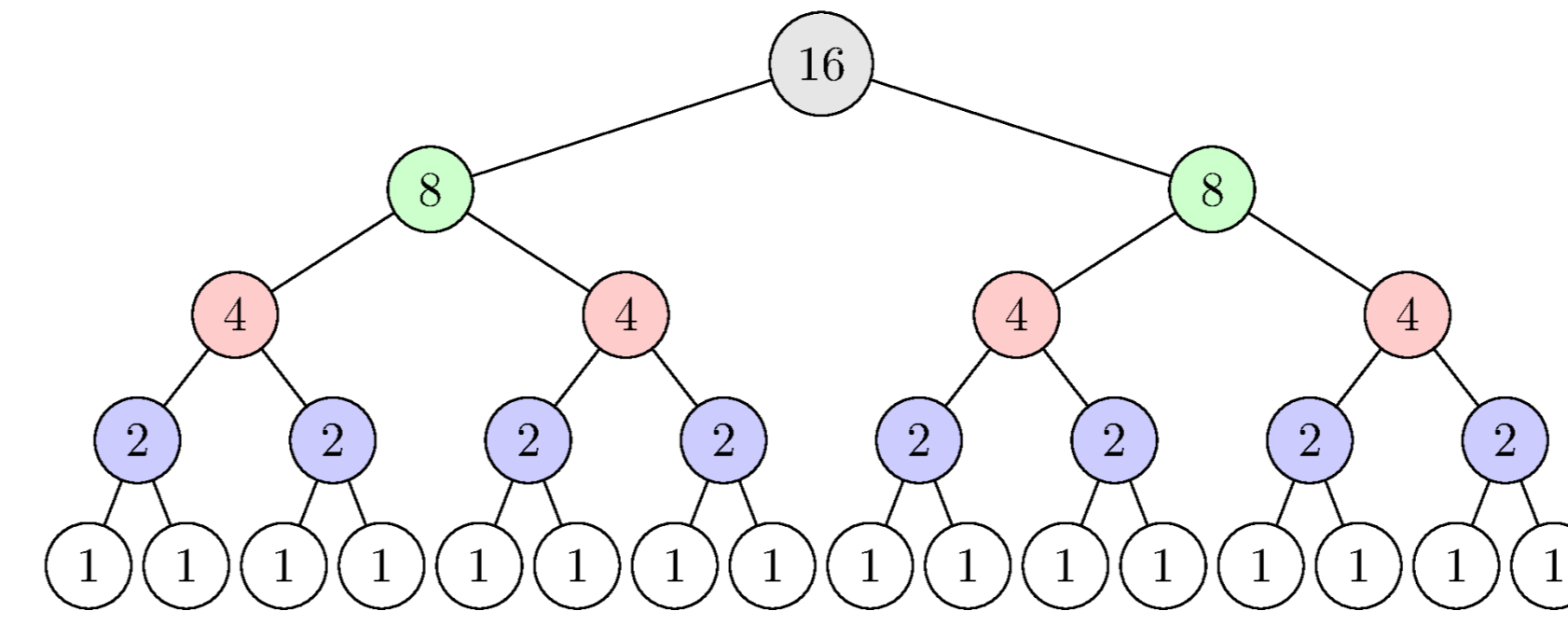
$$\mathcal{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N U_{LJ}(\mathbf{x}_i - \mathbf{x}_j)$$

and comprises  $N(N-1)/2$  monomer-monomer interactions.



