Effect of Non-Conformal Contact in the Self-Limiting Assembly of Curved Particles

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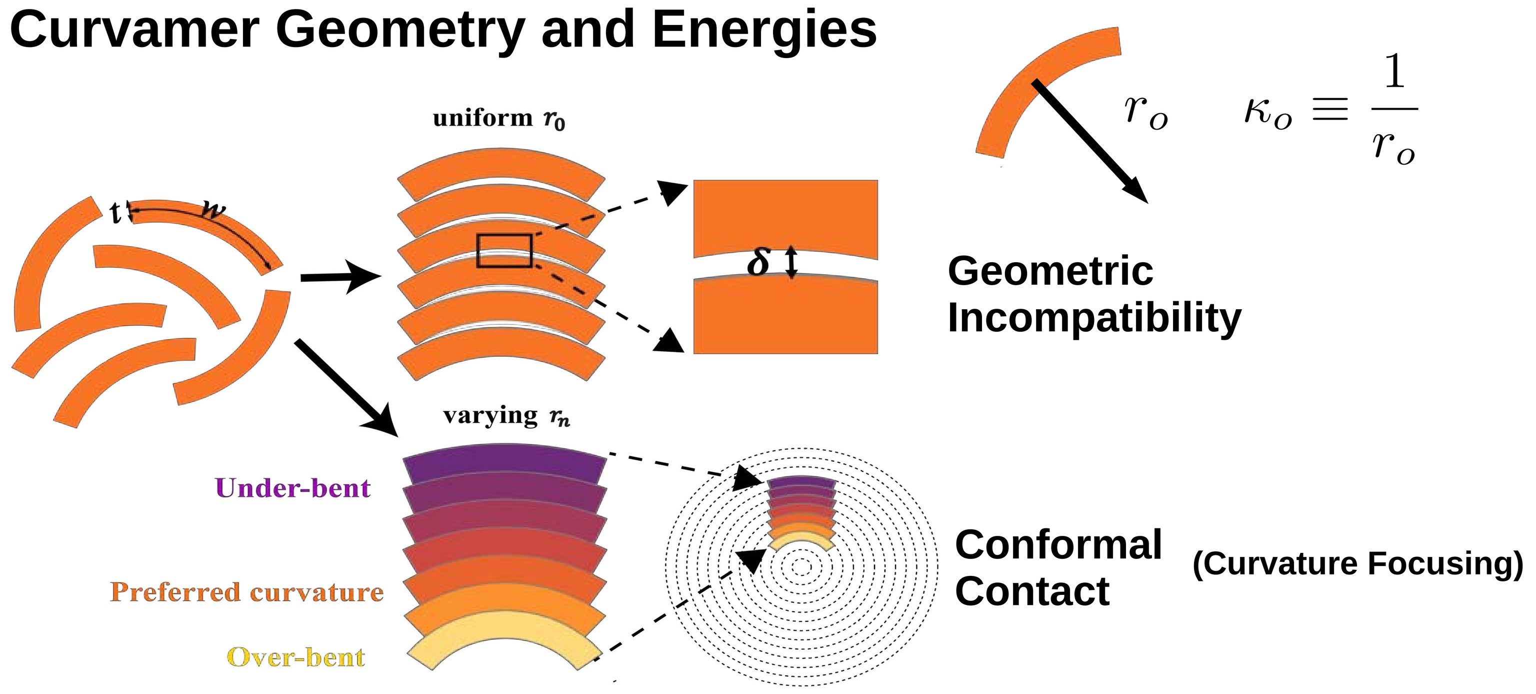
Abstract

When two identically-shaped, curved particles are attracted to each other, they must bend away from their preferred curvature in order to maintain a perfectly gap-less, or conformal, contact surface. This is due to geometric incompatibility between the top surface of one particle and the bottom surface of another. This bending introduces a stress which increases as the particle stack grows in size. Since the stack cannot satisfy both conformal contact and preferred curvature, the system becomes frustrated. We aim to utilize this geometrically-induced frustration as a means to limit the self-assembly size of the particle stack to some programmed finite value. However, one particularly important mode of escaping frustration is non-conformal stacking. Here we study the effect of this escape mode by introducing an harmonic adhesive potential which allows for small openings between stacked particles. We find that the ability to form gaps imposes a theoretical upper bound to the finite self-assembly size of the stack, an understanding of which is critical to determine the feasibility of particle stack sizes for various experimental techniques.

