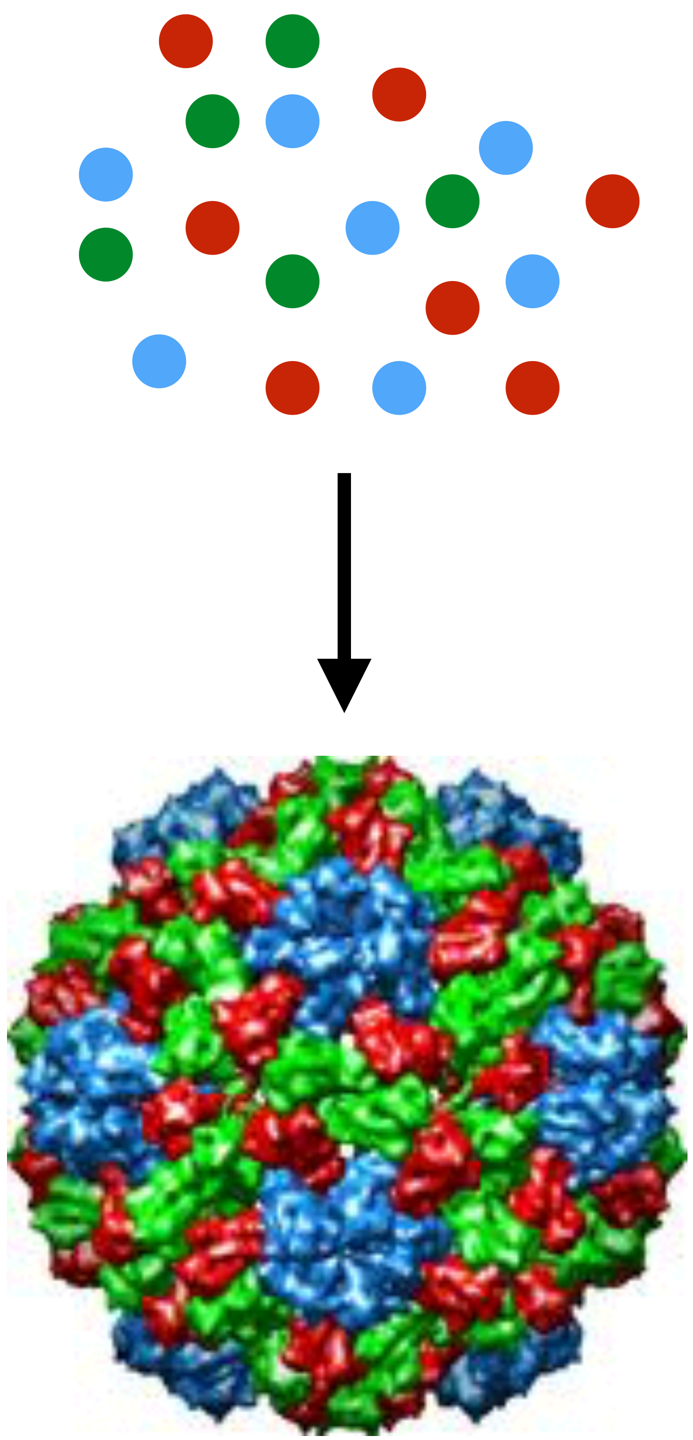
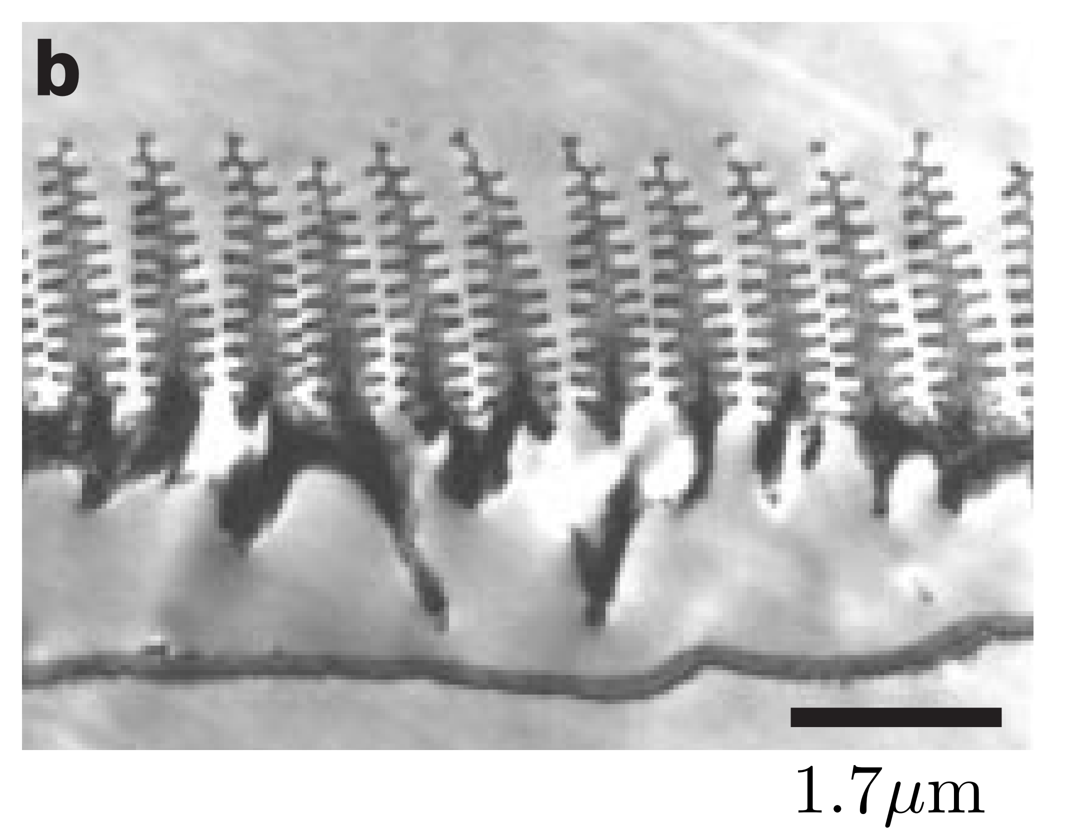
MAE 545: Lecture 23 (12/15)

Self assembly and structural colors

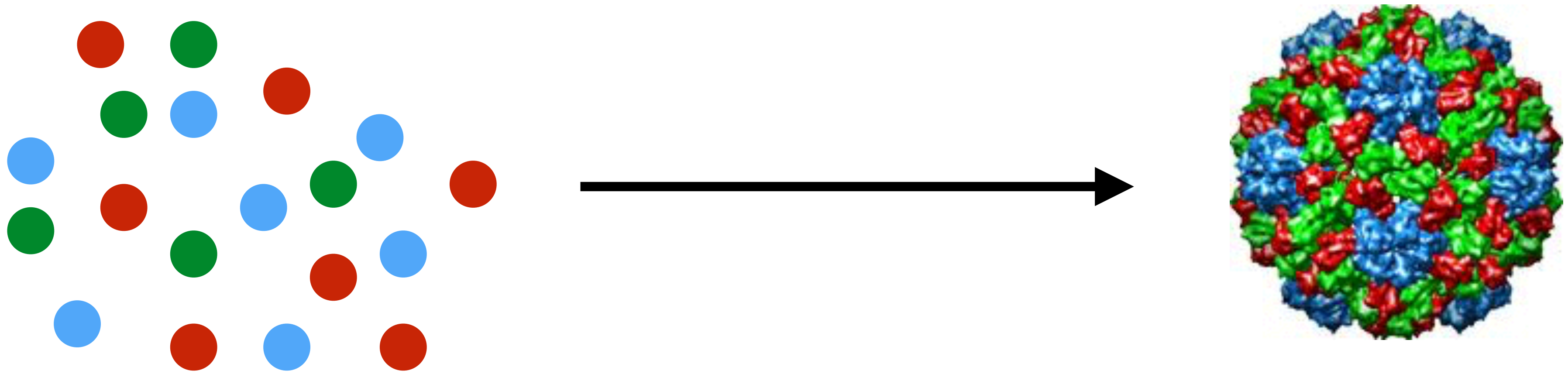




Self-assembly of viral capsids

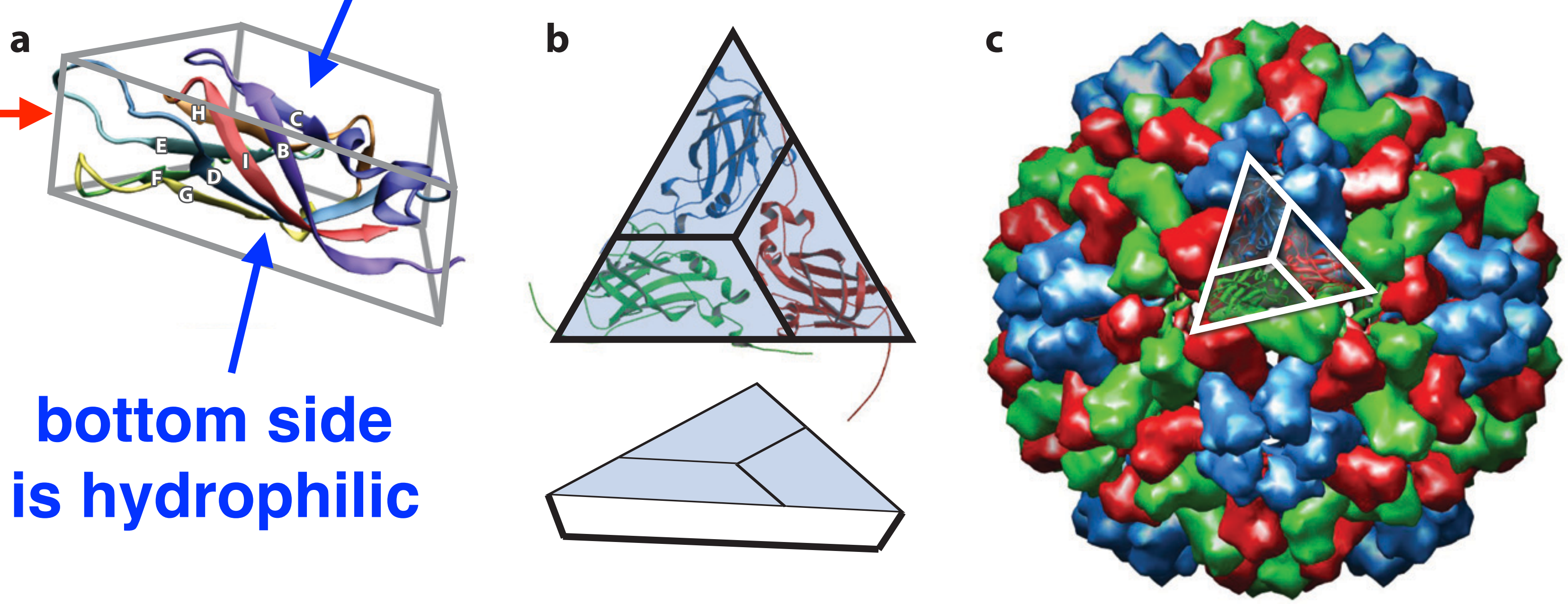
capsid proteins in solution

Cowpea Chlorotic Mottle virus



top side is hydrophilic

all sides are hydrophobic



bottom side is hydrophilic

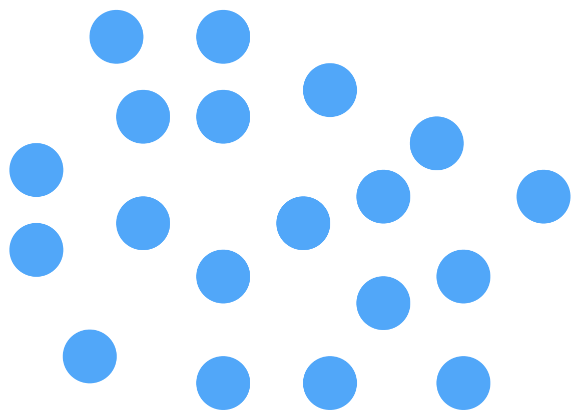
Hydrophilic parts are on the outside and on the inside of assembled capsid.

Hydrophobic parts are at protein junctions and are hidden from water.

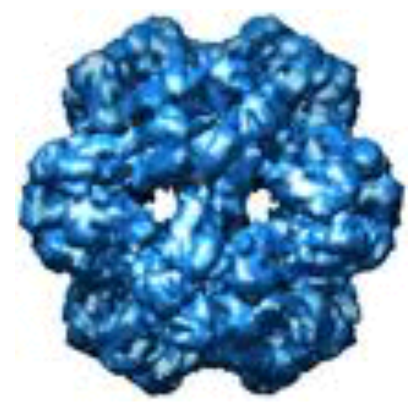
R.F. Bruinsma and W.S. Klug, Annu. Rev. Cond. Matter Phys. 6, 245 (2015)

Self-assembly of viral capsids

capsid proteins in solution



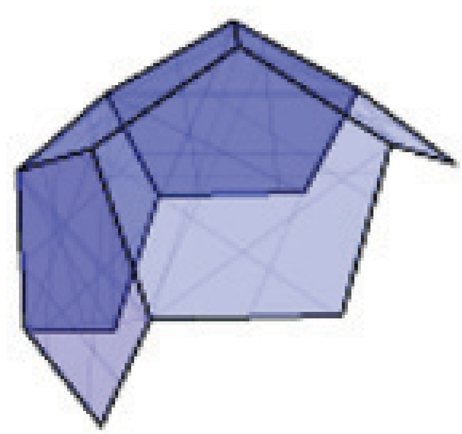
Brome mosaic virus



Note: we only present thermodynamics of self-assembly. Kinetics of self-assembly can be analyzed with master equations.

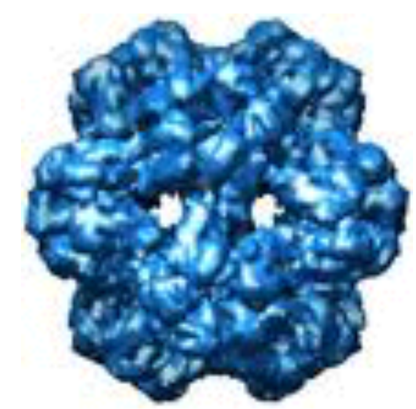
$E(1) = 0 \qquad C(1)$

energy and concentration of protein monomers



$E(n) \qquad C(n)$

energy and concentration of partially assembled capsids containing *n* proteins



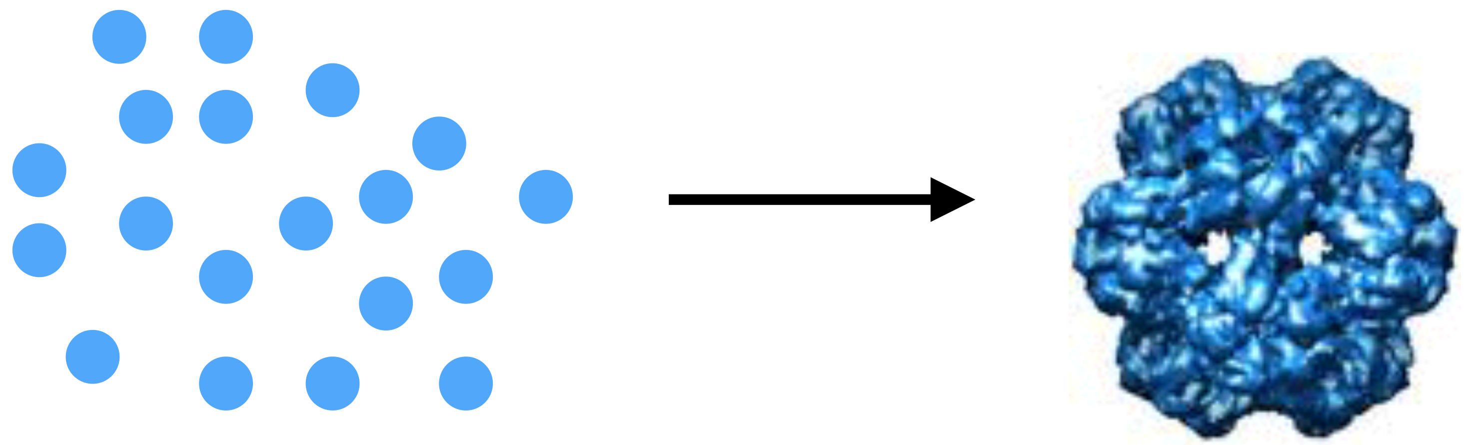
$E(N) \qquad C(N)$

energy and concentration of fully assembled capsids

Self-assembly of viral capsids

capsid proteins in solution

Brome mosaic virus



$$E(n) \qquad C(n)$$

energy and concentration of partially assembled capsids containing *n* proteins

$$E(1) = 0 \qquad C(1)$$

energy and concentration of protein monomers

$$E(N) \qquad C(N)$$

energy and concentration of fully assembled capsids

Total concentration of capsid proteins

$$\boxed{C_{\mathrm{tot}} = \sum_{n=1}^{N} nC(n)}$$

System free energy

$$\boxed{G \sim \sum_{n=1}^{N} \Big[C(n)E(n) + k_B T C(n) \left(\ln(C(n)/C_0) - 1 \right) \Big]}$$

energy **mixing entropy**

Self-assembly of viral capsids

Total concentration of capsid proteins

$$C_{\text{tot}} = \sum_{n=1}^{N} nC(n)$$

System free energy

$$G \sim \sum_{n=1}^{N} \left[C(n)E(n) + k_B T C(n) \left(\ln(C(n)/C_0) - 1 \right) \right]$$

Minimize free energy with respect to concentrations *C*(*n*) subject to the fixed total concentration C_{tot} constraint.