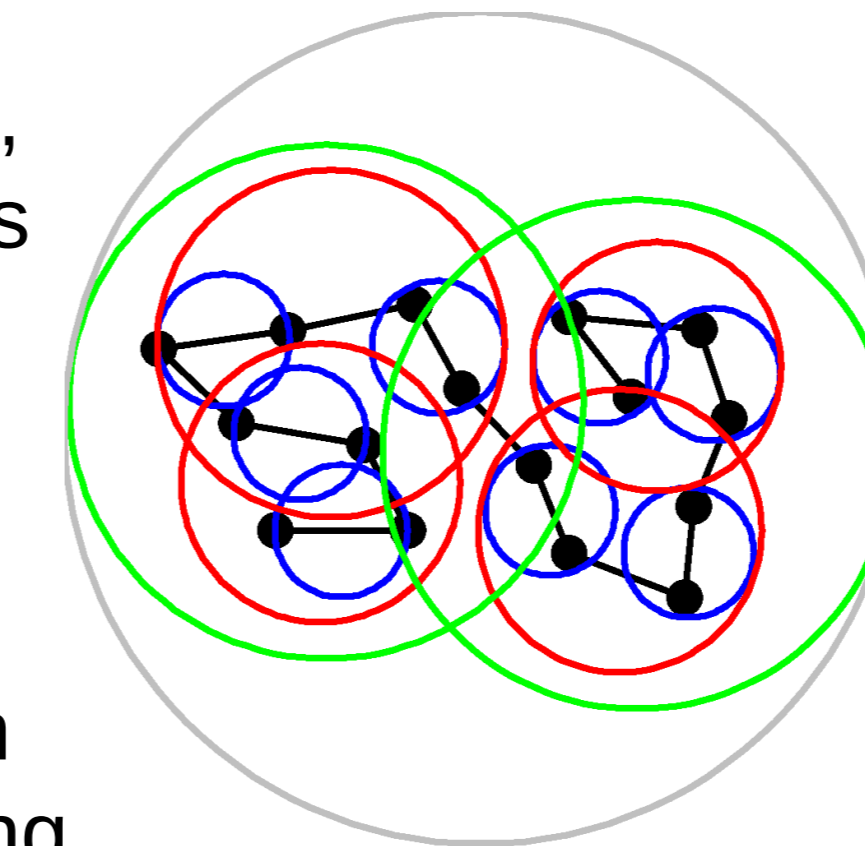
### Tree data structure:

The geometry of the polymer is stored in a binary tree with nodes representing groups of monomers



with individual monomers as leaves. Within each node the position and radius of a sphere containing all its monomers is stored.

If two spheres don't intersect, strict upper and lower bounds for the interaction of their respective groups of monomers can easily be established. The estimate of such a node-node interaction can be improved by estimating the four interactions between the child-nodes instead.



### Inverse Metropolis:

A proposed update from microstate  $\mu$  to microstate  $\nu$  is accepted with probability

$$W_{\text{accept}}(\mu, \nu) = \min \left( 1, e^{-\Delta E/k_B T} \right)$$

with  $\Delta E = \mathcal{H}(\nu) - \mathcal{H}(\mu)$ . The usual procedure is to calculate  $\Delta E$ , determine this probability, and to draw a uniformly distributed random number  $\xi \in [0, 1)$ . The update is accepted if  $\xi < W_{\text{accept}}(\mu, \nu)$ . We reverse this sequence: The last condition is equivalent to

$$\xi < e^{-\Delta E/k_B T}$$

and consequently to

$$\Delta E < -k_B T \ln \xi.$$

Now, we draw  $\xi$  first and estimate  $\Delta E$  with increasing precision until it can be decided whether the condition is fulfilled or violated. Using the binary tree, this can be done in a very efficient way. We are able to investigate system sizes up to  $N = 2^{14}$ , i.e., a Hamiltonian with more than  $10^8$  interactions. Measurements strongly suggest that the complexity for a single pivot step is reduced from  $\mathcal{O}(N^2)$  for a naïve implementation to  $\mathcal{O}(N \log N)$ .