Curvamer Geometry and Energies

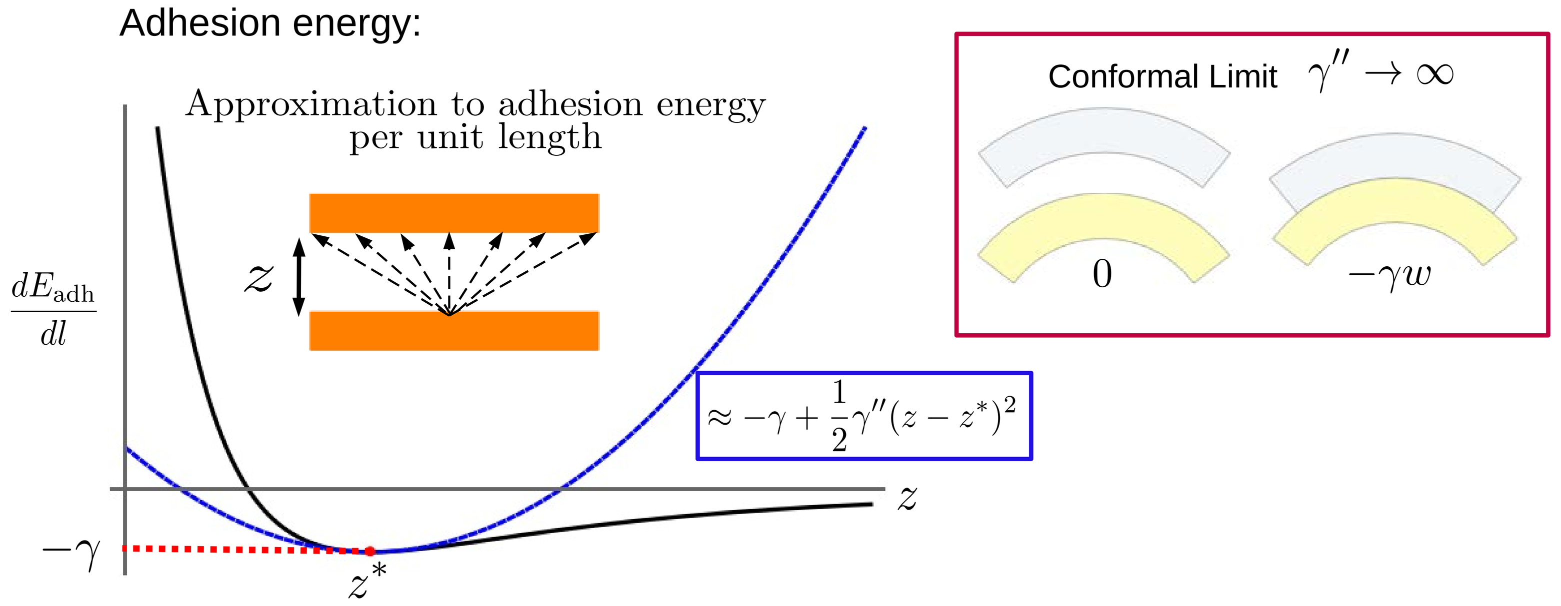


Cannot satisfy both preferred geometry and conformal contact $\Longrightarrow$ System becomes frustrated