Minimize functional

$$H = G + \mu \left[C_{\text{tot}} - \sum_n nC(n) \right]$$

Afterwards set the Lagrange multiplier μ to fix the total concentration C_{tot}.

$$C(n) = C_0 e^{-(E(n)-\mu n)/k_B T} \qquad C(1) = C_0 e^{\mu/k_B T}$$

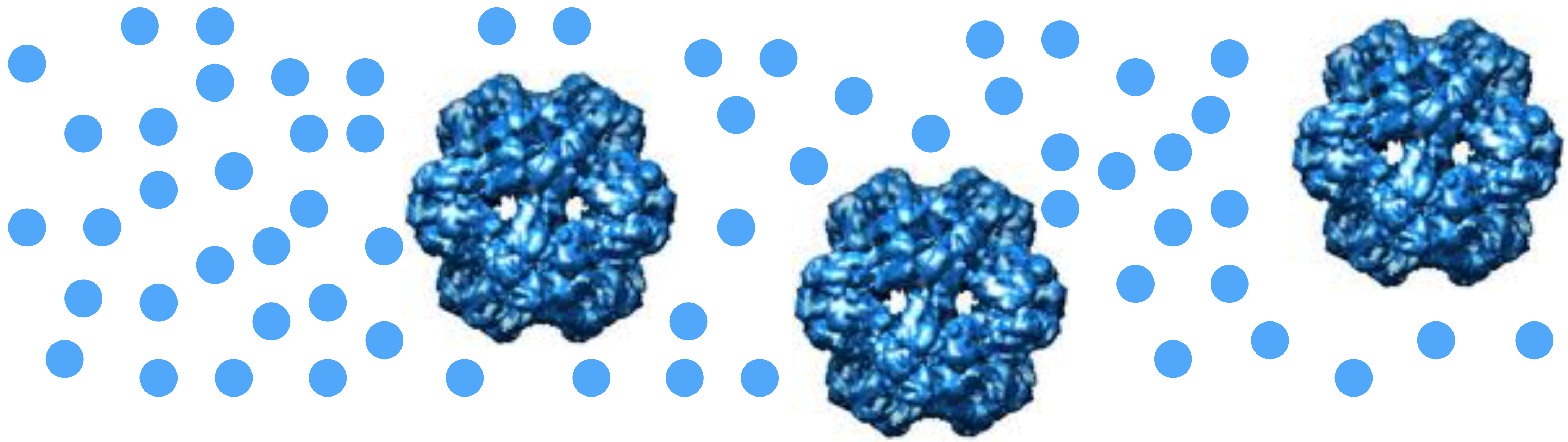
Parameter μ plays a role of chemical potential!

Law of mass action

$$\boxed{\frac{C(n)}{C_0} = \left(\frac{C(1)}{C_0} \right)^n e^{-E(n)/k_B T}}$$

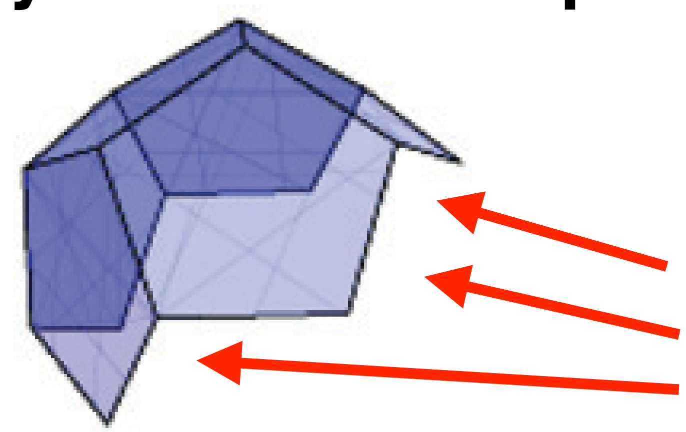
C(1) is determined by fixing the total concentration!

Self-assembly of viral capsids



$$\boxed{\frac{C(n)}{C_0} = \left(\frac{C(1)}{C_0}\right)^n e^{-E(n)/k_B T}}$$

Neglect concentration of partially assembled capsids $C(n) \approx 0$



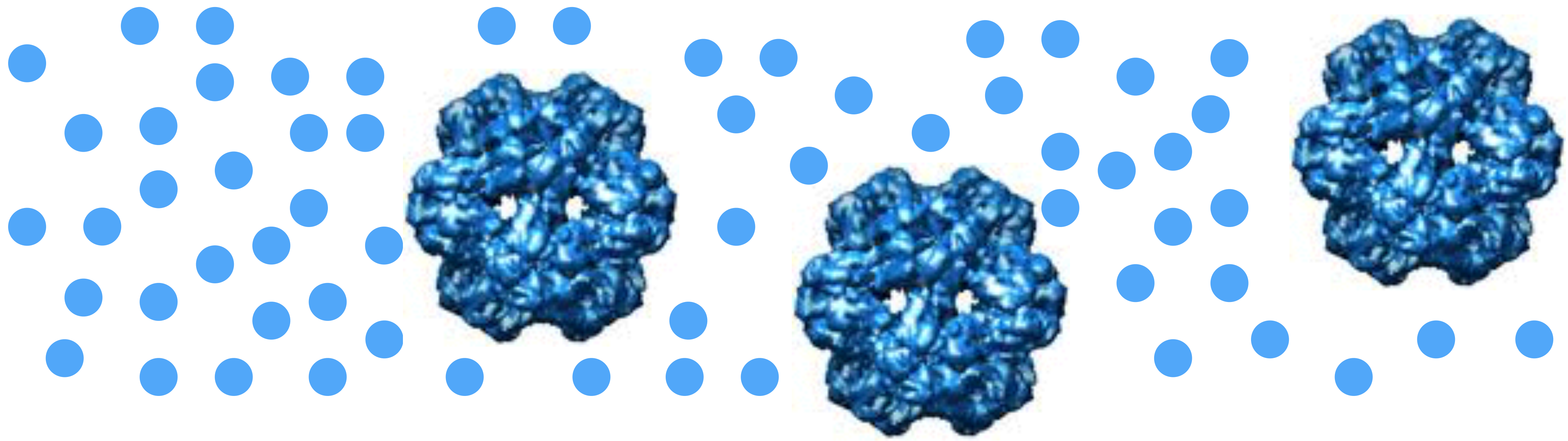
Total protein concentration

$$C_{\text{tot}} \approx C(1) + NC(N)$$

$$\frac{C_{\text{tot}}}{C_0} \approx \frac{C(1)}{C_0} + N\left(\frac{C(1)}{C_0} e^{-E(N)/(Nk_B T)}\right)^N$$

$$\boxed{C^* = C_0 e^{E(N)/(Nk_B T)}}$$

Self-assembly of viral capsids



$$\frac{C_{\mathrm{tot}}}{C_0} \approx \frac{C(1)}{C_0} + N\left(\frac{C(1)}{C^*}\right)^N$$

$$\boxed{C^* = C_0 e^{E(N)/(N k_B T)}}$$

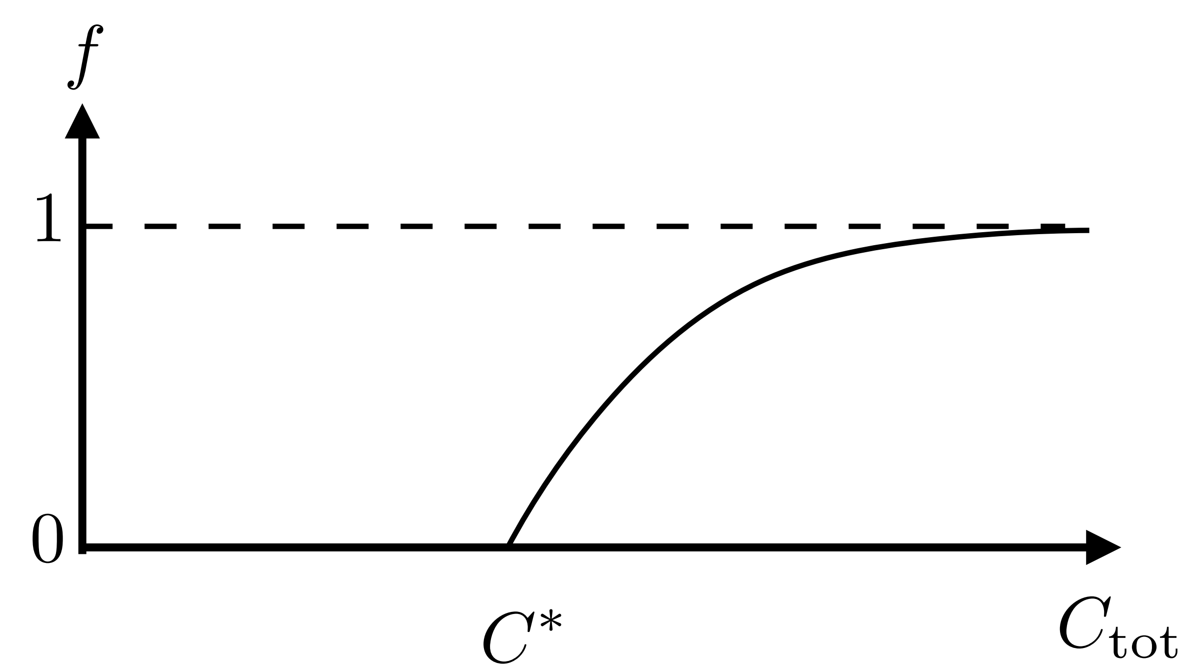
At low concentrations $C_{\mathrm{tot}} \ll C^*$

$$C(1) \approx C_{\mathrm{tot}}$$

At large concentrations $C_{\mathrm{tot}} \gg C^*$

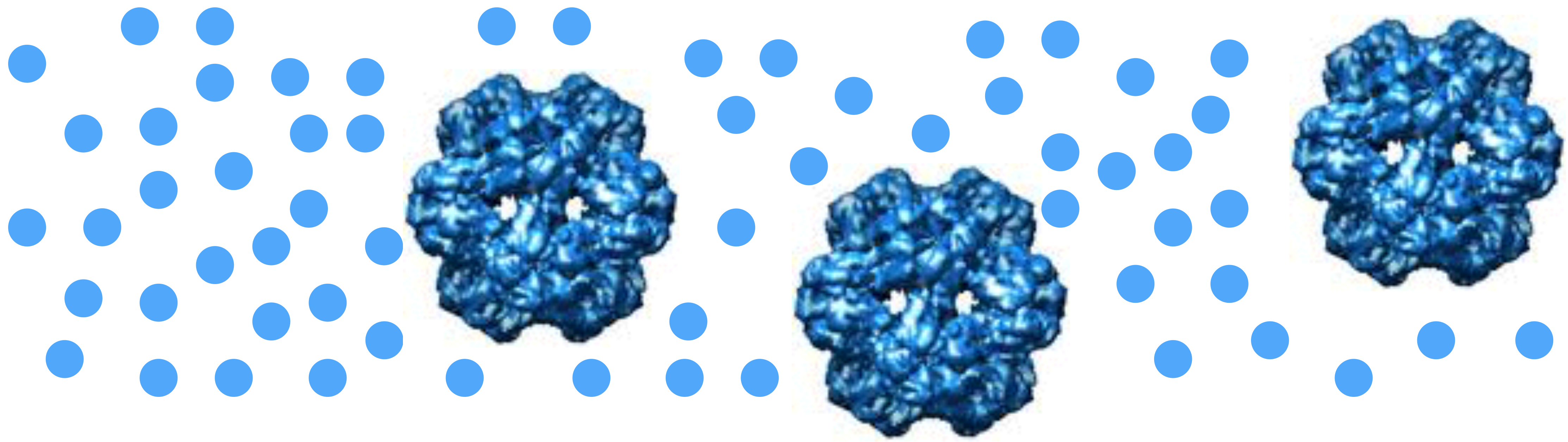
$$C(1) \approx C^* \left(\frac{C_{\mathrm{tot}}}{N C_0}\right)^{1/N} \approx C^*$$

Fraction of proteins assembled in capsids $f = 1 - \dfrac{C(1)}{C_{\mathrm{tot}}}$



This generic profile is also observed for assembly of more complex viral capsids!

Self-assembly of viral capsids



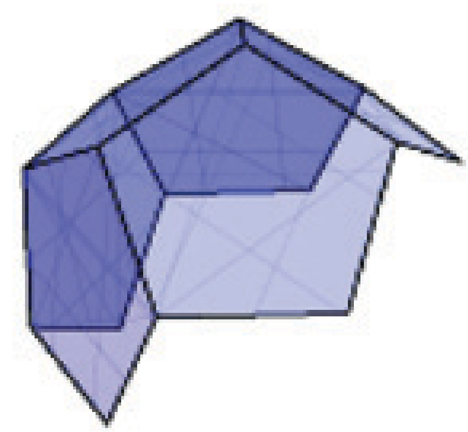
$$\boxed{\frac{C(n)}{C_0} = \left(\frac{C(1)}{C_0}\right)^n e^{-E(n)/k_B T}}$$

Can we really neglect partially assembled capsids at large protein concentrations?

$$\frac{C(N/2)}{C(N)} = \left(\frac{C(1)}{C_0}\right)^{-N/2} e^{-[E(N/2)-E(N)]/k_B T}$$

$$C(1) \approx C^* = C_0 e^{E(N)/(N k_B T)}$$

$$\boxed{\frac{C(N/2)}{C(N)} \approx e^{-[E(N/2)-E(N)/2]/k_B T} \ll 1}$$

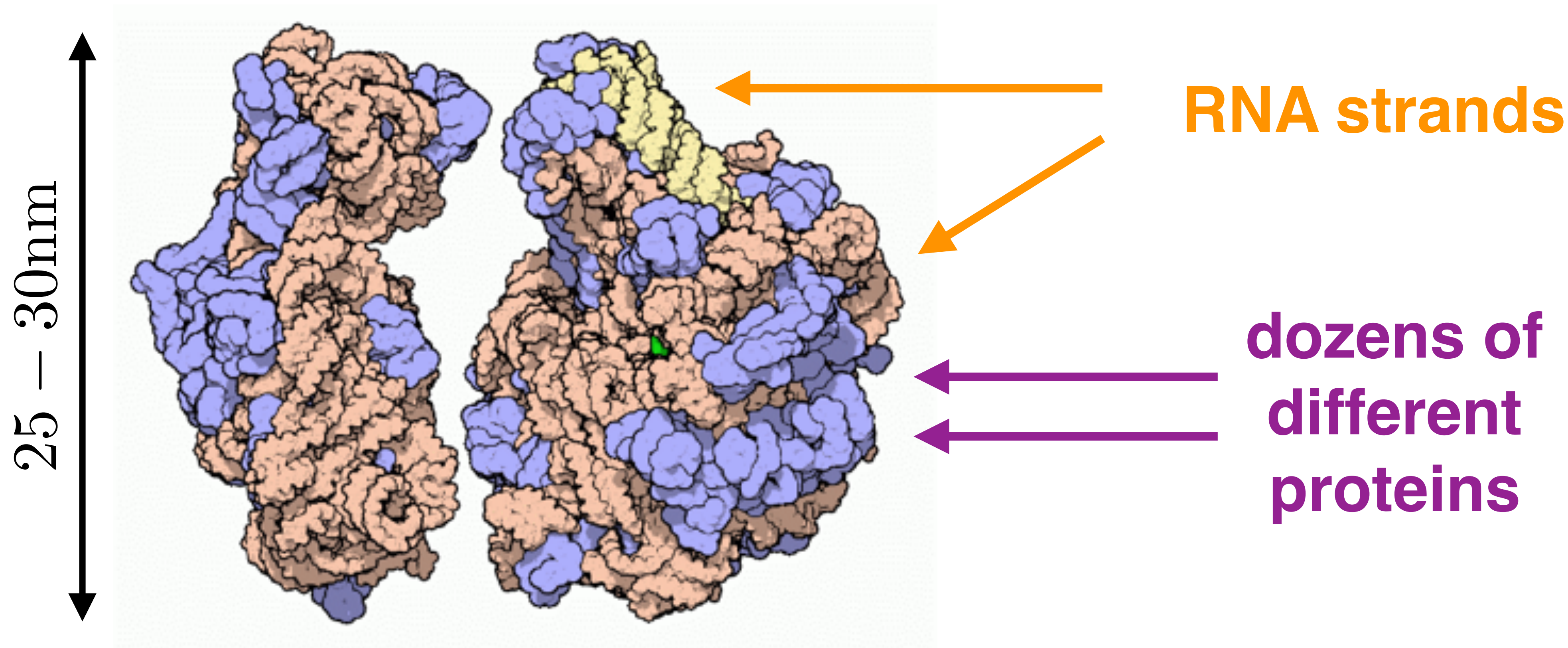


For Cowpea Chlorotic Mottle Virus the scission energy is

$$2E(N/2) - E(N) \sim 100 k_B T$$

Complex self-assembly

Ribosomes are huge multi-protein complexes that are important for the synthesis of new proteins.



