

Effect of stoichiometry on locally favoured structures in the Kob-Andersen mixture

1. Locally Favoured Structures

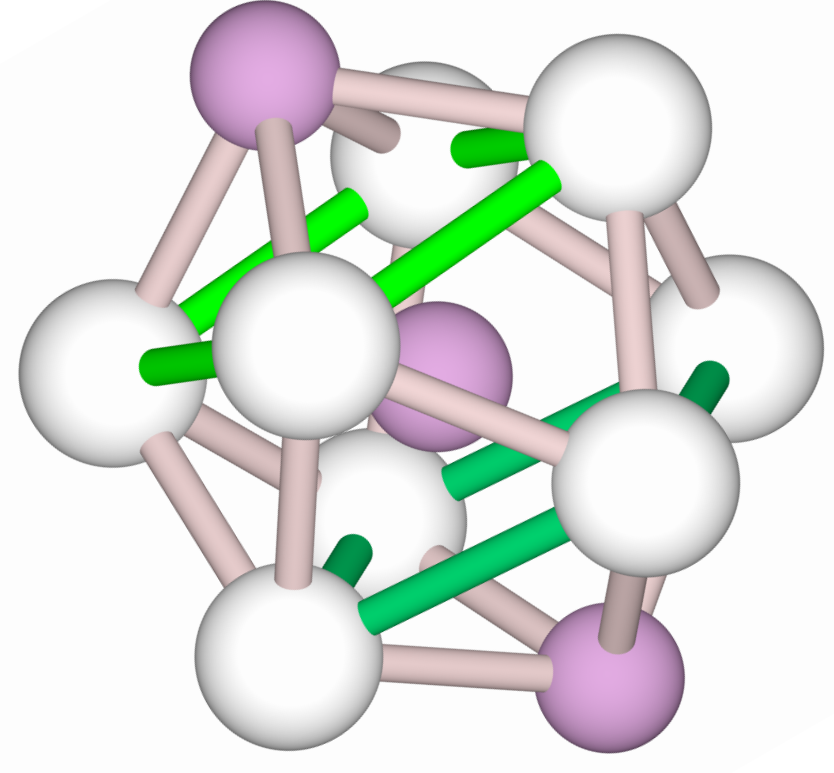


Fig. 1 A bicapped square antiprism with A (white) and B (purple) particles.

The **Kob-Andersen** (KA) binary mixture is a model glassformer homologous to $\text{Ni}_{80}\text{P}_{20}$, a **metallic glass** [1]. It is composed of 80% **large** (A) and 20% **small** (B) Lennard-Jones particles of equal mass that interact with non-additive interaction potentials. Locally ordered structures (bicapped square antiprims, also known as **11A**) are typically formed upon cooling [2]. One particular 11A structure (**A_8B_3**) is, *a priori*, compatible with a bulk crystal structure, analogous to the 3D tessellation seen in the Al_2Cu crystal structure, yet the typical **concentration** of A_8B_3 in a KA mixture is **very low**.

In order to determine whether the **stoichiometry** of the mixture is a factor in the frustration of crystallization, we vary it from the normal 4:1 ratio and analyse the change in the distribution of locally favoured structures.