Main Idea: Use geometric frustration as a mechanism to limit self-assembly

Bending energy: $E_B = \frac{1}{2}Bw(\kappa - \kappa_o)^2$

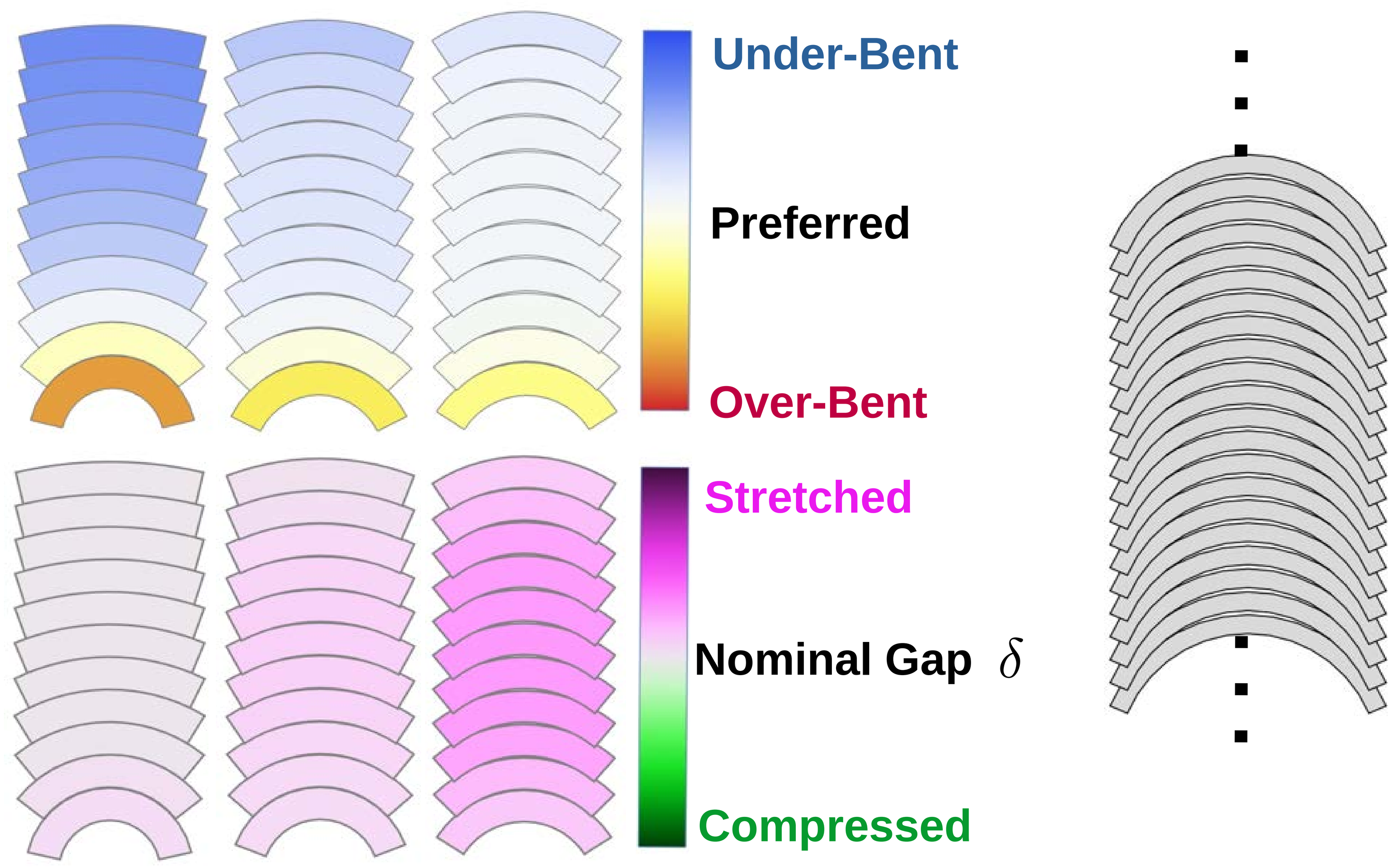
Adhesion energy:



Non-conformal stacking is likely a major method for the system to escape frustration.

An harmonic potential allows for pairs to stack with gaps, via an effective particle interaction range.