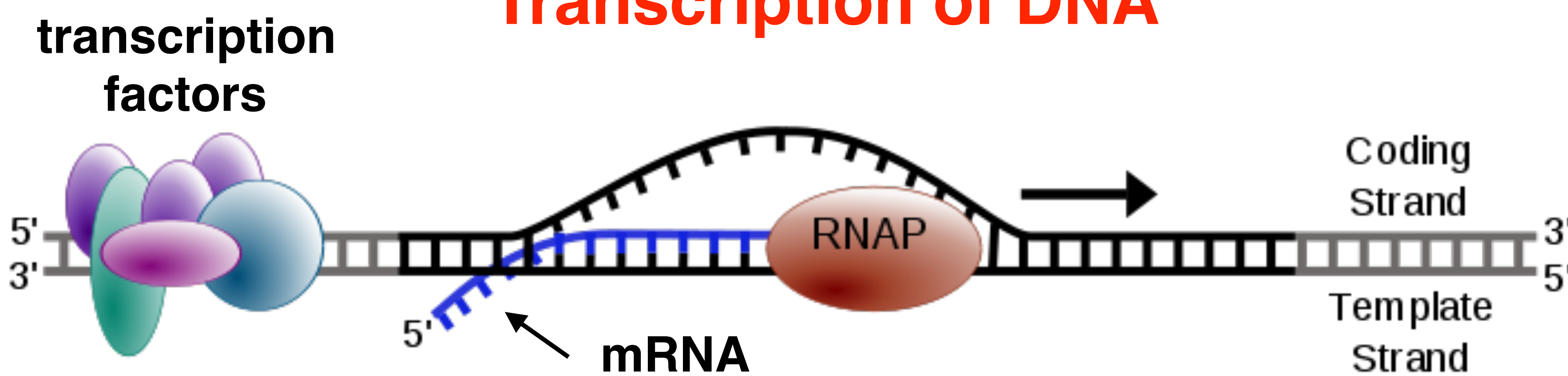
Multiple proteins fit together like a puzzle to make the desired structure.

Matching pieces are characterized with strong (specific) binding due to the shape complementarity.

Non-matching pieces bind weakly (non-specifically).

Production of new proteins

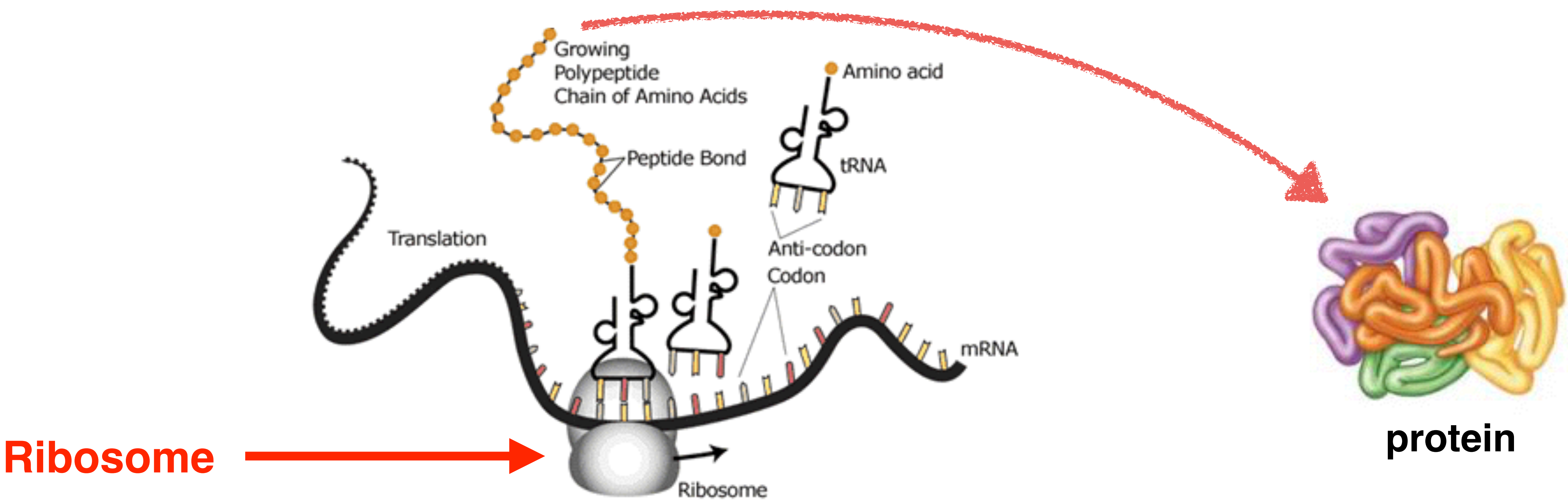
Transcription of DNA



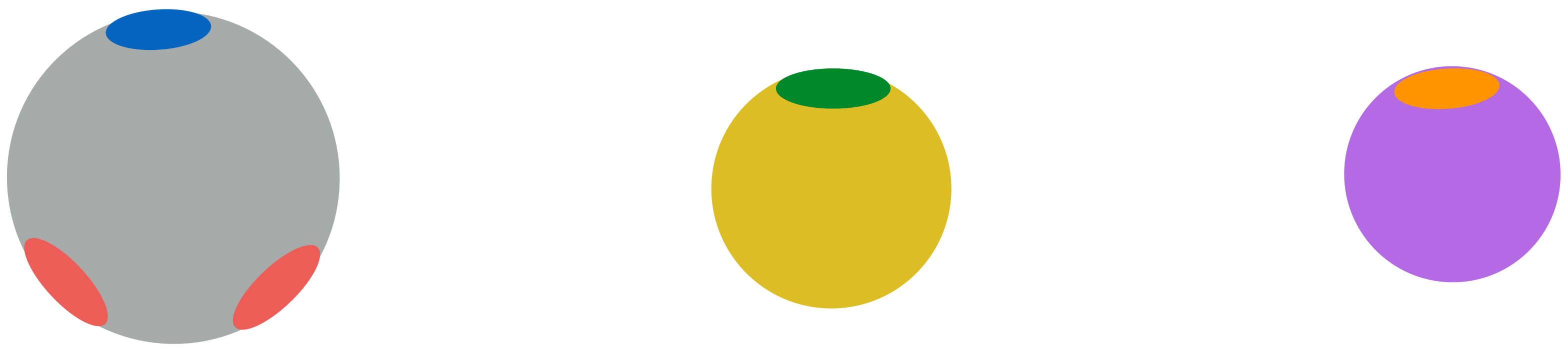
Transcription factors are proteins, which bind to specific locations on DNA, and they help recruiting RNA polymerase (RNAP) that makes a messenger RNA (mRNA) copy of certain DNA segment.

Note: some transcription factors (repressors) also prevent transcription.

Translation of mRNA

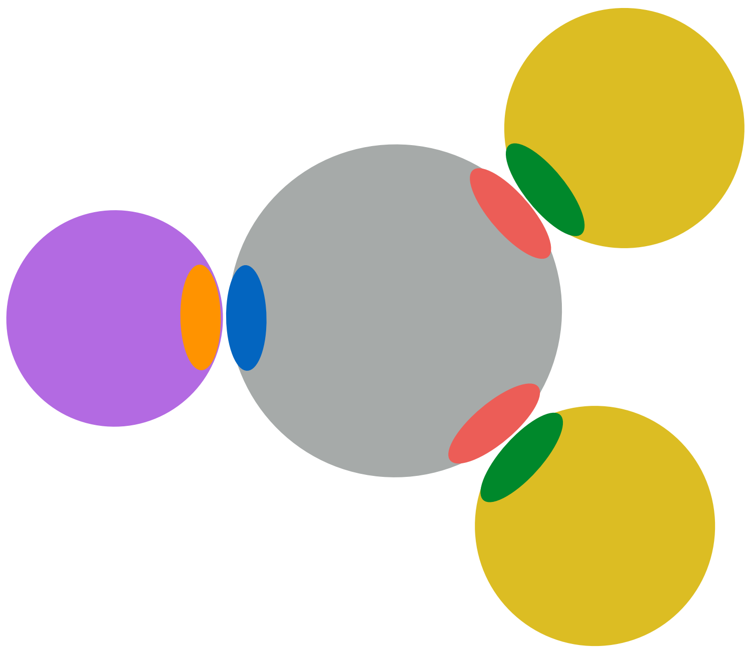


Patchy particles

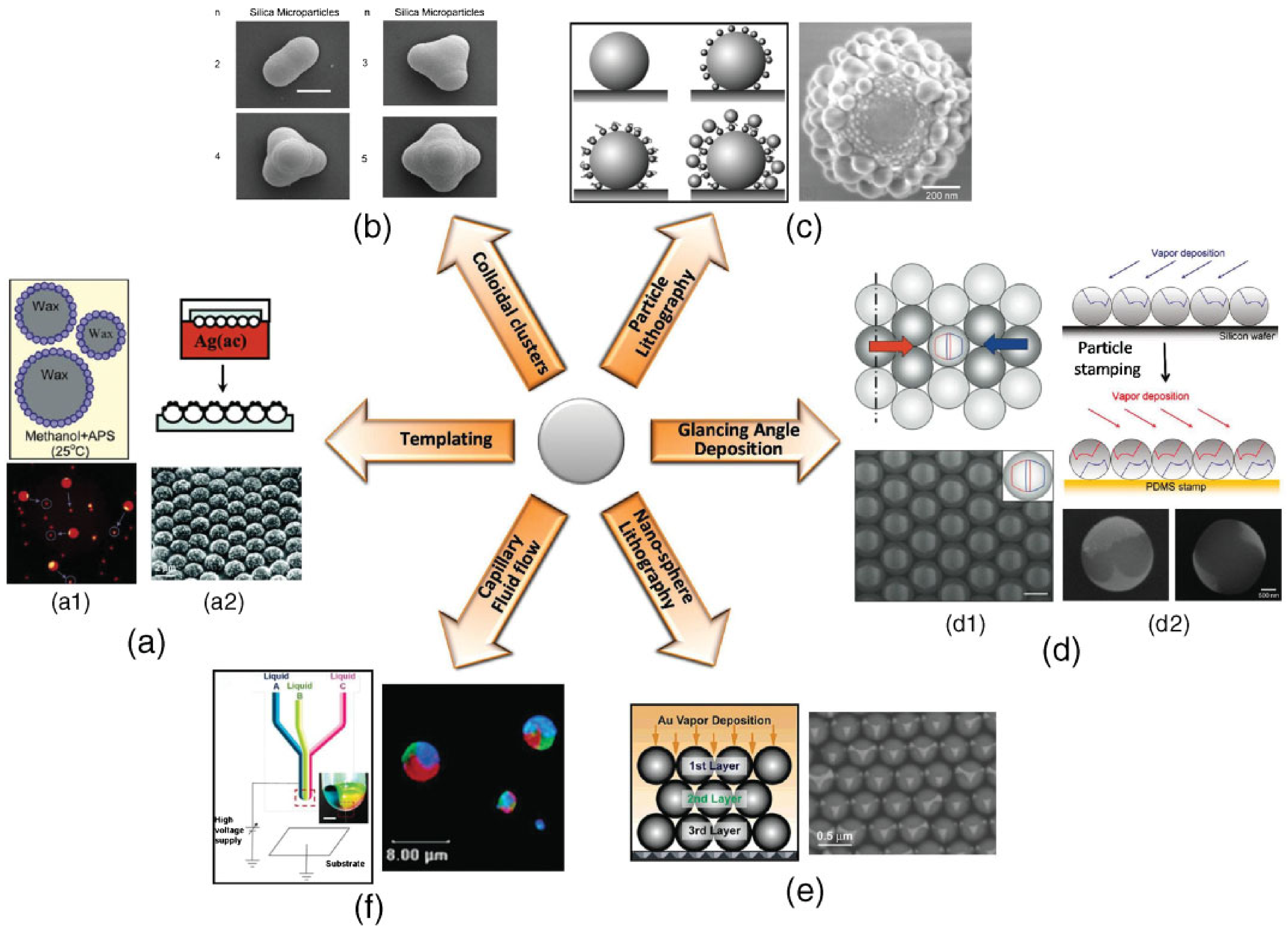


Particles with patches of different chemical/physical properties.

Patches can be designed to bind strongly only with certain partners.



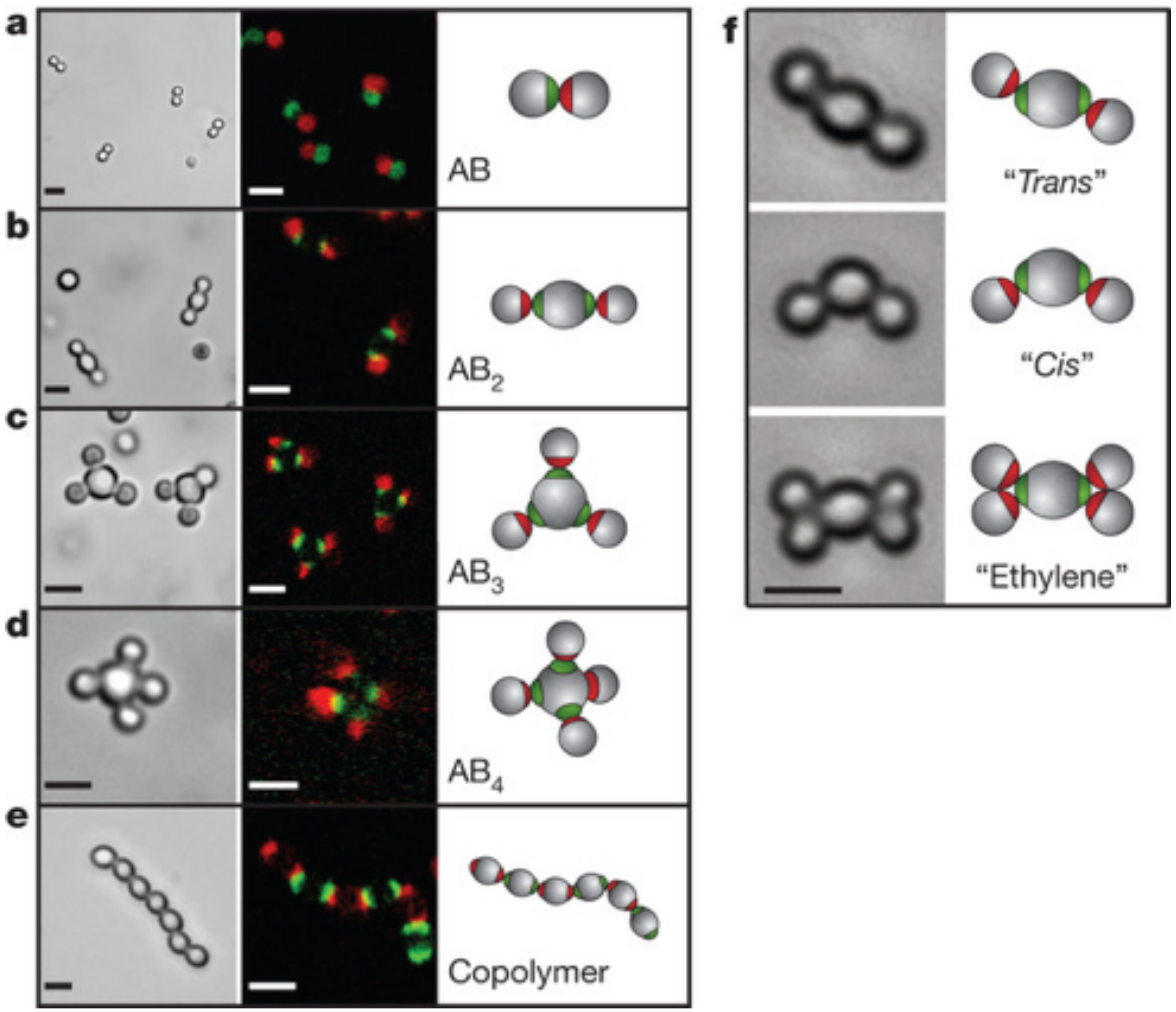
Experimental approaches for making patchy particles



A.B. Pawar and I. Kretzschmar, Macromol. Rapid Common. 31, 159 (2010)