2. Slow Relaxation

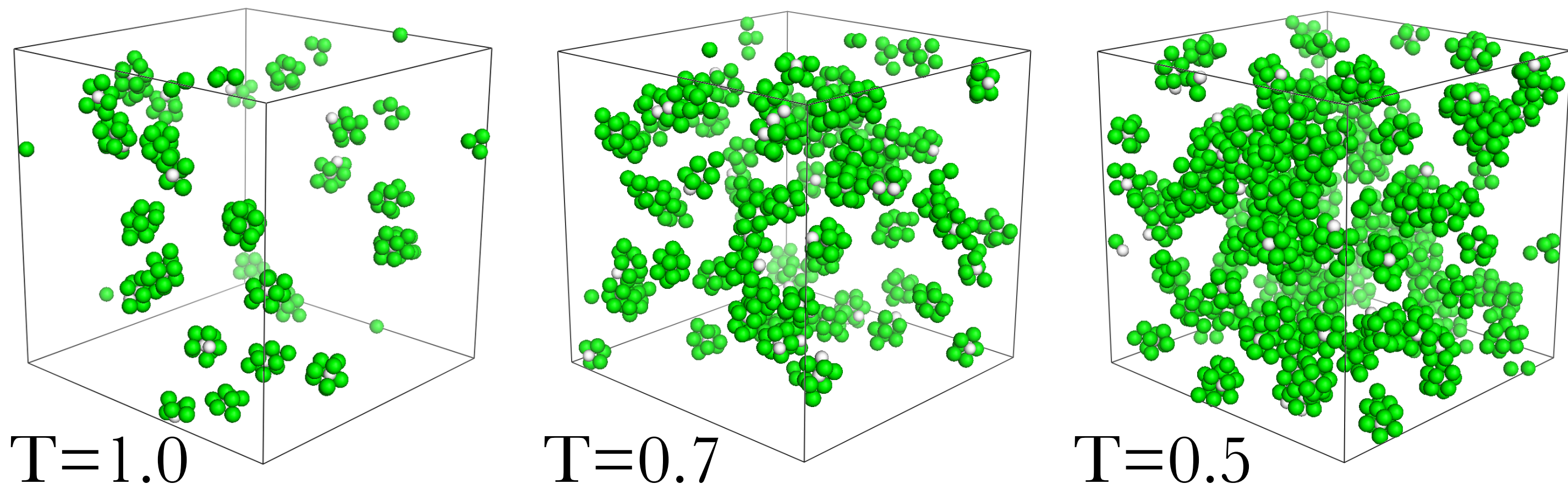
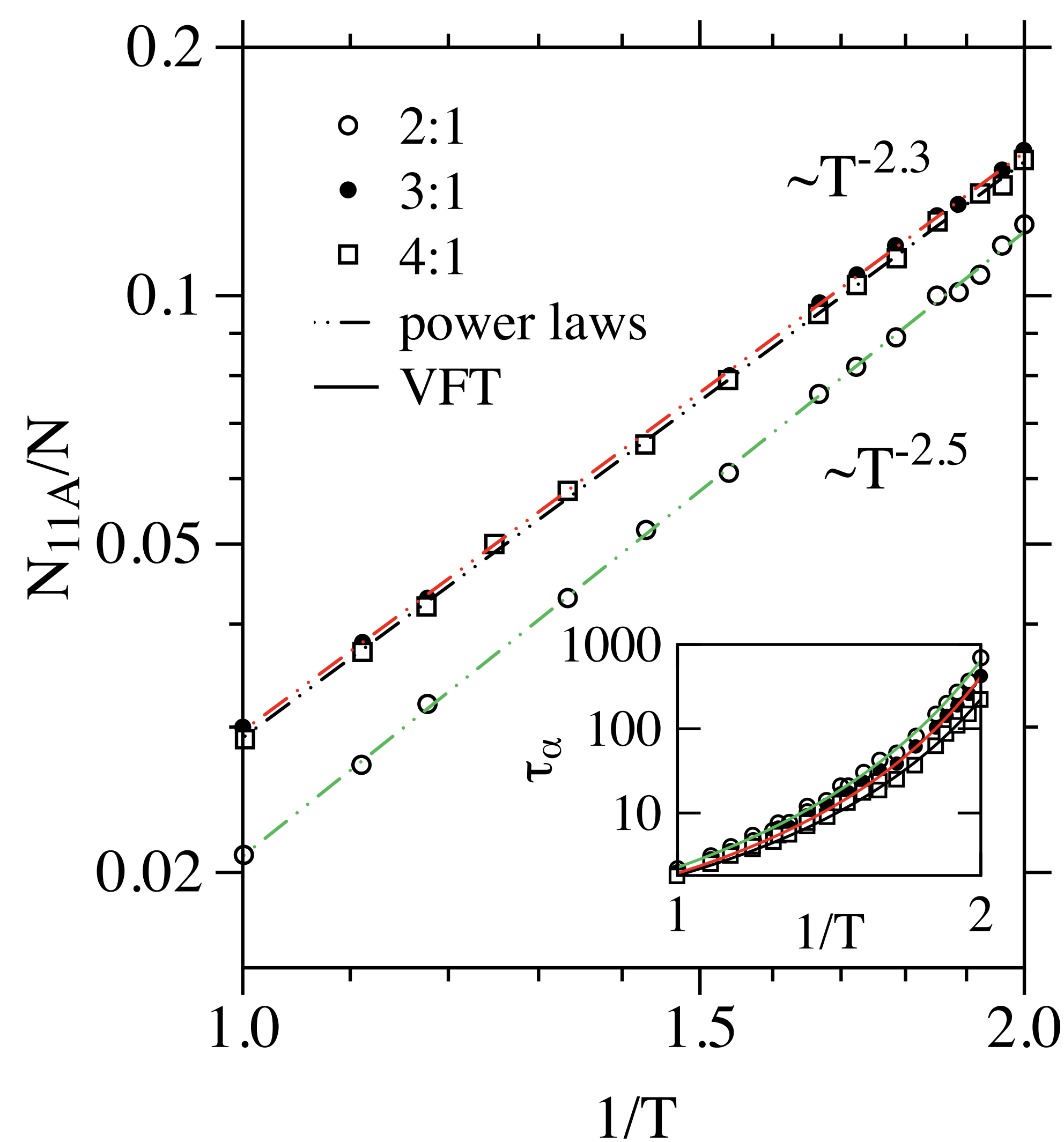