Mechanically-Equilibrated Solutions and Infinite Stacks

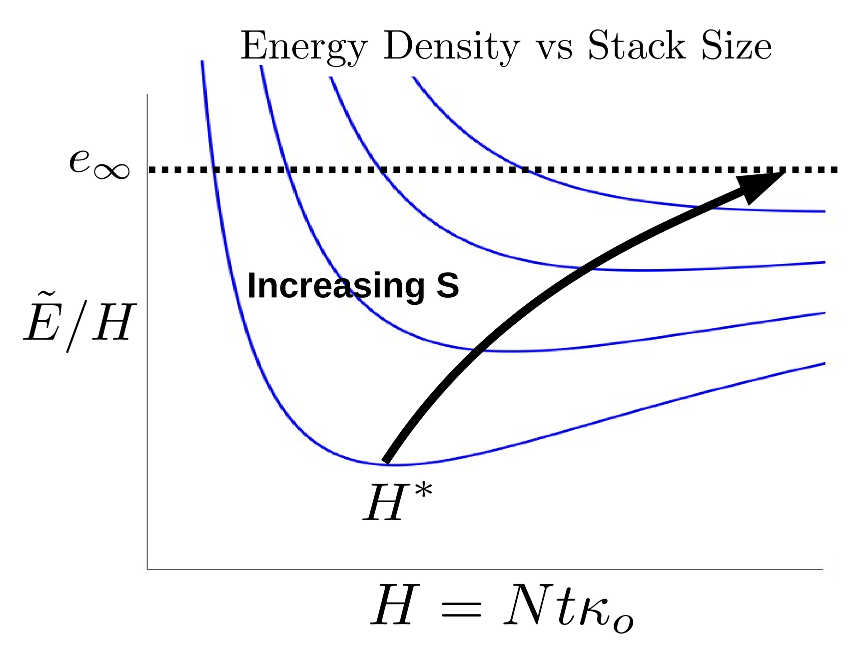


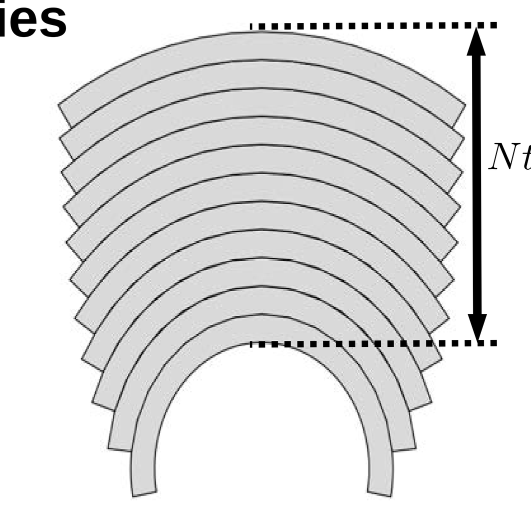
Gaps grow as the effective interaction range increases, but if it increases too much finite solutions disappear and only infinite stacks of identically curved particles becomes possible.

Thus a maximum mechanically-equilibrated stack size is introduced.

What it the mechanical reason finite solutions disappear?
Is this also true for higher order approximations?

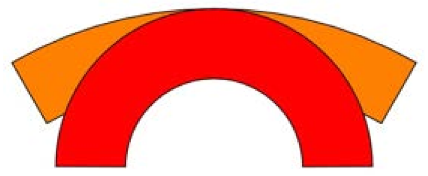
Self-Limitation and Characteristic Energies



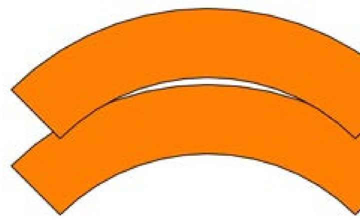


Self-limitation occurs at the minimum of the energy density curve.

Bending energy to flatten
(intra-particle stiffness) $\epsilon_B = wB\kappa_o^2$

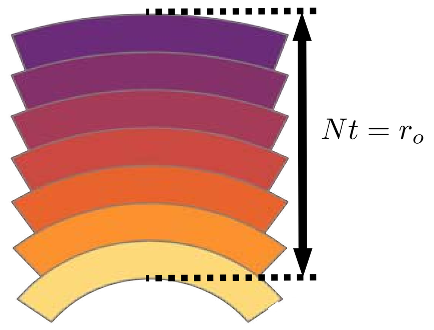


Energy for stiff particles to adhere
(inter-particle gap stiffness) $\epsilon_A = \gamma'' w \delta^2$



