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The free energy of singular sticky-sphere clusters YOAV KALLUS, Santa Fe Institute, MIRANDA HOLMES-CERFON, Courant Institute of Mathematical Sciences — Many model systems for self-assembly use colloidal particles with an interaction range much smaller than their diameter. The cluster chemistry of such particles can be studied in a universal approach, independent of the particular interaction potential shape, by use of the “sticky sphere” limit. Rigid clusters—contact arrangements such that no nonrigid motion is available without breaking at least one contact—take the place of energy minima, with energy determined by the number of contacts. The relative stability of rigid clusters with the same number of contacts is determined by entropic contributions, such as the vibration entropy. The harmonic approximation gives the leading asymptotic term in the vibration entropy if the cluster has no zero-frequency modes, but diverges otherwise. We derive the leading asymptotic term for singular clusters. We use our result to characterize the free-energy landscape of a system of sticky spheres by calculating the free energy of rigid clusters of up to $N = 19$ particles, which have been previously enumerated.

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