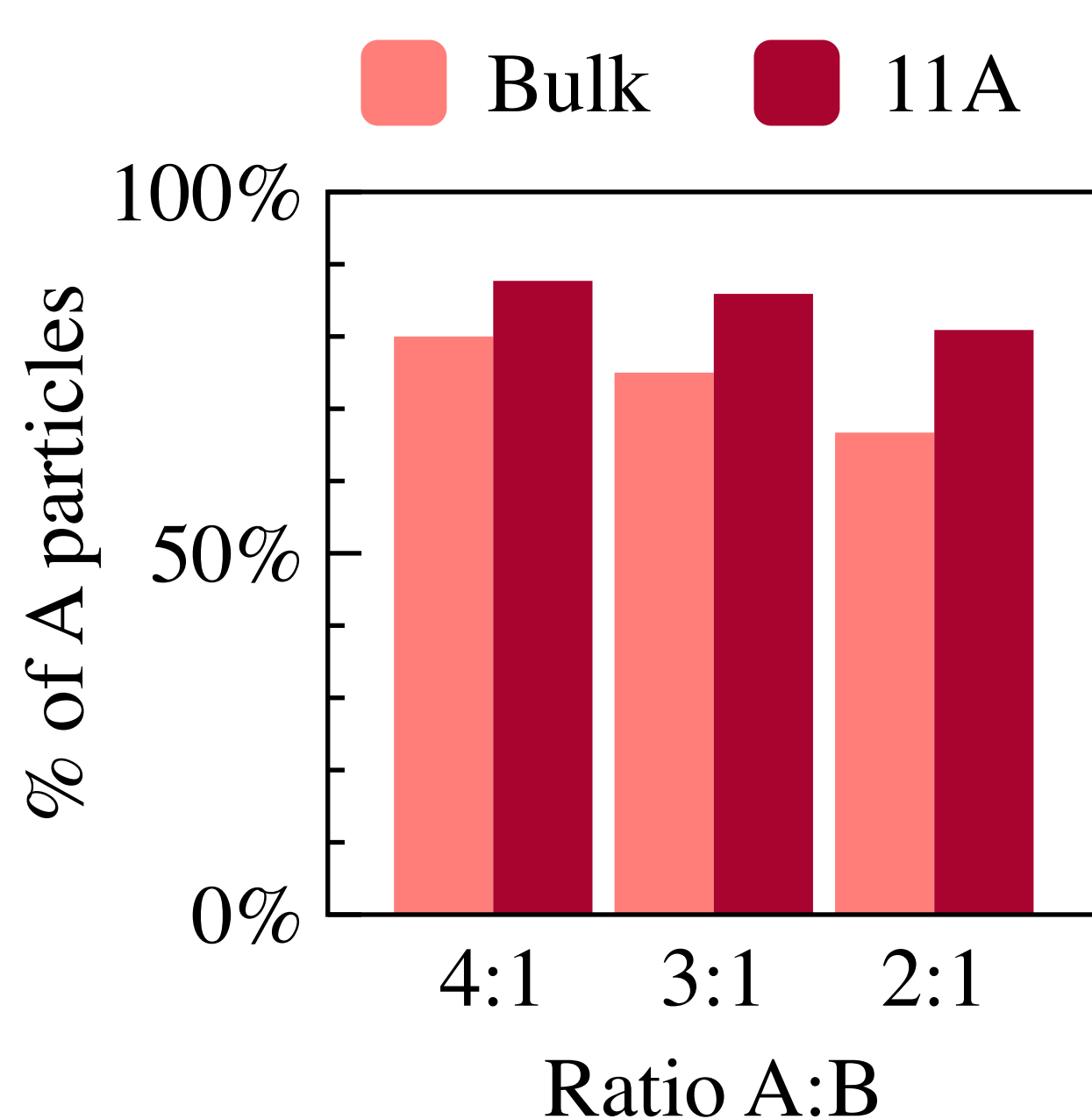
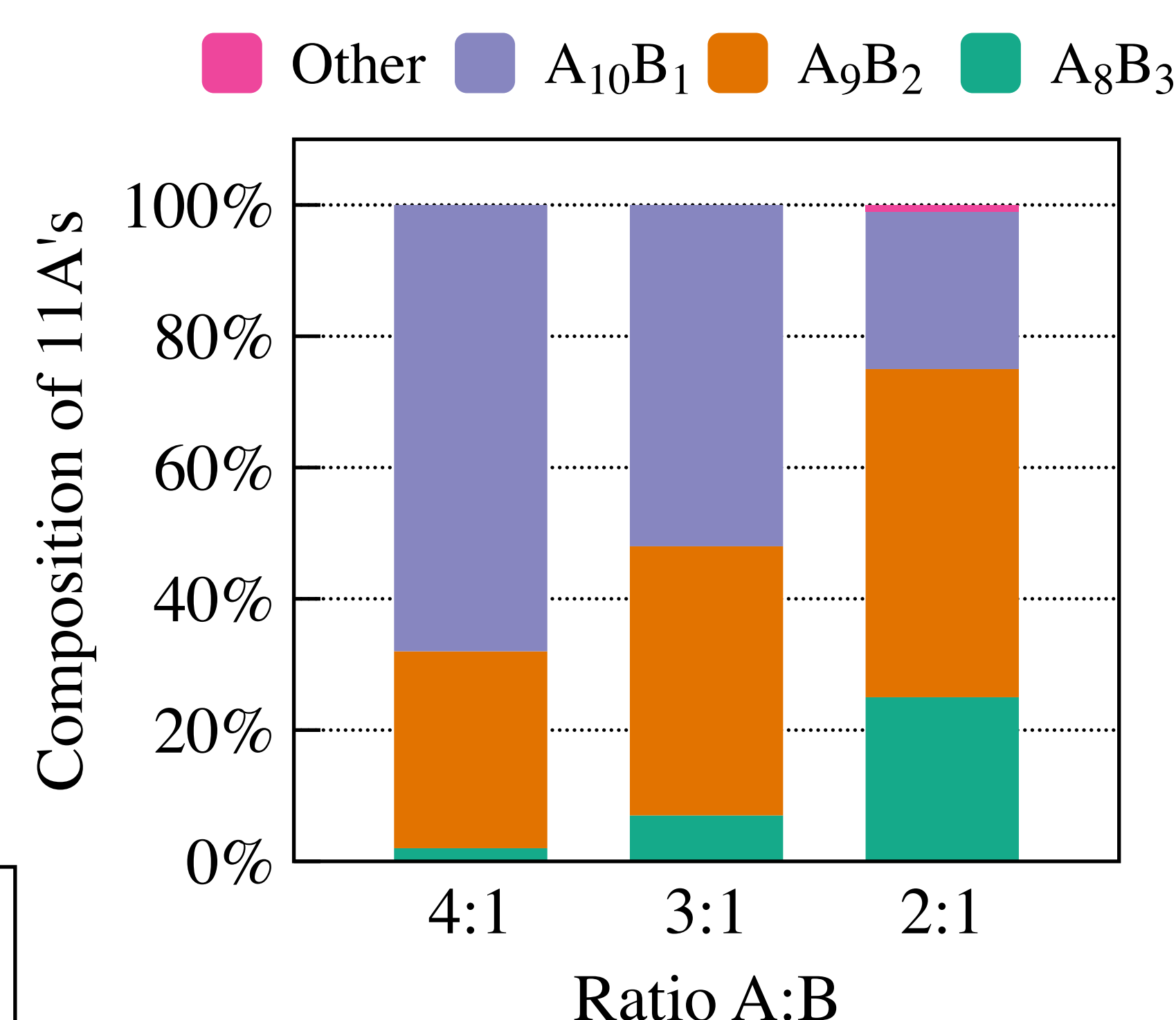
Fig. 2 Increase in number of 11A clusters with decreasing the temperature of the normal KA 4:1 mixture. Only cluster particles are shown.