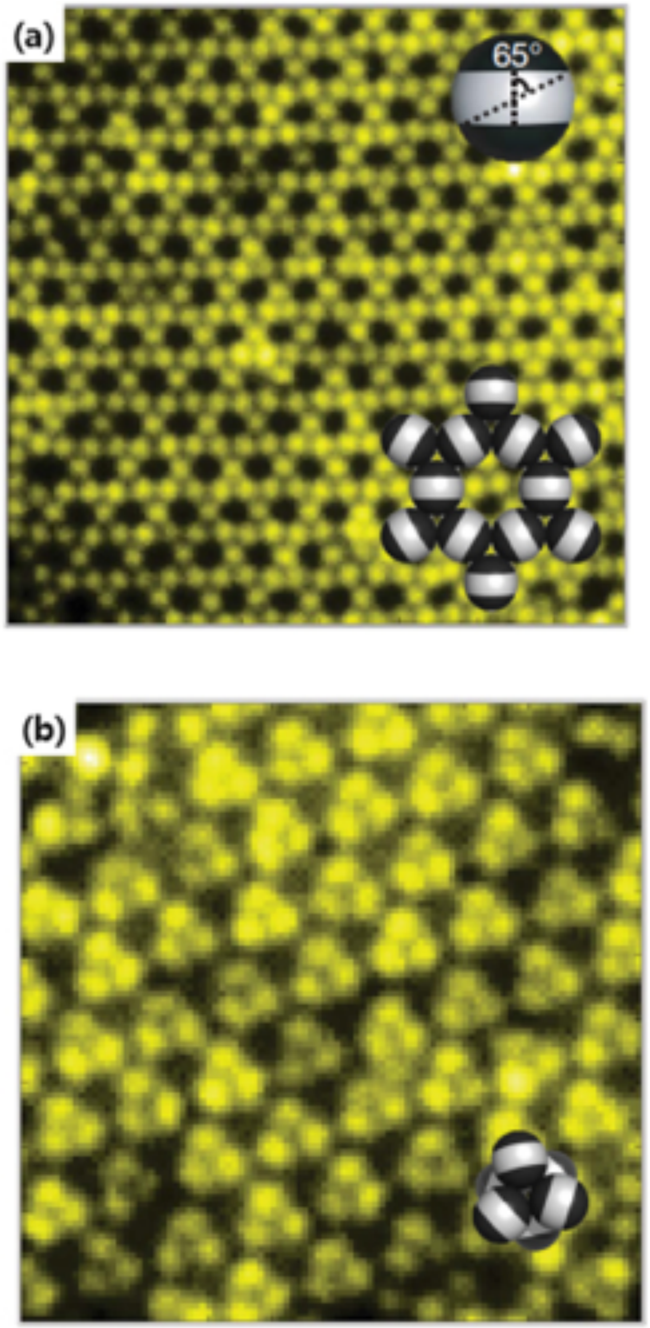
Self-assembly of patchy particles

simple molecule-like structures



Y. Wang et al., Nature 491, 51 (2012)

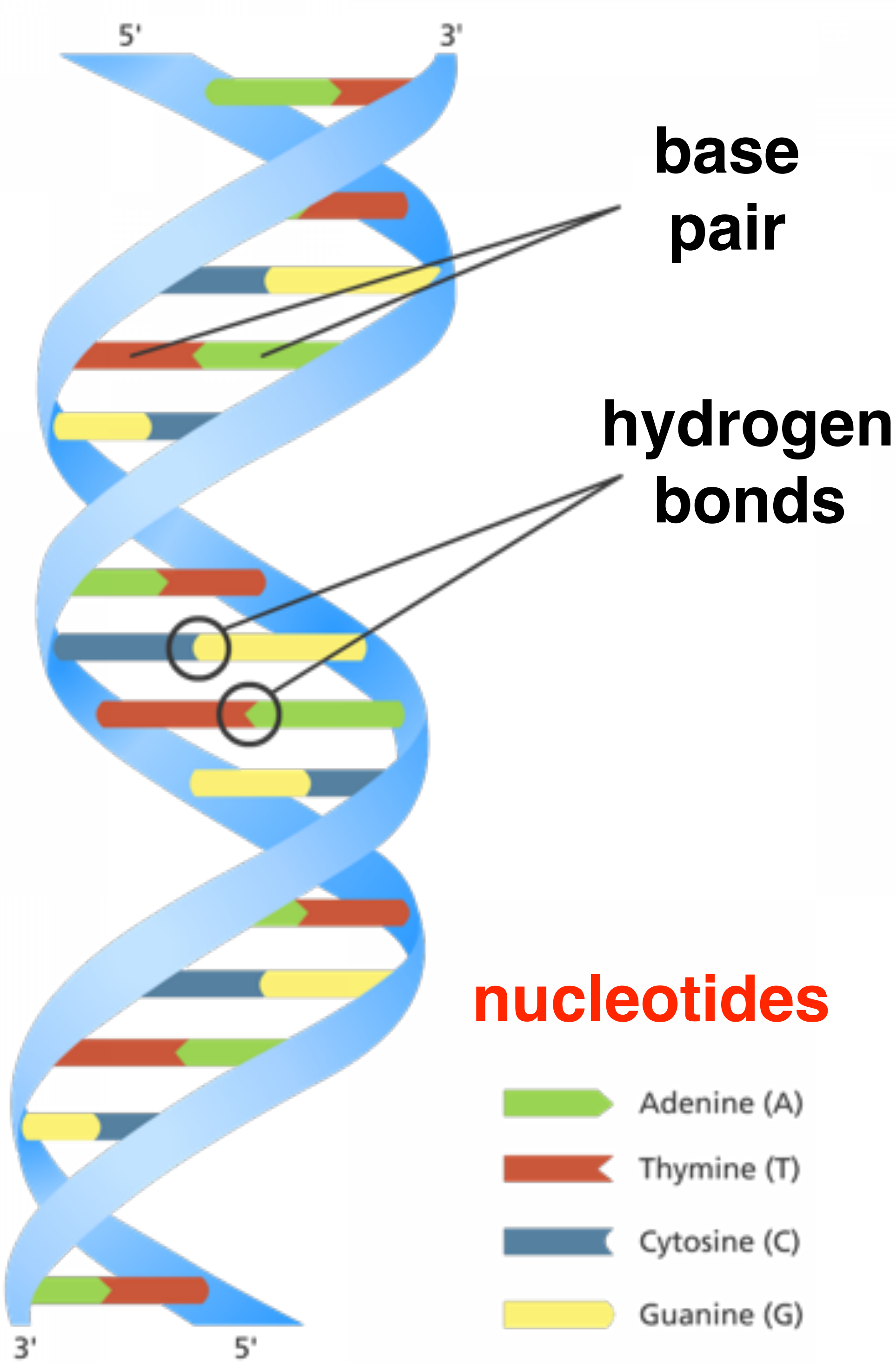
crystal structures



G.-R. Yi et al., J. Phys.: Condens. Mat. 25, 193101 (2013)

DNA

Double stranded DNA forms, when the opposite strands are complementary (A-T, G-C)



Binding energy between two DNA strands *a* and *b* with sequences *s* of length N.

$$\boxed{E_{\text{int}}\left(\{s_i^a\},\{s_i^b\}\right) \approx \sum_{i=1}^{N} M(s_i^a, s_i^b)}$$

$$M(C,G) = M(G,C) \approx -4k_BT$$

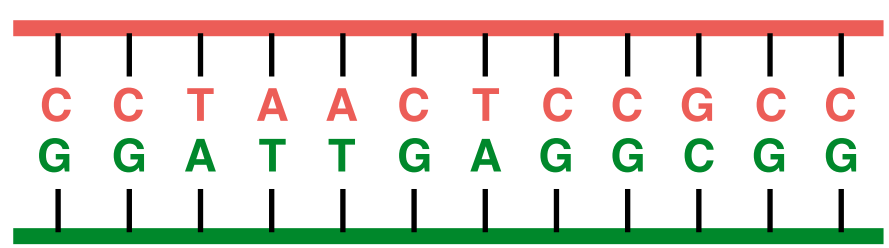
$$M(A,T) = M(T,A) \approx -2k_BT$$

room temperature

$$M(A,C) = M(C,A) \approx 0$$

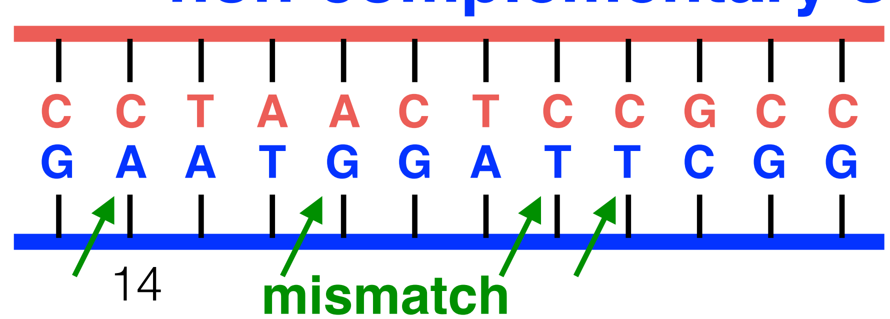
$$M(G,T) = M(T,G) \approx 0$$

Strong binding between complementary sequences



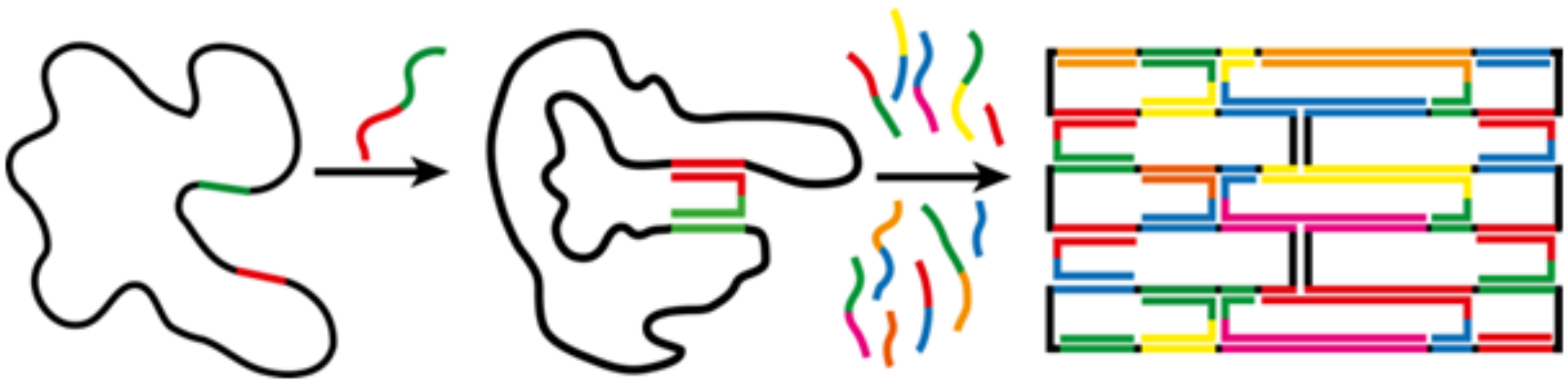
$E_{\text{int}} \approx -40k_BT$

Weaker binding between non-complementary sequences



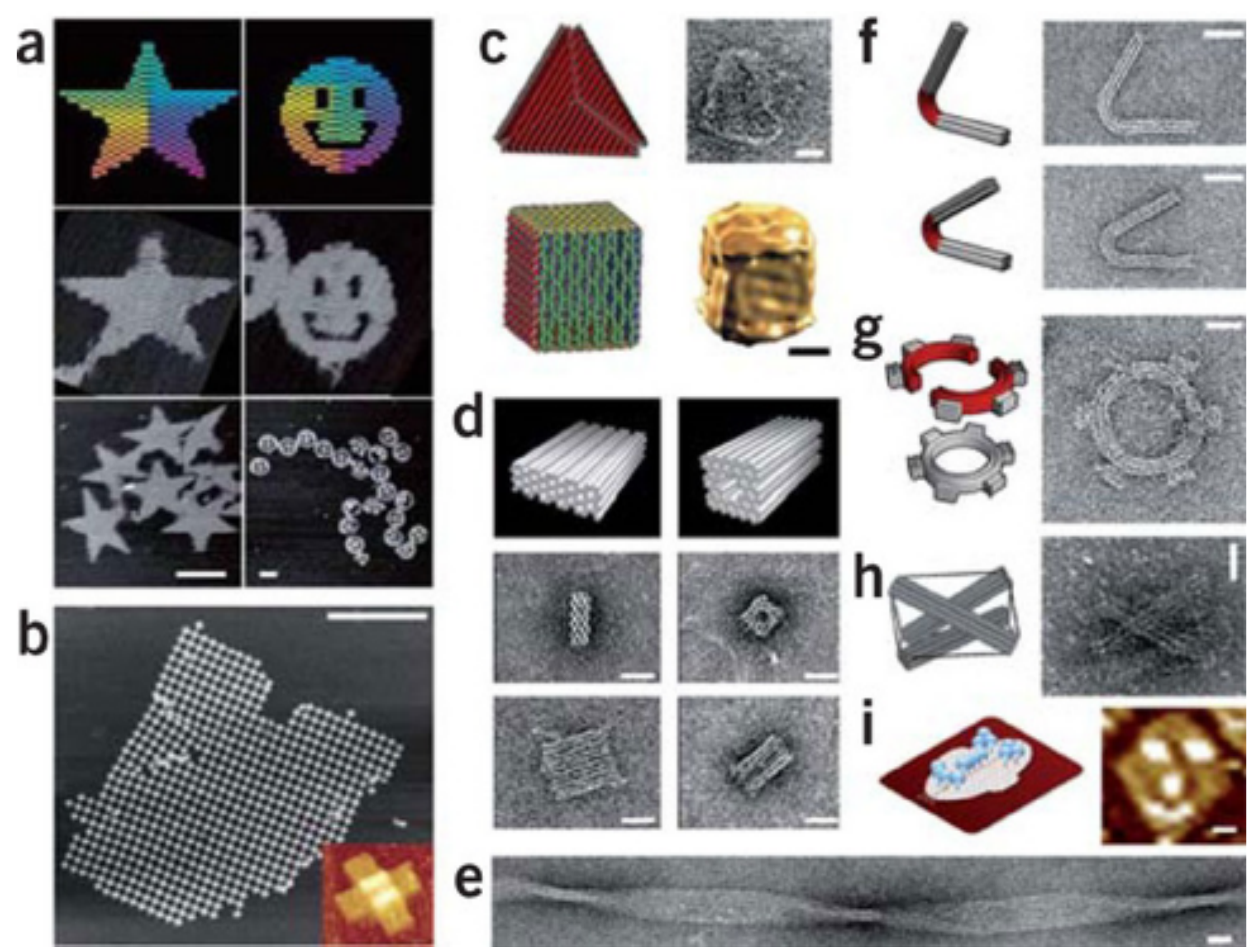
$E_{\text{int}} \approx -26k_BT$

Scaffold DNA origami



Short strands (synthetic DNA) act like staples that fold the scaffold (virus DNA) into desired structure.

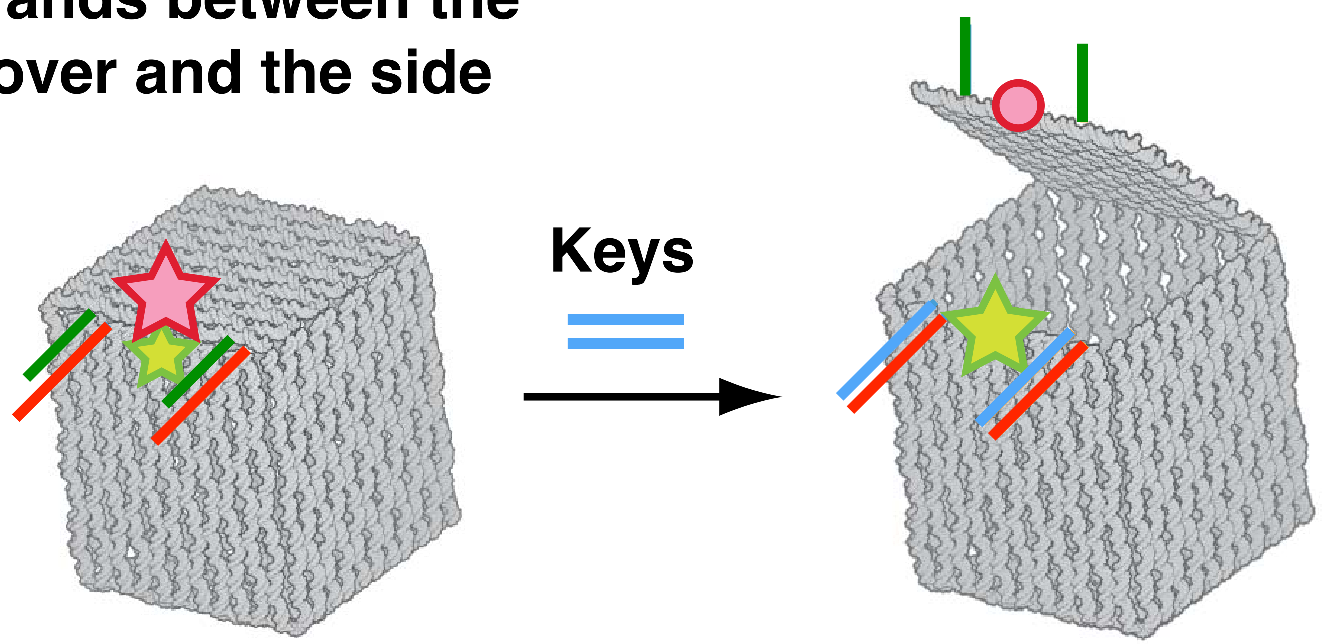
Different colors of staples correspond to different complementary sequences.