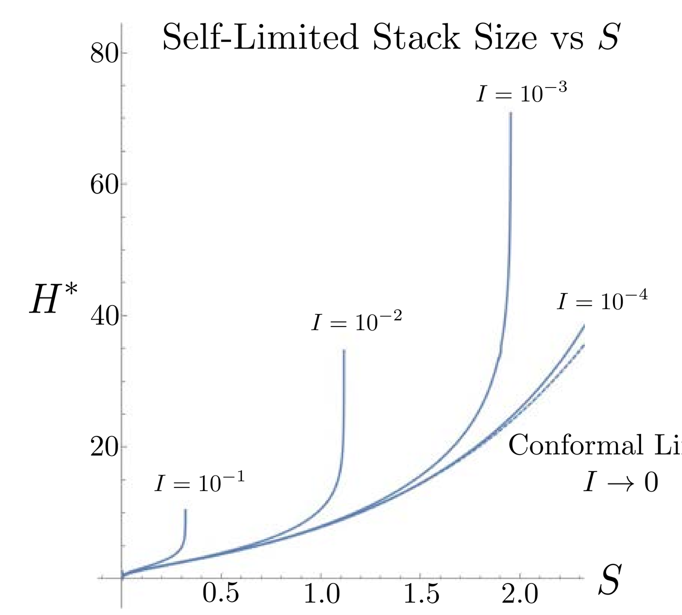
Cohesive boundary cost
(cost to not bind at the boundary when H=1 or Nt = ro) $\epsilon_C = \gamma w t \kappa_o$

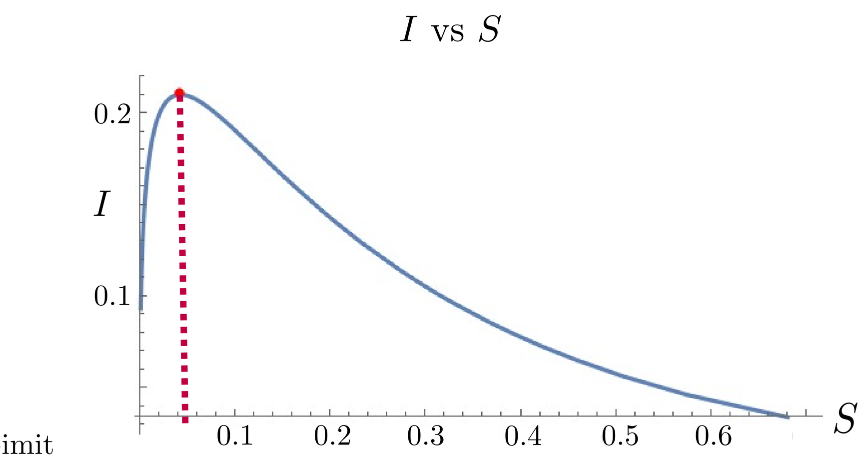
$\epsilon_{bind} = -\frac{\gamma w(N-1)}{N} = -\gamma w + \frac{\gamma w}{N} = -\gamma w + \gamma w t \kappa_o$



Dimensionless System Parameters

$$S = \frac{\epsilon_C}{\epsilon_B} \qquad I = \frac{\epsilon_C}{\epsilon_A}$$





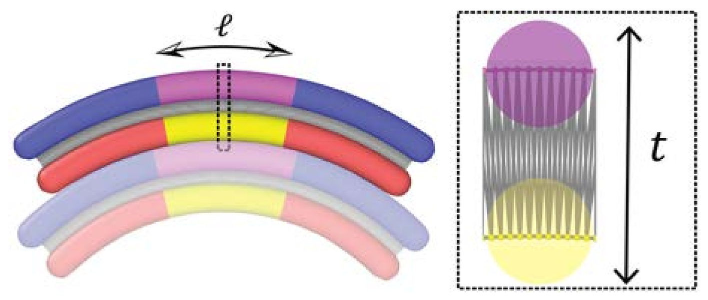
$I_{\max} = 0.211$
$S^* = 0.042$
$H^*(I_{\max}, S^*) = 3.01$