By varying the density of the mixture to give a constant **pressure** reference for the different stoichiometries, we determined the empirical scaling law relating the **fraction** of particles in **11A** structures to the temperature decrease, coupling it to the Vogel–Fulcher–Tammann increase of the **relaxation time**.



3. Change in Composition

Changing the stoichiometry leads to an **increase** in the relative fraction of **A_8B_3** clusters. However, they only represent a minor fraction of the 11A structures, suggesting that further frustration mechanisms occur.



11A clusters are primarily composed of **A particles**, with a greater percentage of A particles present in the 11A clusters than in the overall solution.

4. Minimum Energy of a Cluster

Cluster	Energy (ϵ)
$A_{10}B_1$	-39.44
A_9B_2	-41.59
A_8B_3	-43.62

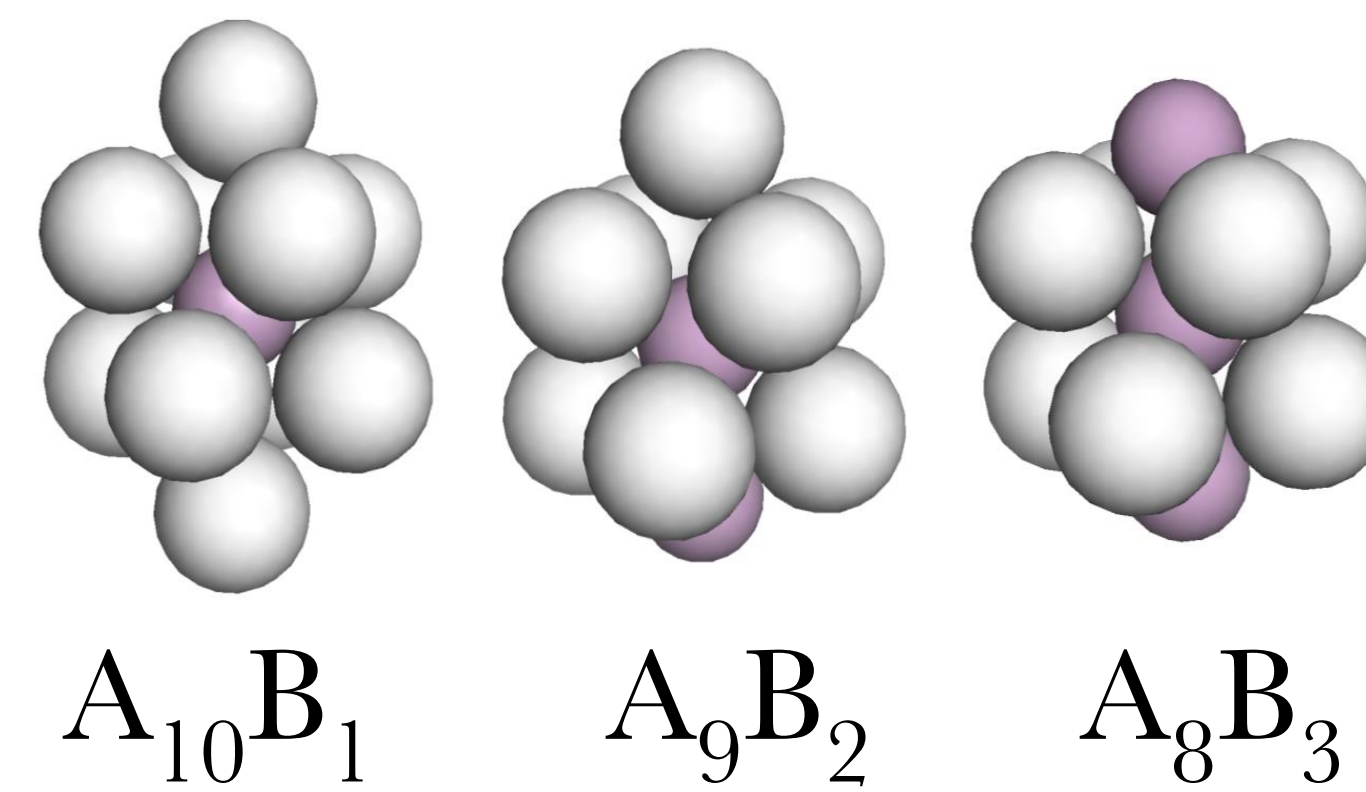
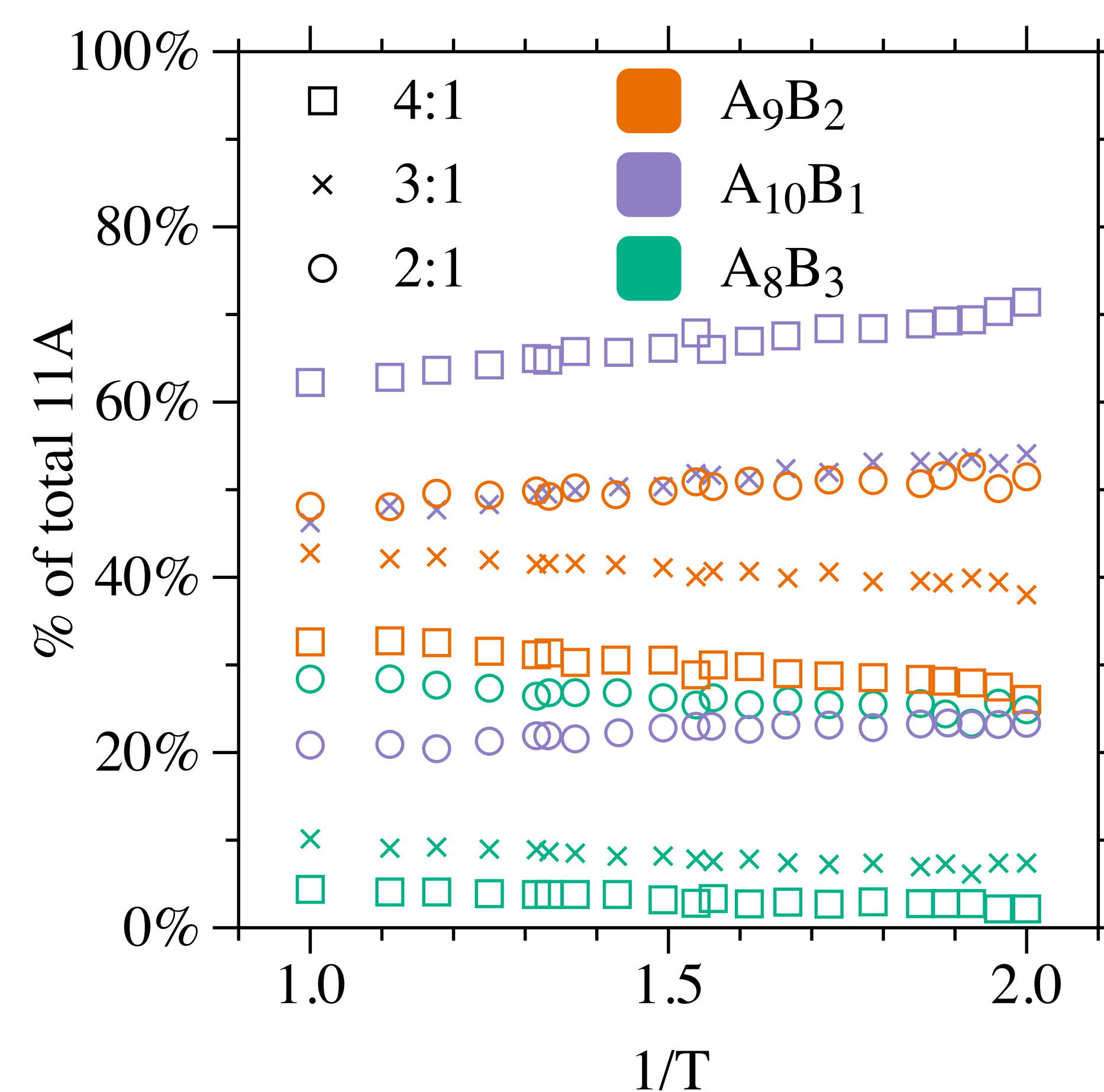