C.E. Castro et al., Nat. Methods 8, 221 (2011)

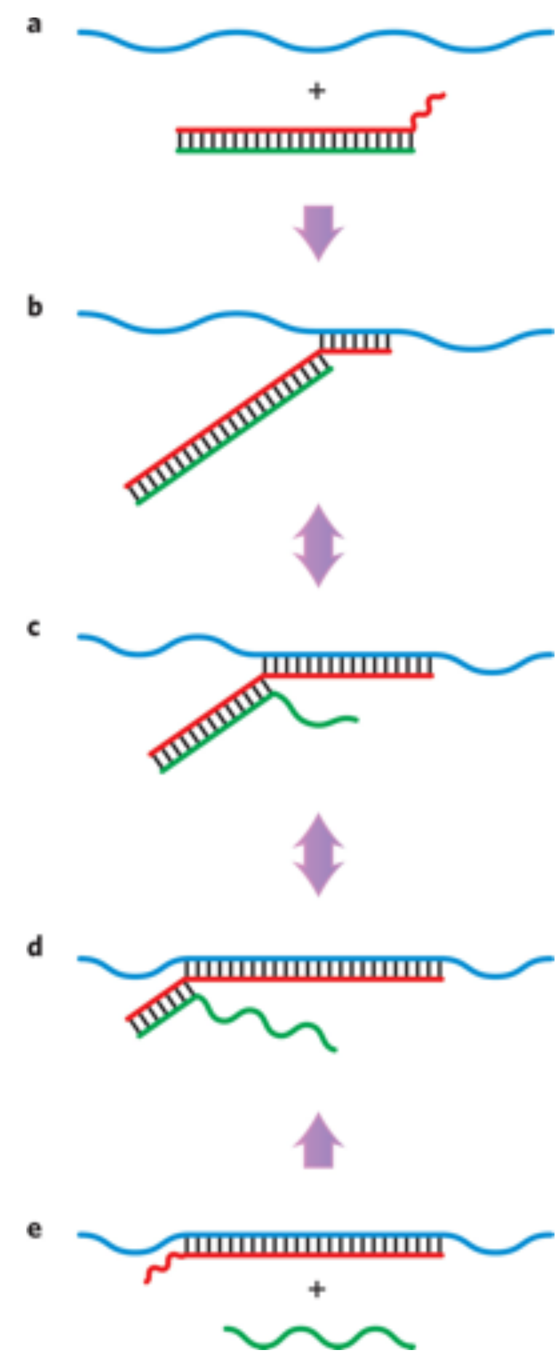
Actuation of DNA origami with a toehold exchange of DNA strands

Box is closed by binding of complementary DNA strands between the cover and the side



Longer strands (keys) bind to their complementary DNA strands on the side of the box to release the cover.

Toehold exchange



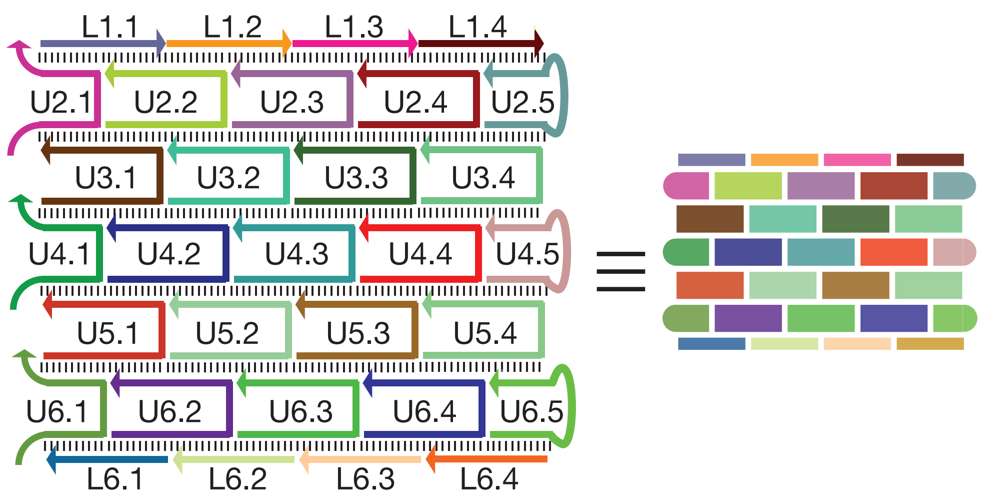
E.S. Andersen et al., Nature 459, 73 (2009)

DNA brick origami

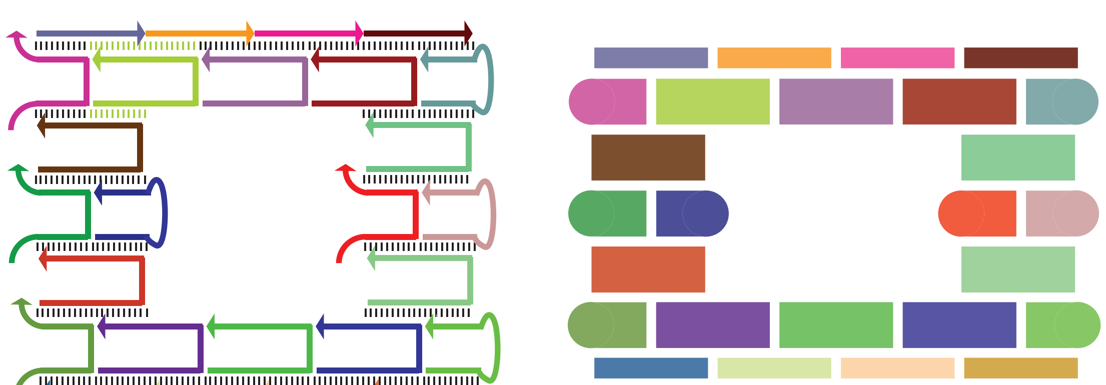
Short staple DNA strands are designed to fit like bricks in a wall. Sequence of DNA strands determine, which “bricks fit together”.

Single stranded DNA building brick (42 bases)

“Brick-wall” diagram



Design of arbitrary structure by removal of certain DNA strands (bricks) from mixture.



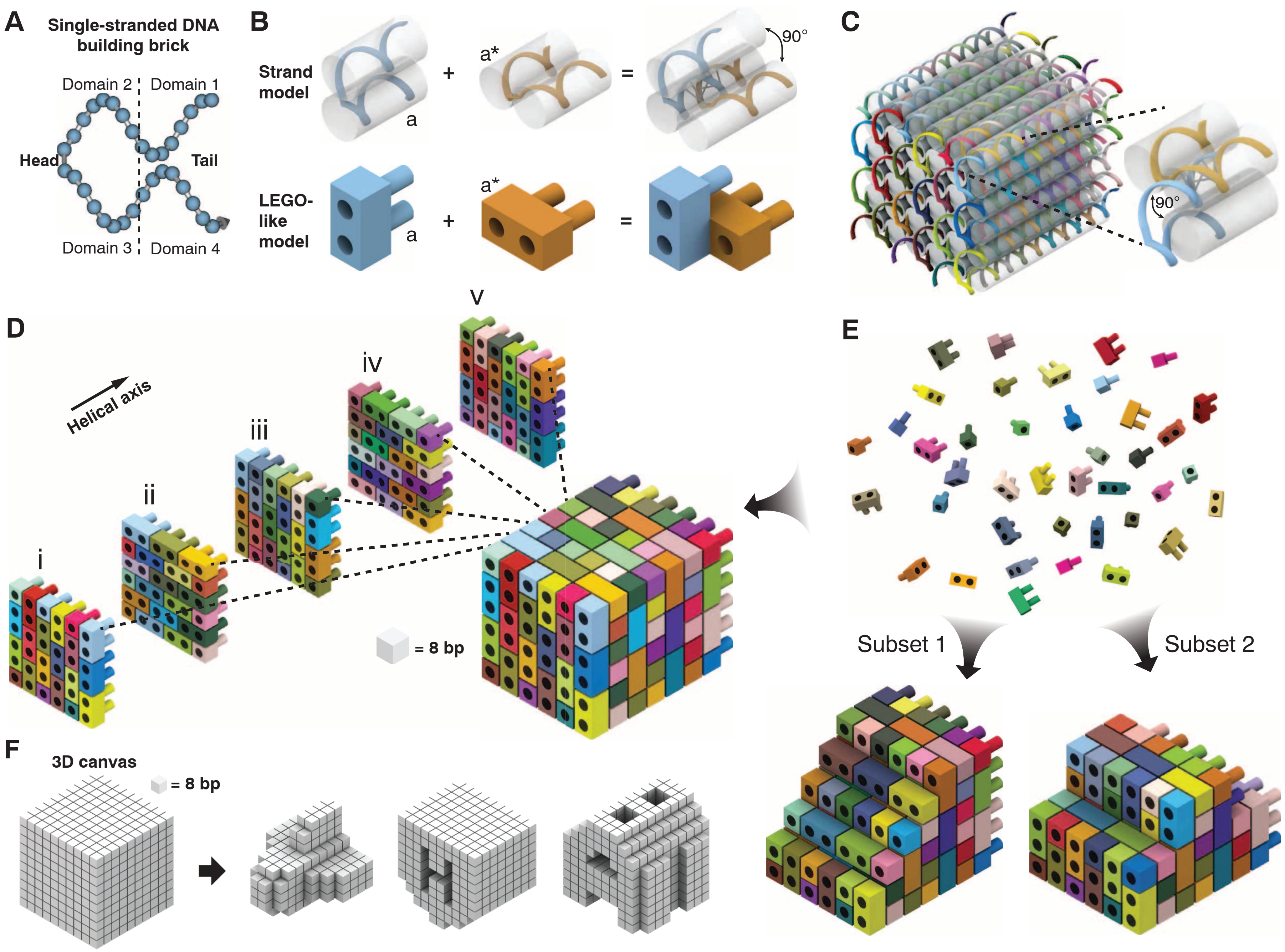
Example of generated structures

B. Wei et al., Nature 485, 623 (2012)

DNA brick origami

Short staple DNA strands are designed to fit together like lego blocks. Sequence of DNA strands determine, which "lego blocks fit together".

Single stranded DNA building brick (32 bases)



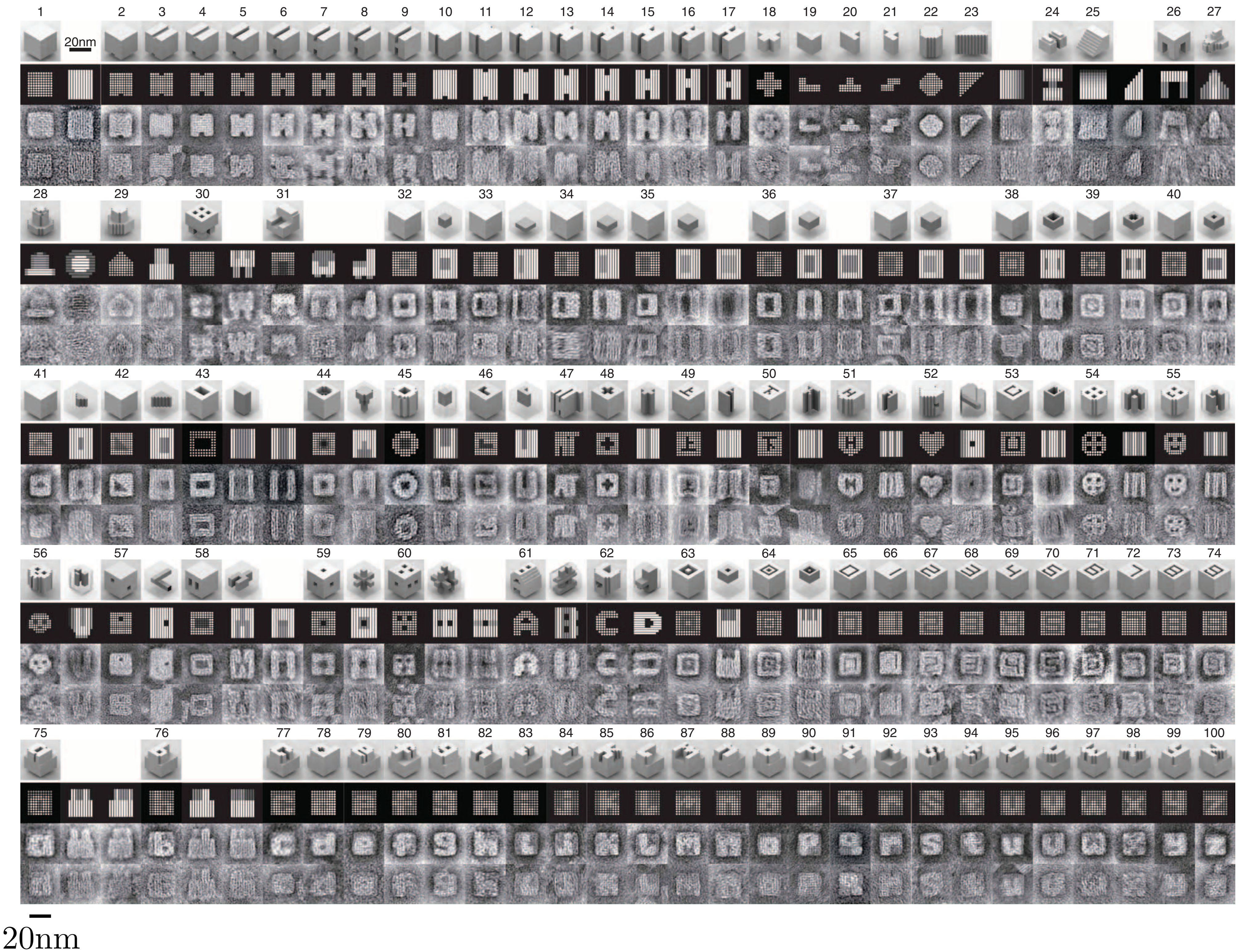
10x10x10 canvas

Design of arbitrary structure by removal of certain DNA strands (bricks) from mixture.