Theoretical Takeaways

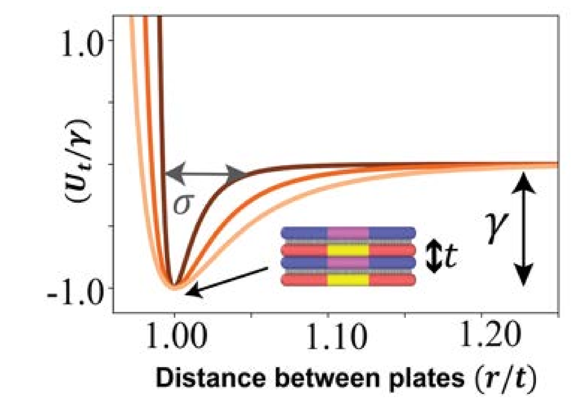
Non-conformal contact is a frustration escape mode which can be characterized by dimensionless parameter I, a function of geometric and particle interaction parameters. Non-zero I allows gaps to form within the particle stack but also introduces a maximum self-limiting stack size. The greatest range of self-limiting stack sizes is obtained by minimizing I, which can best be accomplished by having short range particle interactions and adjusting geometric constants. For the maximum value of I that still allows self-limitation, the corresponding stack size is H = 3.

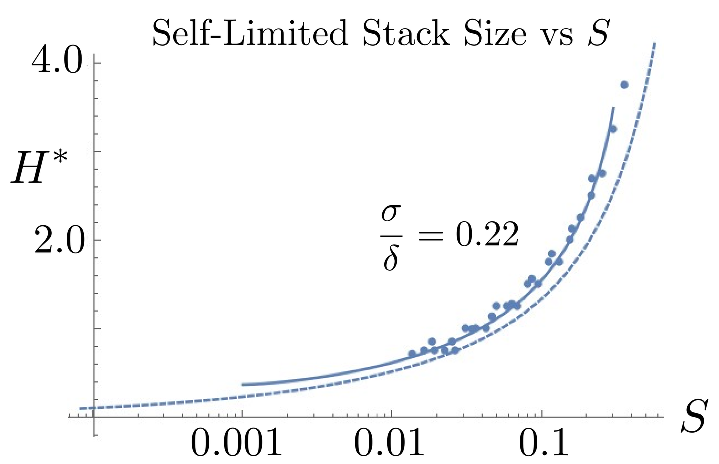
Molecular Dynamics Simulations

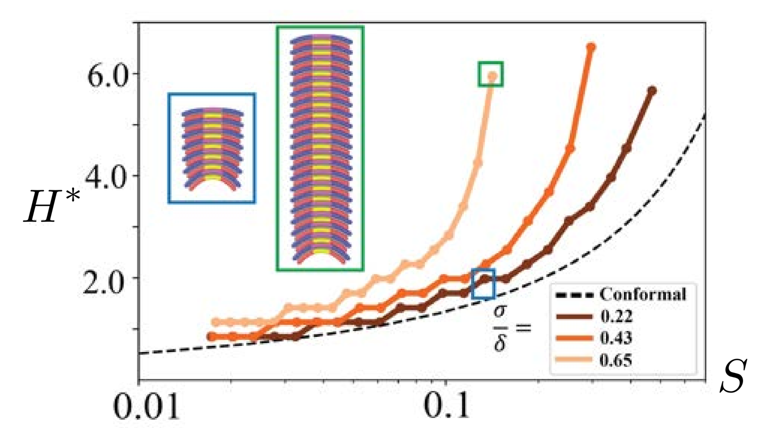
Bead-spring model of a curvamer



Interaction potential between two flat plates







Relevance to MRSEC

Geometric frustration, which utilizes incompatible geometry in building block design, is a mechanism Brandeis MRSEC IRG-1 is studying to achieve the controllable, finite-sized self-assembly of equilibrium sub-units into structures much larger than individual sub-units. Here we explore one building block design, that of curved particles, in order to determine the robustness and scalability of many-particle stacks.

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