Fig. 3 Energy minimised 11A clusters with A particles in white and B particles in purple.

Using an **energy minimization** algorithm (GMIN[3]) we determined the energies of **isolated** 11A clusters.

$A_{10}B_1$ is the **highest energy** cluster, its **high concentration** in the mixtures has to therefore have an **entropic** (rotational symmetry around a larger radius of gyration) [4] or a **kinetic** origin (assembly of the clusters), or both.

5. Temperature Dependence



With decreasing temperature, the composition of 11A clusters changes gradually. One observes that decreasing the temperature **decreases** the fraction of particles in **A_8B_3** or leaves it unchanged for all the stoichiometries. In the case of 2:1, the reduction in temperature favours **A_9B_2** clusters.

Altering the ratio of A:B particles in the KA mixture leads to an increase of crystal forming A_8B_3 11A clusters from 3% to 25% of the total 11A composition.

However, for kinetic and/or entropic reasons, the majority of the 11A clusters remain non-tassellating in Euclidean space, leading to **frustration** and slow dynamics.

References & Acknowledgements

- [1] Kob W, Andersen HC. Phys. Rev. E. **51**, 4626 (1995).
- [2] Speck T, Malins A, Royall CP. Phys. Rev. Lett. **109**, 195703 (2012)
- [3] Wales DJ. <http://www-wales.ch.cam.ac.uk/GMIN/> 2014
- [4] Malins A et al. Journal of Physics: Condensed Matter. **21**, 425103 (2009).

The authors acknowledge the support of ERC project NANOPRS, Grant PHYS RQ8903. C.P. Royall is also supported by the Royal Society.