Y. Ke et al., Science 338, 1177 (2012)

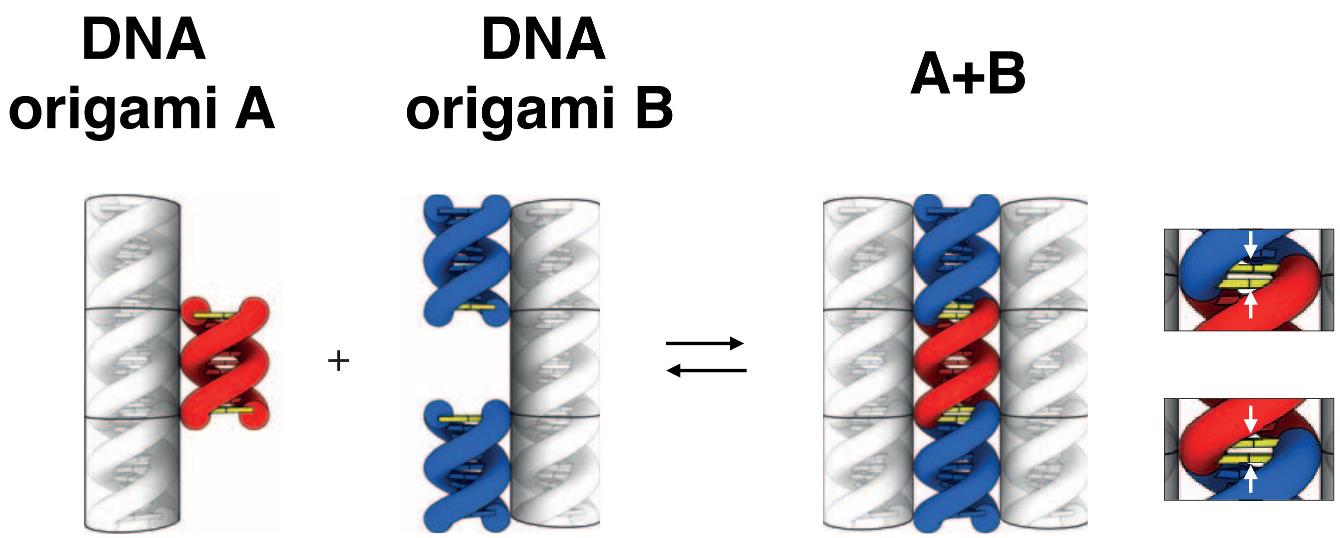
DNA brick origami

Example of generated 3D structures

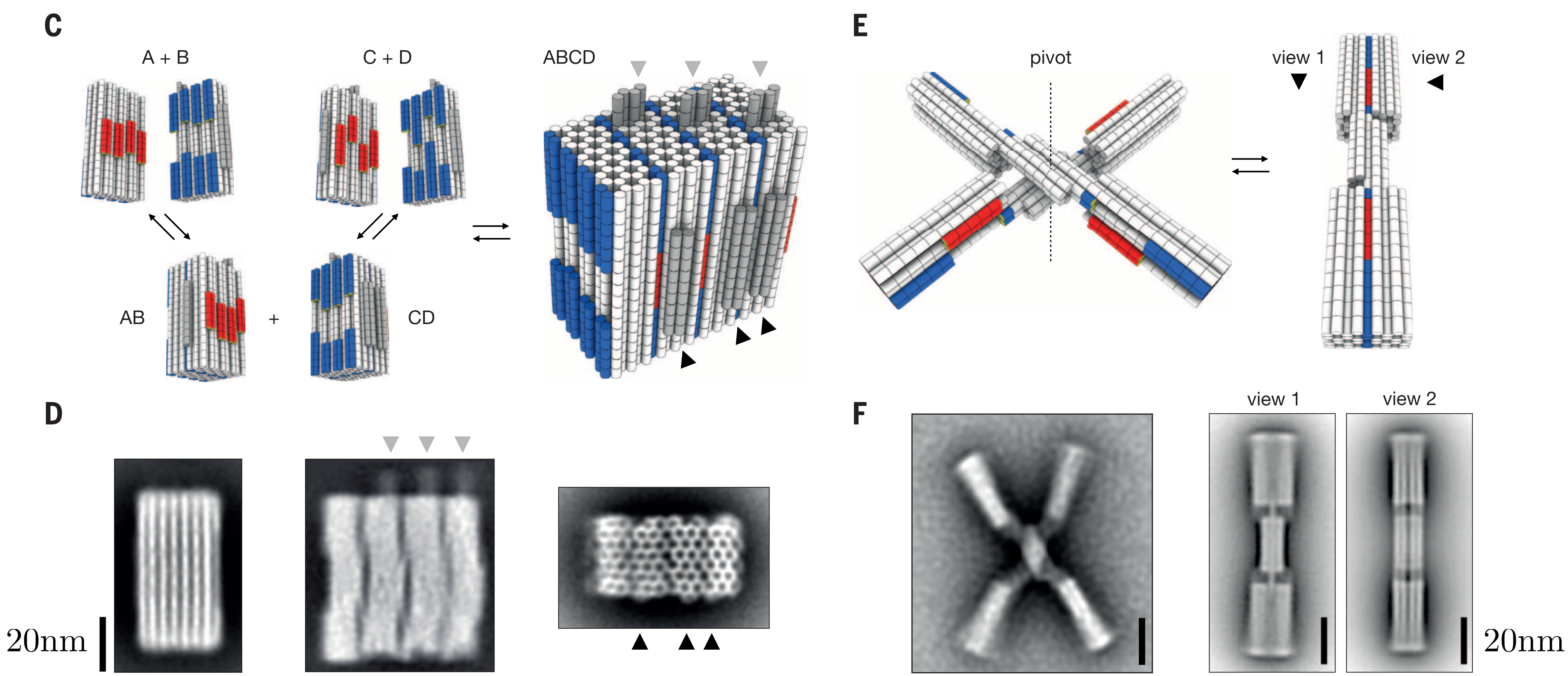


Y. Ke et al., Science 338, 1177 (2012)

Shape complementarity with DNA origami



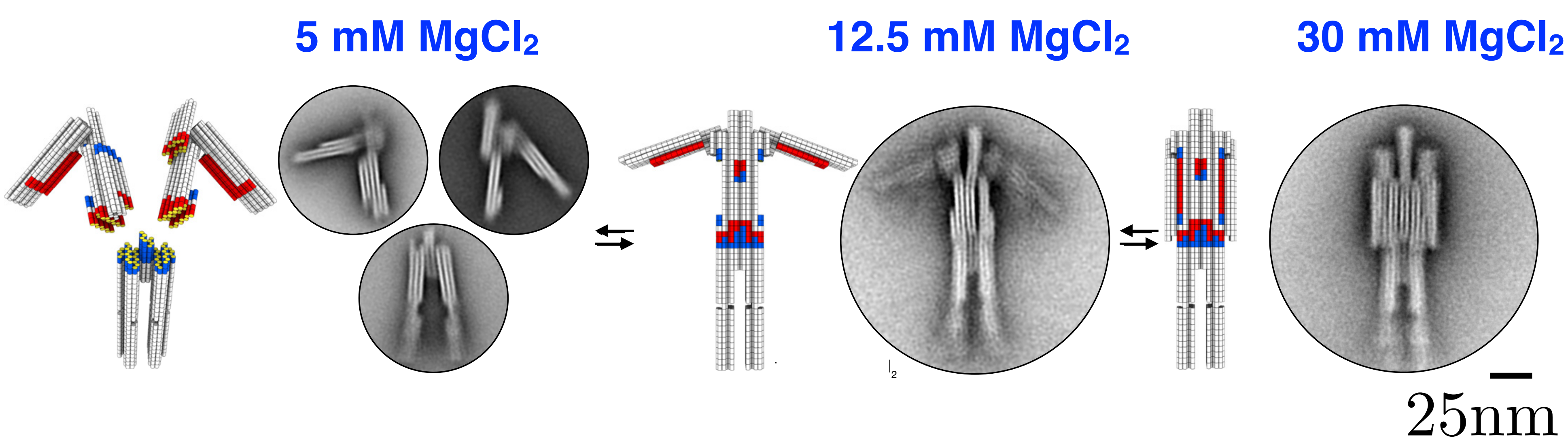
binding can be strengthened by additional complementary nucleotides (yellow)



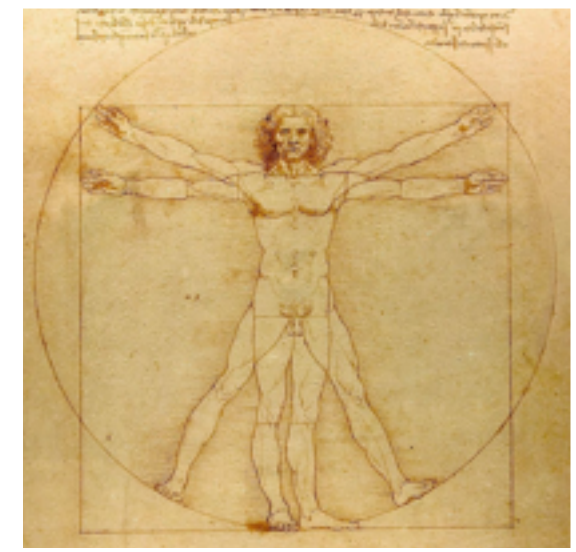
T. Gerling et al., Science 347, 1446 (2015)

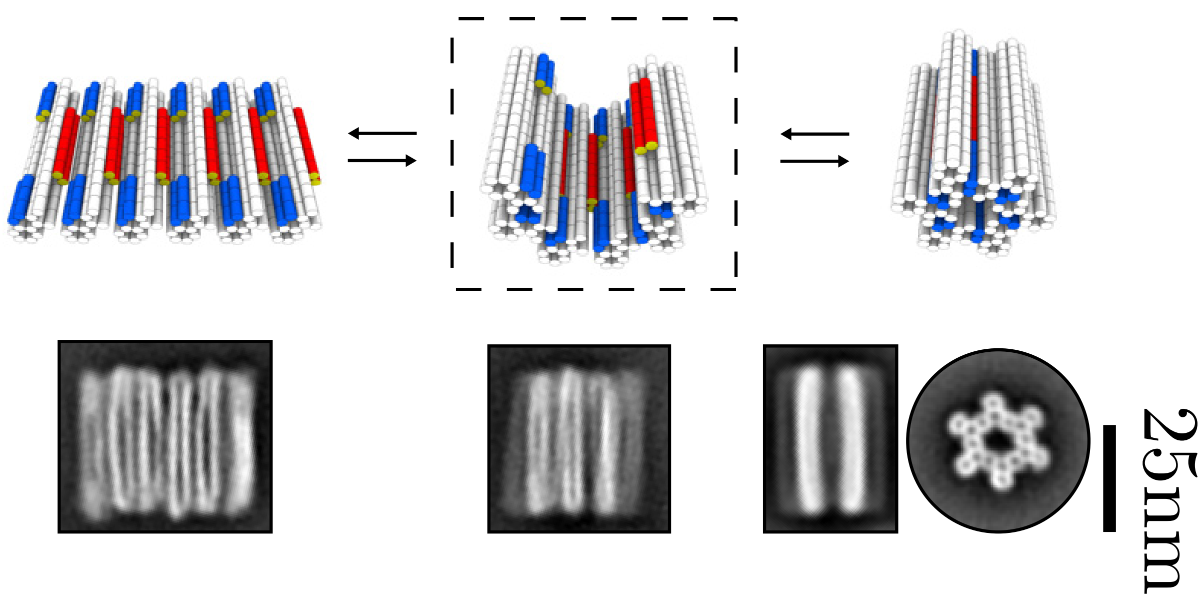
Actuation of DNA origami

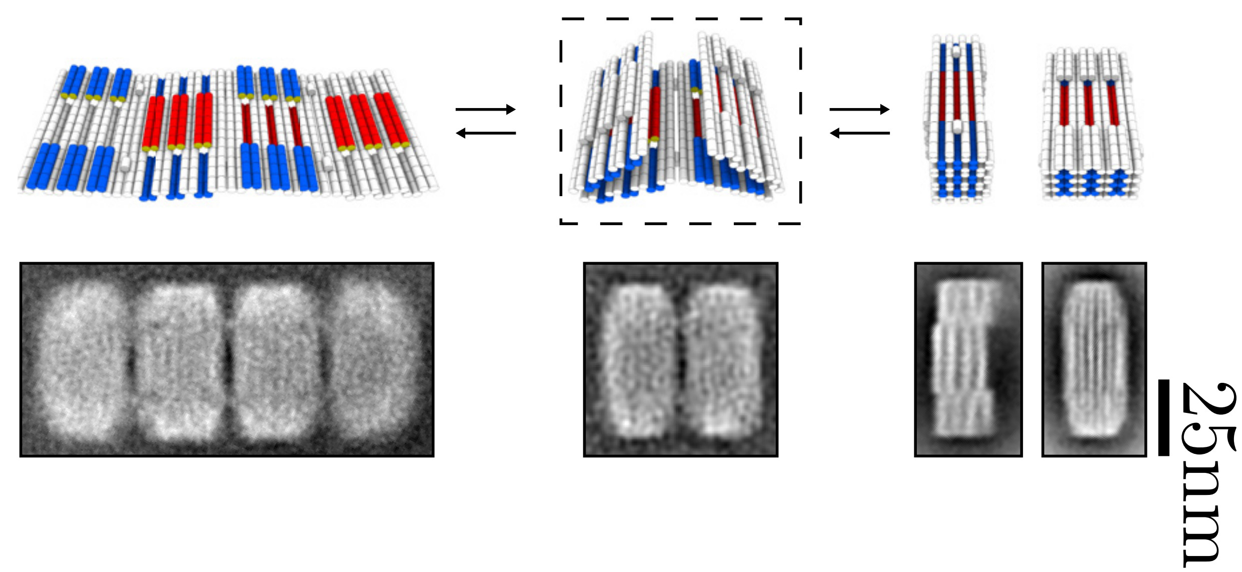
Assembly of structures is controlled by temperature and external salt, which screens the electrostatic interaction between charged DNA strands.



Vitruvian man by da Vinci

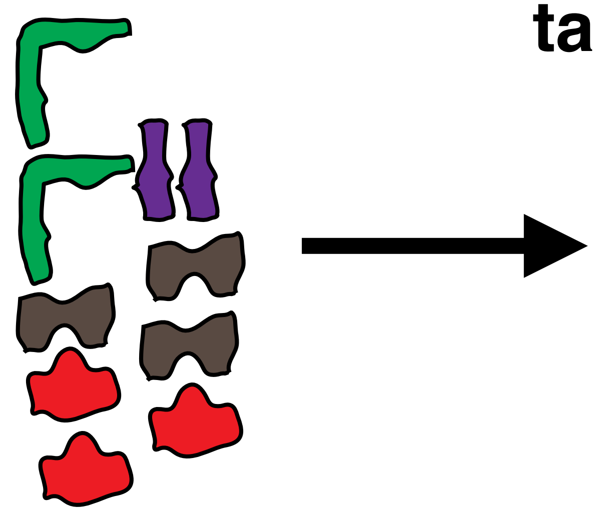




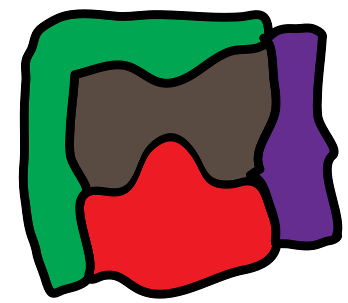


T. Gerling et al., Science 347, 1446 (2015)

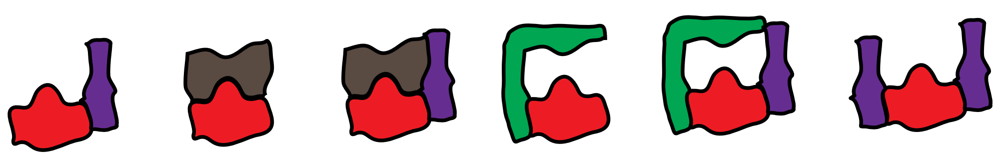
Potential issues with self-assembly



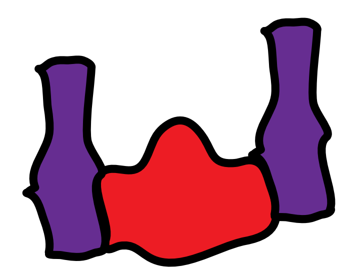
target structure



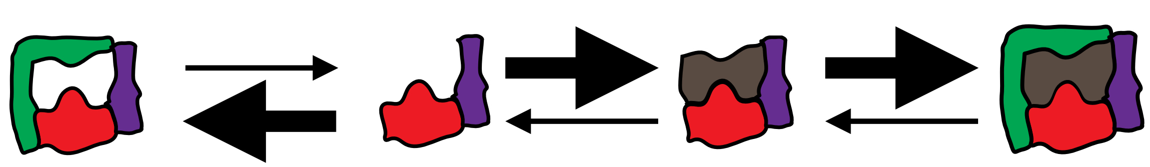
There are exponentially many competing structures. Entropic effects may dominate for large structures!



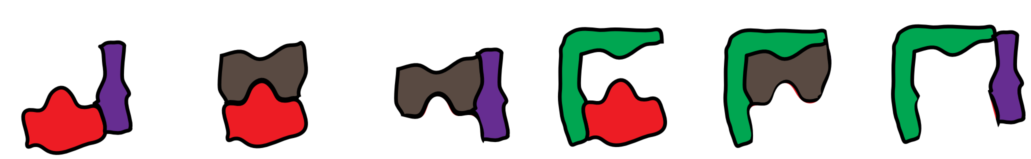
If non-specific interactions are too strong, we may get incorrectly bound structures.



If specific interactions are too strong, we may get trapped in incomplete structures. E.g. green piece has to unbind, before the brown piece can bind correctly, but this unbinding is exponentially slow!



Kinetic arrest: target structure can be self-assembled in many different ways. All components may be used up before generating target structures! This may result in many incomplete structures.
Solution: nonuniform concentrations of components may guide certain assembly pathways.

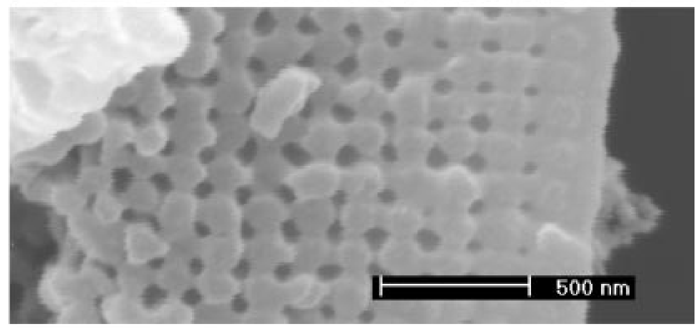


A. Murugan et al., Nat. Comm. 6, 6203 (2015)

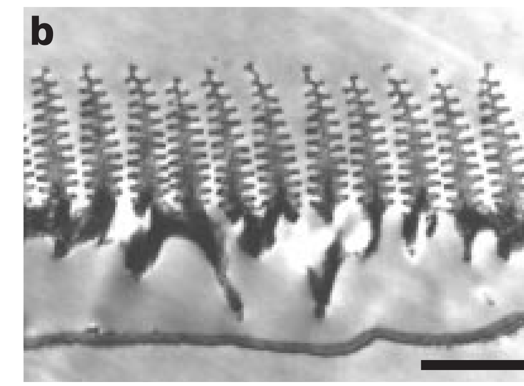
Structural colors

Structural colors of animals and plants appear due to the selective reflection of ambient light on structural features underneath the surface.