## Theta-Temperature

### Using end-to-end distance:

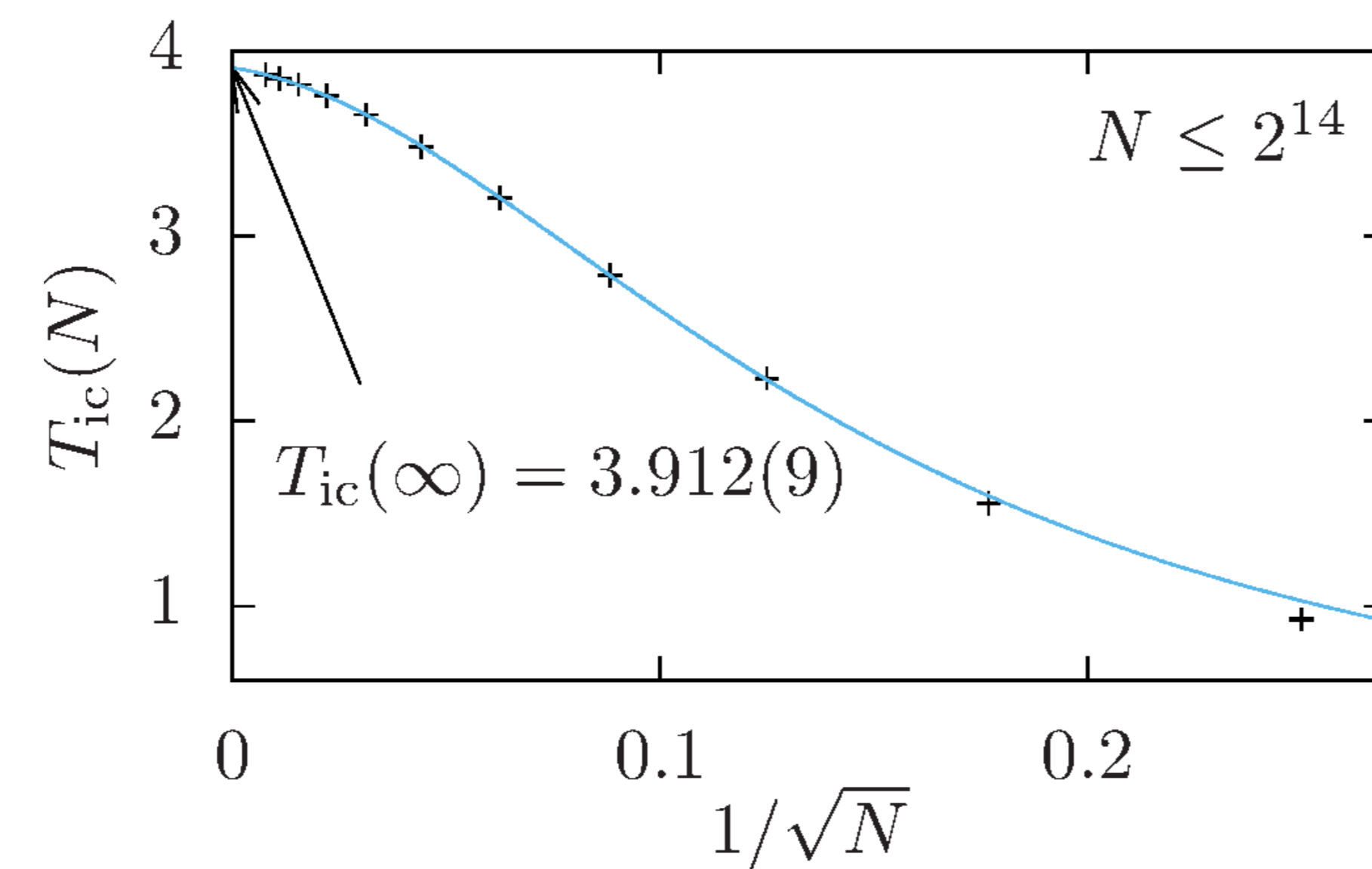
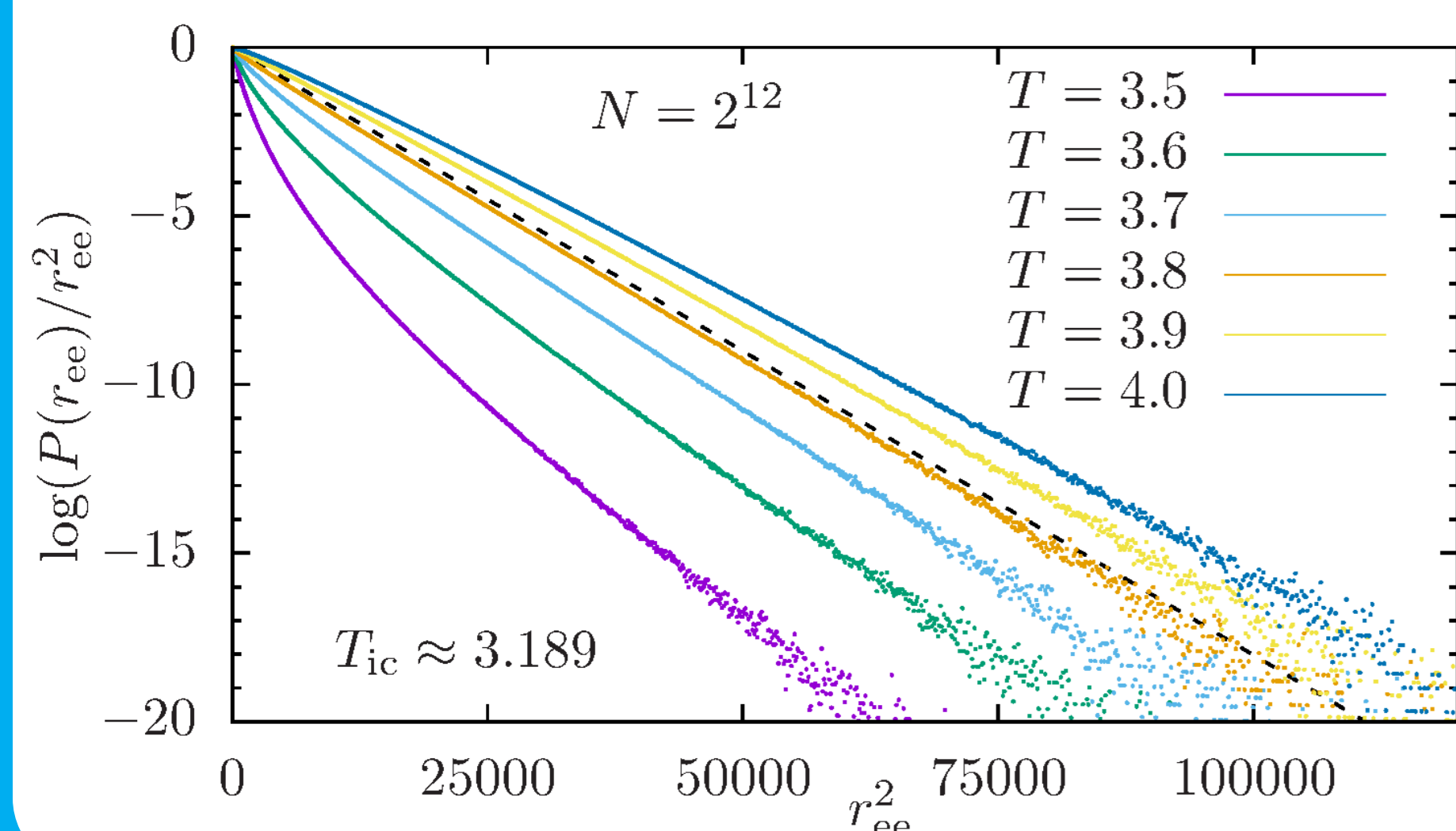
At the  $\Theta$ -point the polymer should behave like an ideal chain. This means that the absolute end-to-end distance

$$r_{ee} = |\mathbf{x}_N - \mathbf{x}_1|$$

is expected to be distributed according to

$$\log(P(r_{ee})/r_{ee}^2) \propto r_{ee}^2.$$

A proxy  $T_{ic}$  for the  $\Theta$ -temperature can be found by measuring this distribution and determining the temperature for which the above relation holds.



### Using Boyle temperature:

At the critical temperature  $T_\Theta$  for an infinitely large polymer the attractive forces are perfectly balanced by the excluded volume. Its finite-size equivalent is the Boyle temperature  $T_B$  which is the temperature at which the second virial coefficient

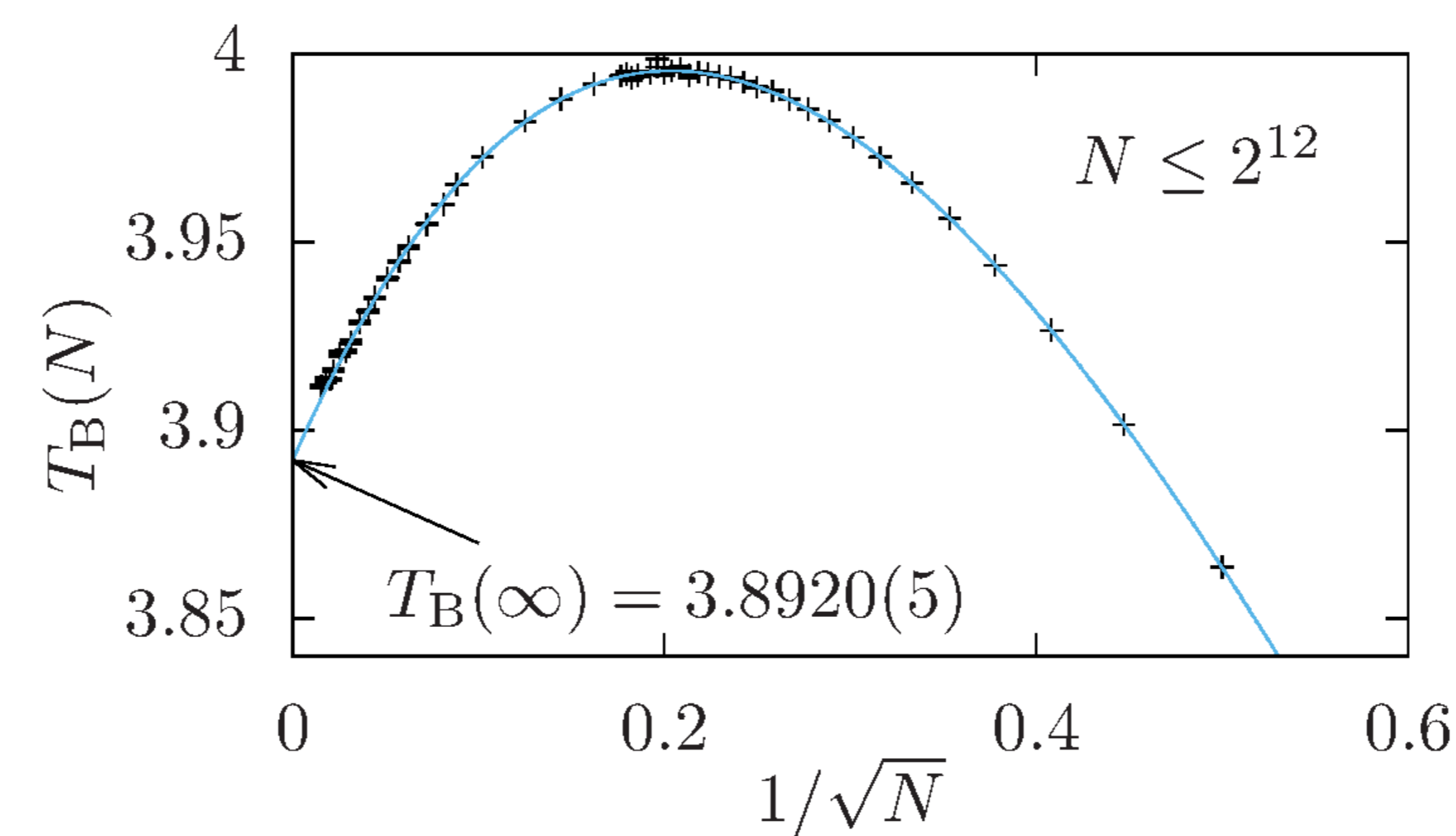
$$A_2(T, N) = \frac{\int e^{-\frac{\mathcal{H}(\mathbf{X}) - \mathcal{H}(\mathbf{Y})}{T}} \left( 1 - e^{-\frac{U(\mathbf{X}, \mathbf{Y})}{T}} \right) d\mathbf{X} d\mathbf{Y}}{2Z(N, T)^2},$$

$$= \frac{1}{2} \langle 1 - e^{-\frac{U}{T}} \rangle,$$

vanishes. Here, the interaction of two chains with conformations  $\mathbf{X}$  and  $\mathbf{Y}$  is given by

$$U(\mathbf{X}, \mathbf{Y}) = \sum_{i=1}^N \sum_{j=1}^N U_{LJ}(\mathbf{x}_i - \mathbf{y}_j)$$

Using the binary tree, the interaction energy between two polymers and consequently  $A_2$  and  $T_B$  can be determined very efficiently.



## Conclusion

The proposed Metropolis algorithm in combination with the binary tree data structure allows for the investigation of very long chains. The two methods of finding the  $\Theta$ -temperature agree very well in the thermodynamic limit, but produce surprisingly different results for finite  $N$ . We find no evidence for logarithmic corrections.

## Acknowledgment

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## References

- [1] T. Vogel, M. Bachmann, and W. Janke, Phys. Rev. E **76**, 061803 (2007).
- [2] N. Clisby, J. Stat. Phys. **140**, 349 (2010).
- [3] S. Schnabel and W. Janke, Comput. Phys. Comm. **256**, 107414 (2020).
- [4] P. Grassberger and R. Hegger, J. Chem. Phys. **102**, 6881 (1995).