Peacock feather eyes

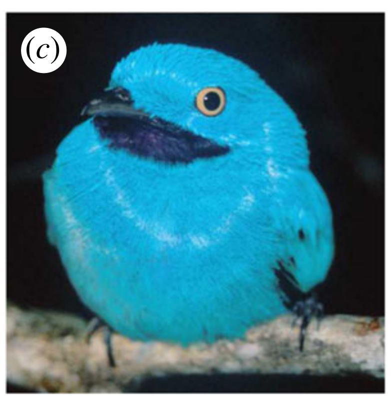


Morpho butterfly

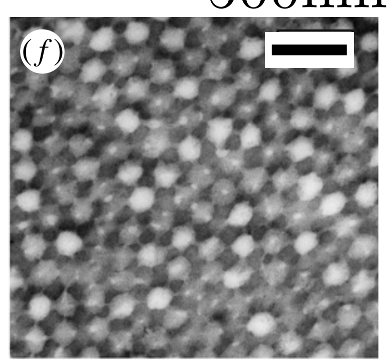


$1.7\mu m$

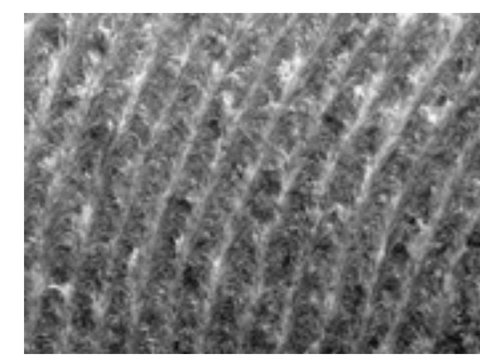
Plum-throated Cotinga



500nm

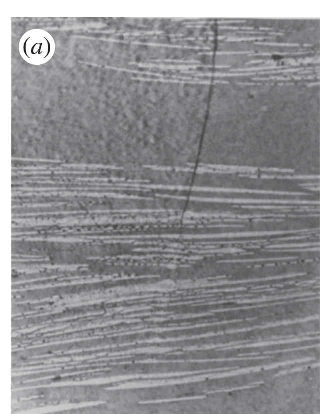


Marble berry



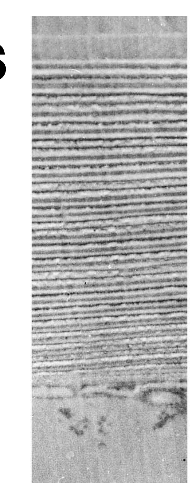
250nm

bleak fish



$1\mu m$

Chrysina aurigans beetle



$1\mu m$

Dynamic structural colors

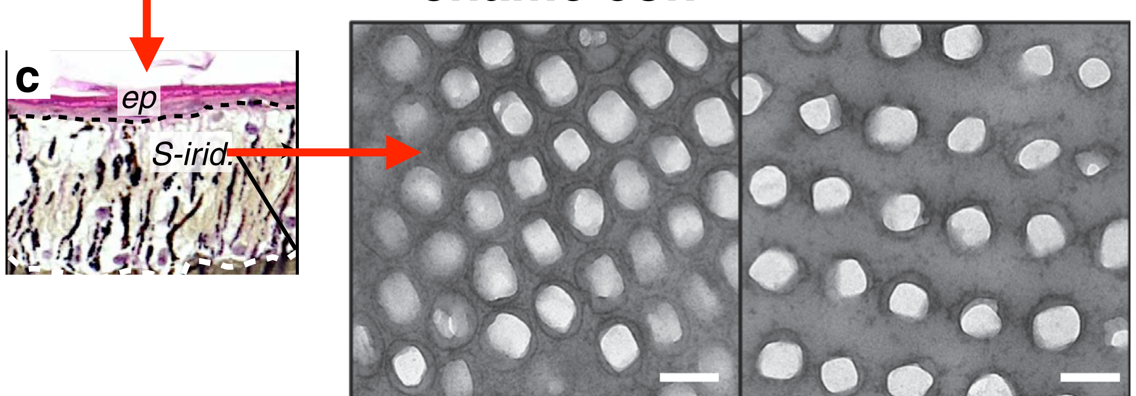
Chameleon (speed 8x)

J. Teyssier et al., Nat. Comm. 6, 6368 (2015)

Changes in osmotic concentration lead to the swelling of cells in excited chameleon. This changes the spacing of periodic structure from which the ambient light is reflected.

skin

relaxed chameleon **excited chameleon**

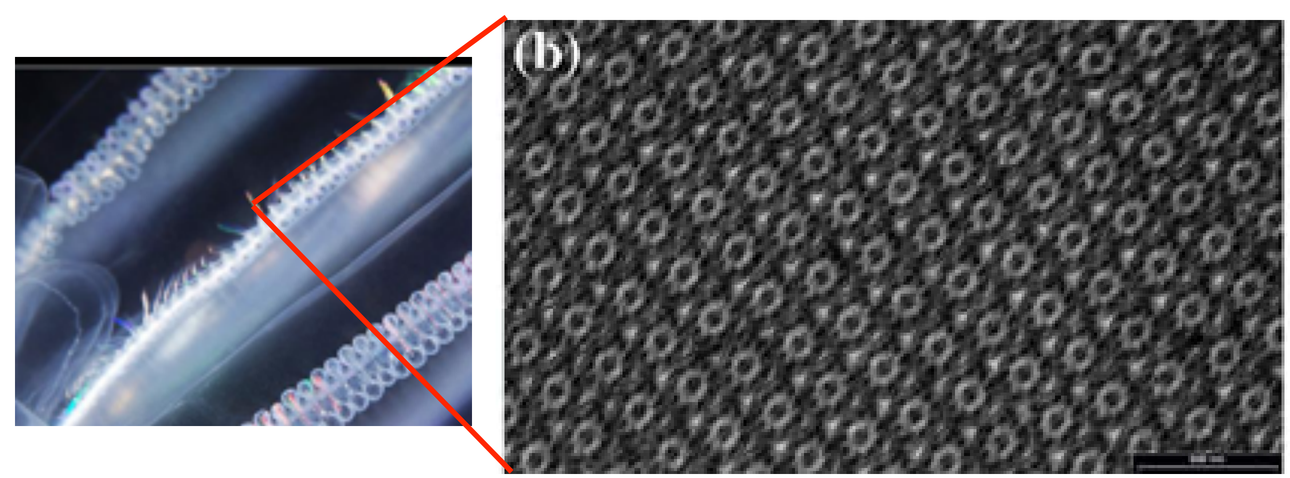


200nm 200nm

Comb Jelly (real time)

https://www.youtube.com/watch?v=Qy90d0XvJIE

Rainbow color waves are produced by the beating of cilia, which change the orientation of periodic structure from which the ambient light is reflected.



$1\mu m$

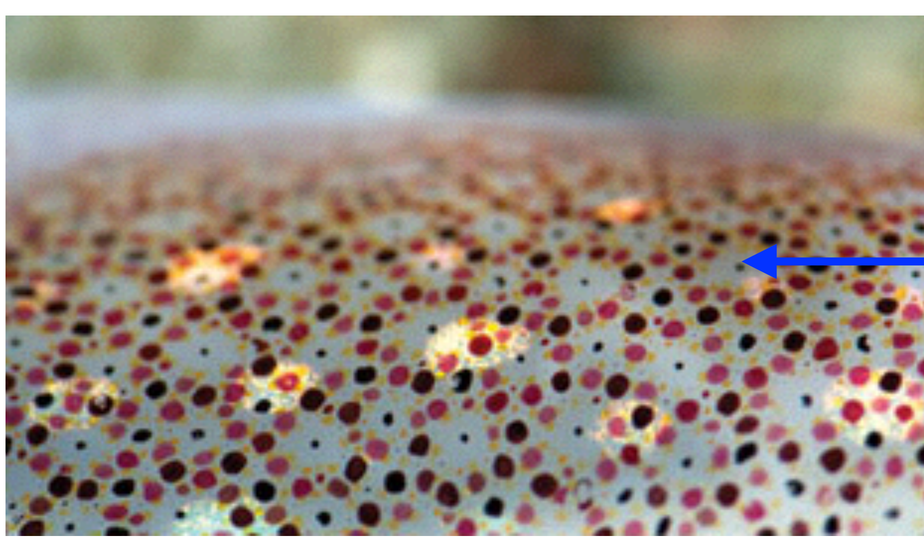
Dynamic colors in cephalopods

octopus

https://www.youtube.com/watch?v=9MB2ltsAPnQ

squid

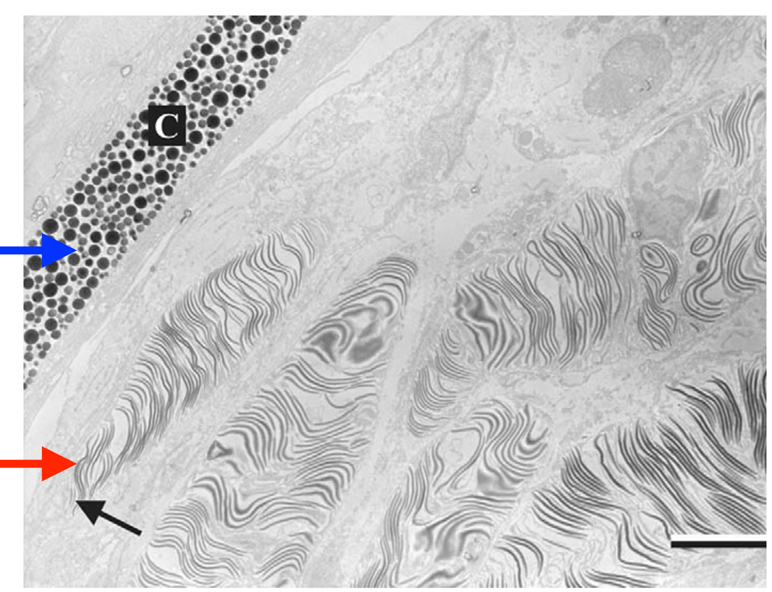
Dynamical color change in cephalopod is achieved by modulation of size and spacing of both the pigment cells and the cells reflecting light.



squid skin surface

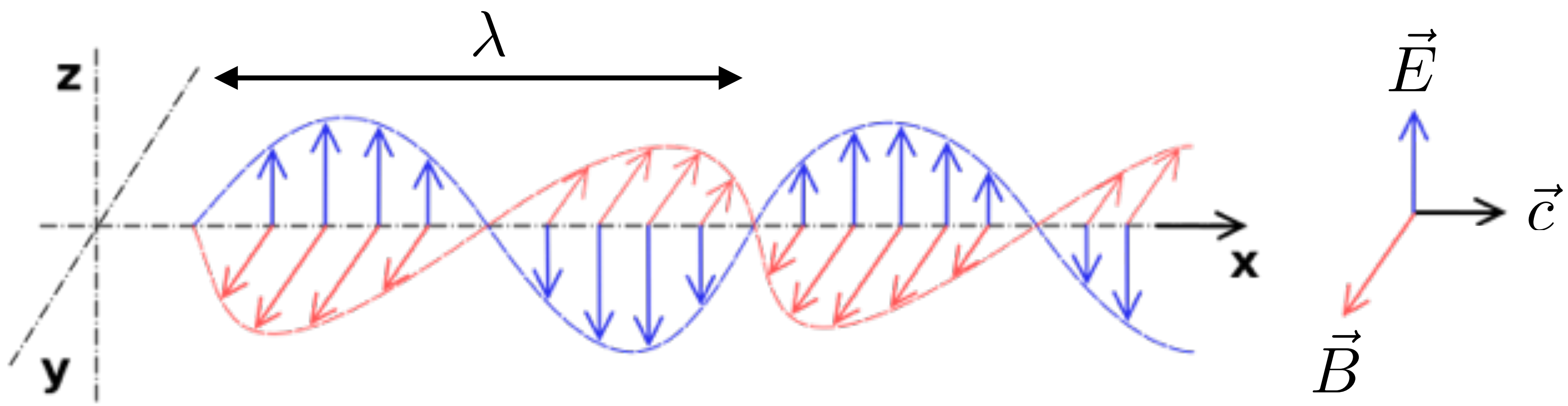
chromatophores (pigment cells)

iridophores (reflecting light)



$7.5\mu\mathrm{m}$

Electromagnetic waves



electric field

magnetic field

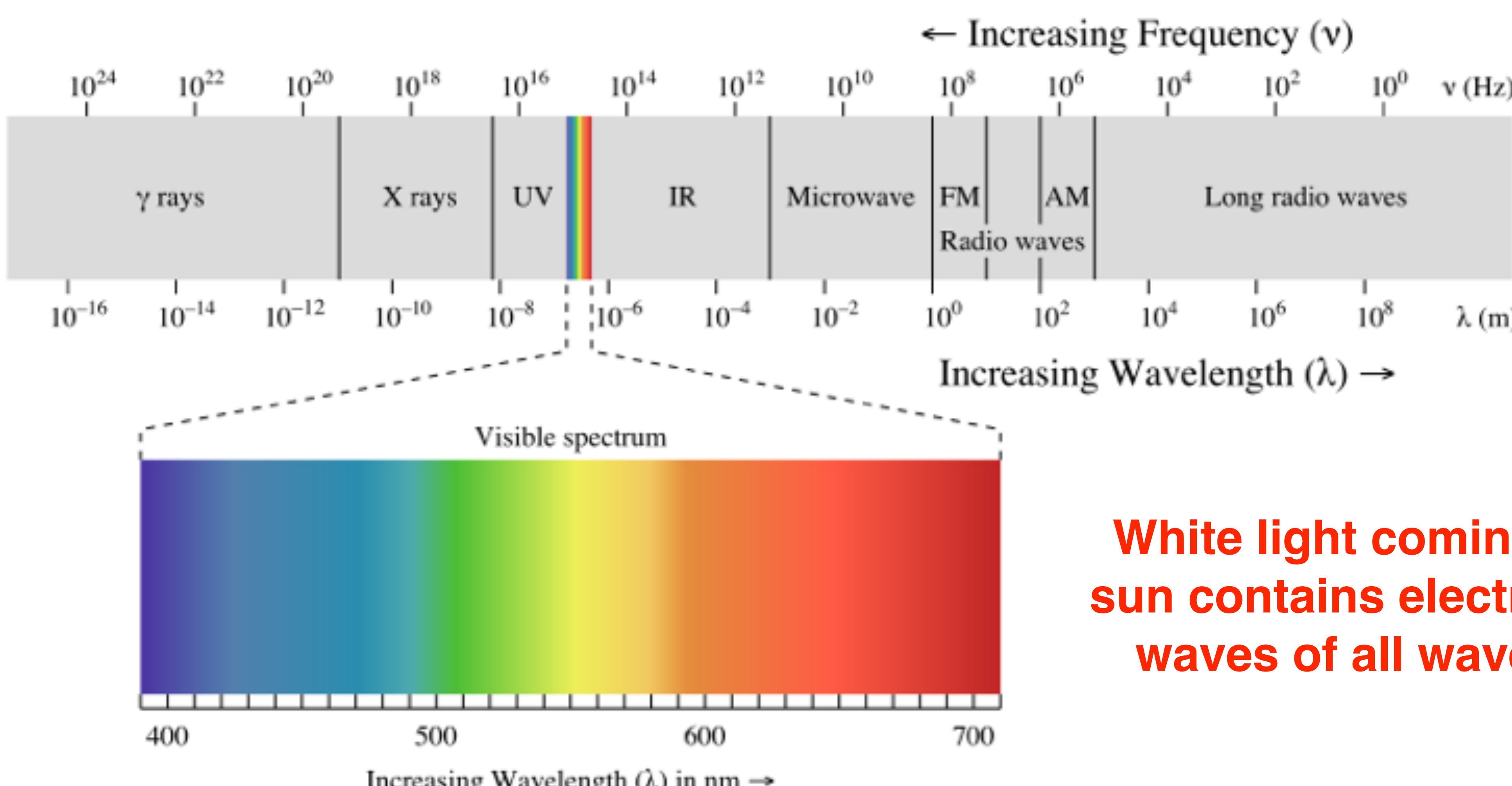
$$\vec{E}(x,t) = \vec{E}_0 e^{2\pi i(\nu t - x/\lambda)}$$

$$\vec{B}(x,t) = \vec{B}_0 e^{2\pi i(\nu t - x/\lambda)}$$

$$c^2 \vec{B}_0 = \vec{c} \times \vec{E}_0$$

speed of light

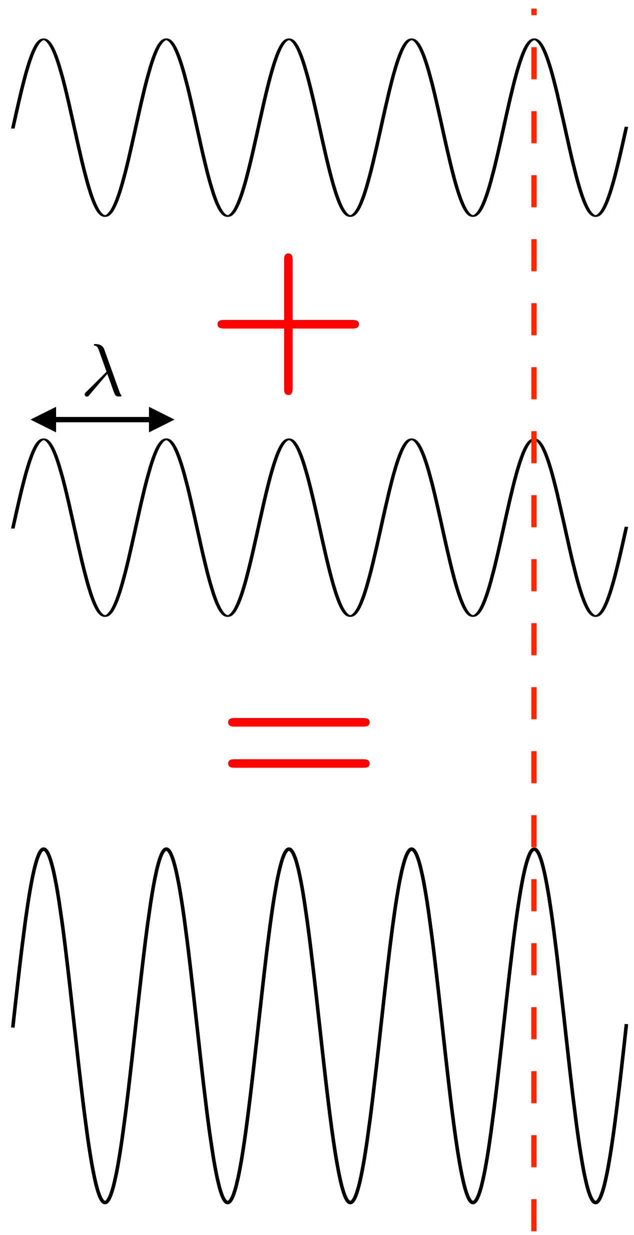
$$c = \lambda\nu = 3 \times 10^8 \mathrm{m/s}$$



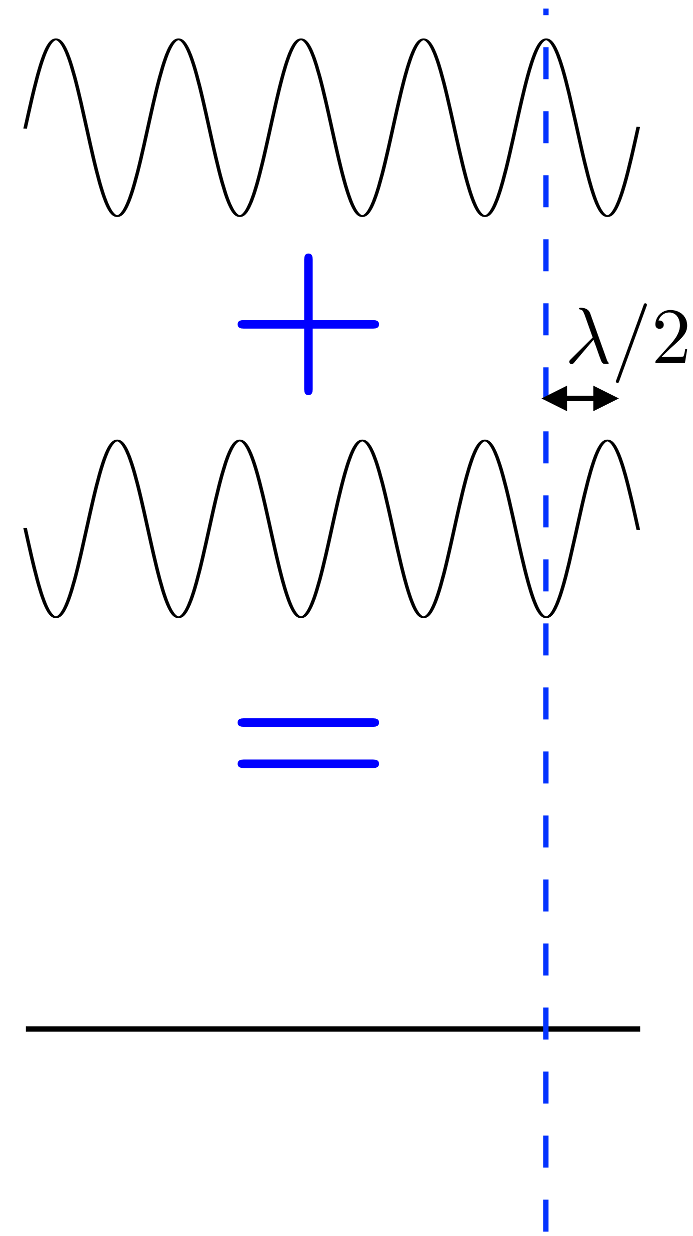
White light coming from the sun contains electromagnetic waves of all wavelengths!

Interference

constructive interference



destructive interference



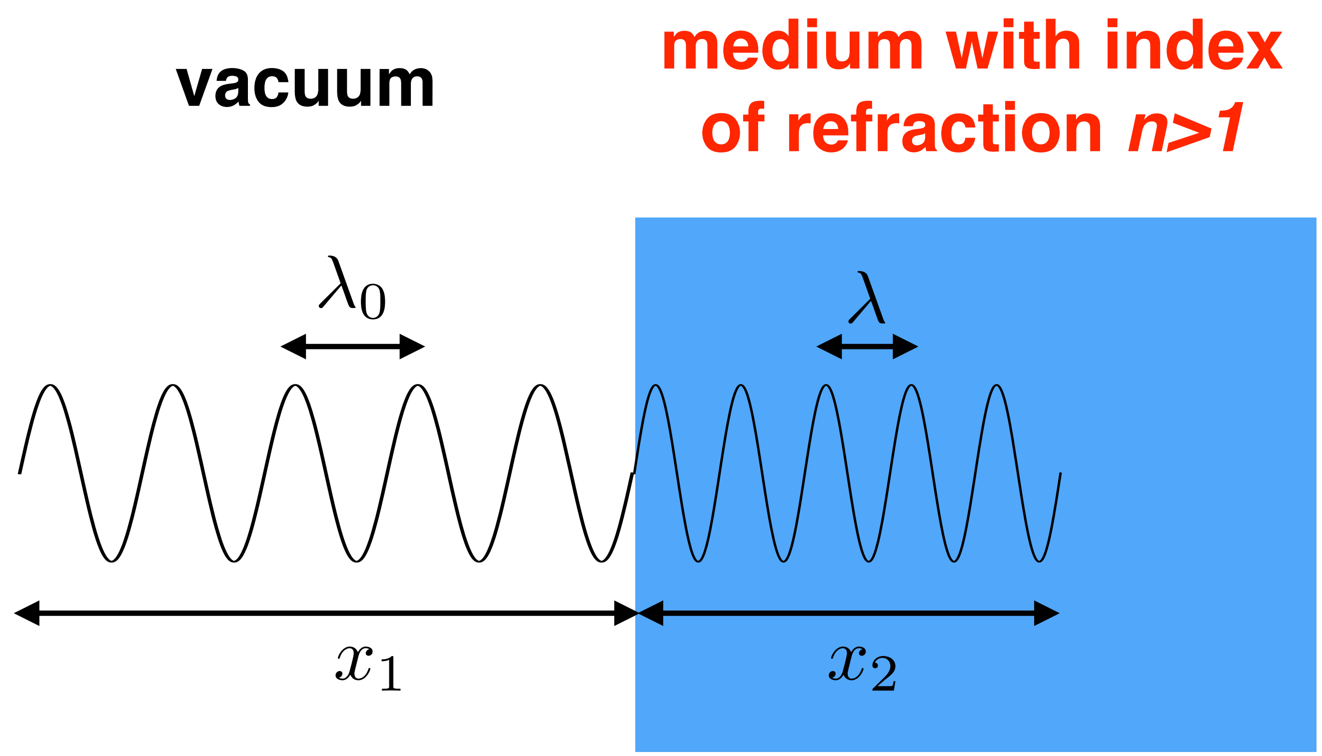
Constructive interference occurs when the two waves are in phase: waves offset by $m\lambda$ **,**

$$m = 0, \pm 1, \pm 2, \ldots$$

Destructive interference occurs when the two waves are out of phase: waves offset by $(m + 1/2)\lambda$ **,**

$$m = 0, \pm 1, \pm 2, \ldots$$

Propagation of light in medium



speed of light	$c_0 = 3 \times 10^8 \mathrm{m/s}$	$c = c_0/n$
frequency	ν_0	$\nu = \nu_0$
wavelength	λ_0	$\lambda = \lambda_0/n$
	$c_0 = \nu_0 \lambda_0$	$c = \nu \lambda$

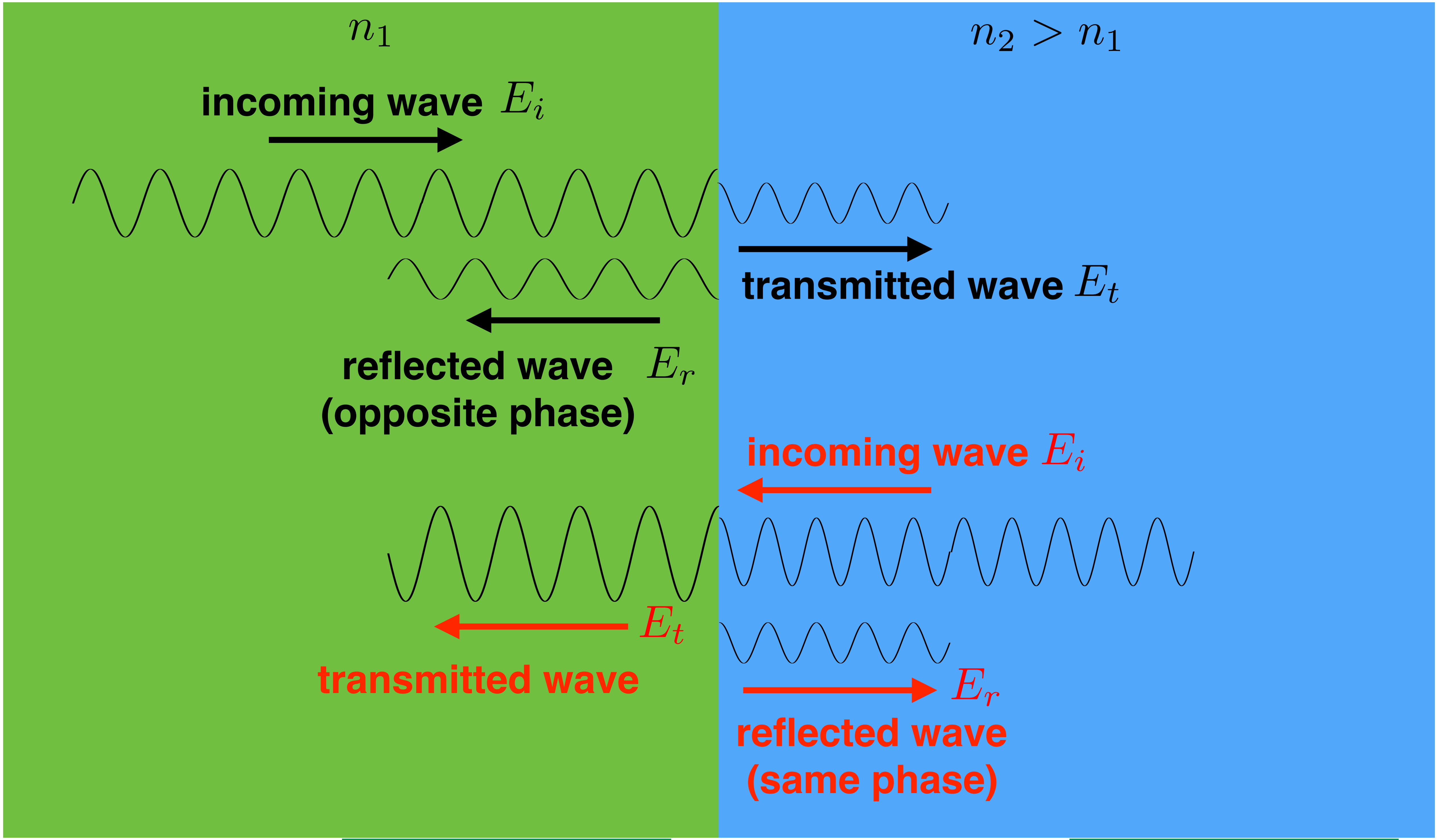
---

total number of cycles

$$\boxed{\frac{x_1}{\lambda_0} + \frac{x_2}{\lambda} = \frac{x_1 + n x_2}{\lambda_0}}$$

Optical path length is geometric distance multiplied by the index of refraction!

Reflection of light at the interface between two media



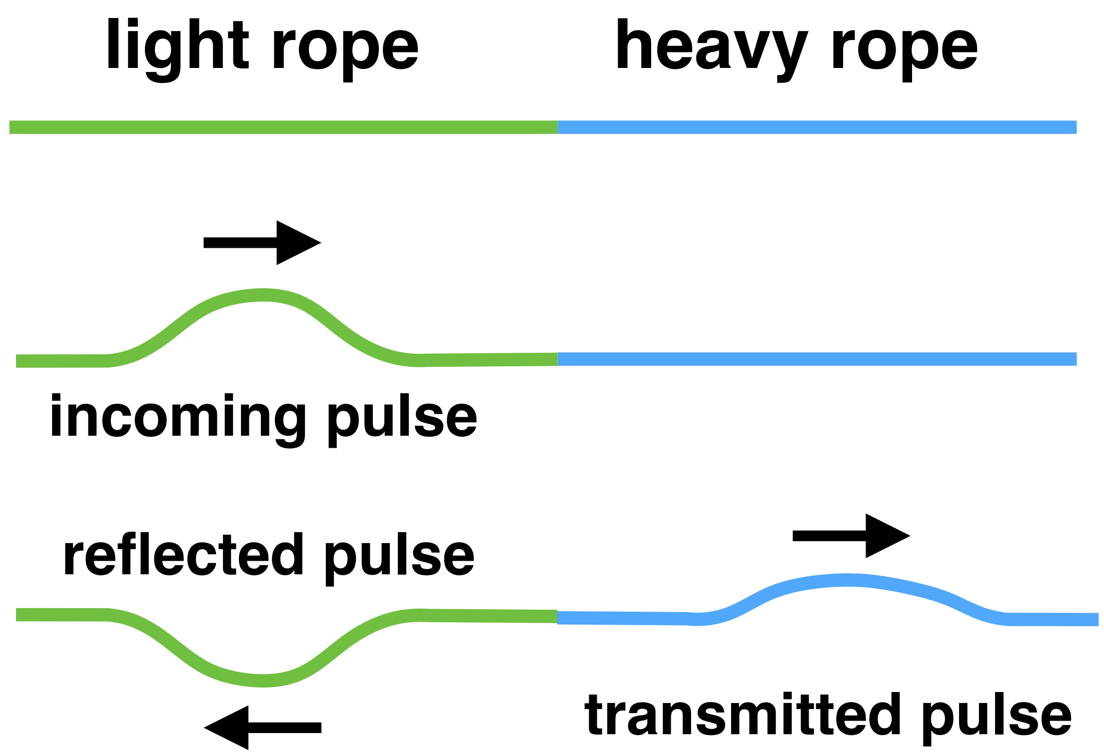
amplitude of reflected electric field

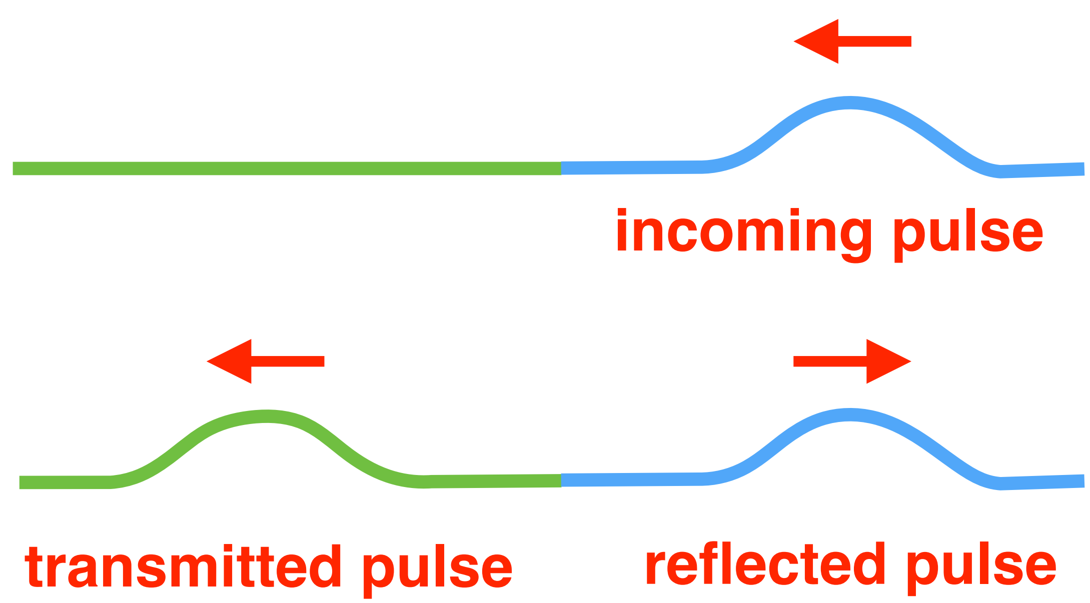
$$\frac{E_r}{E_i} = \frac{n_1 - n_2}{n_1 + n_2}$$

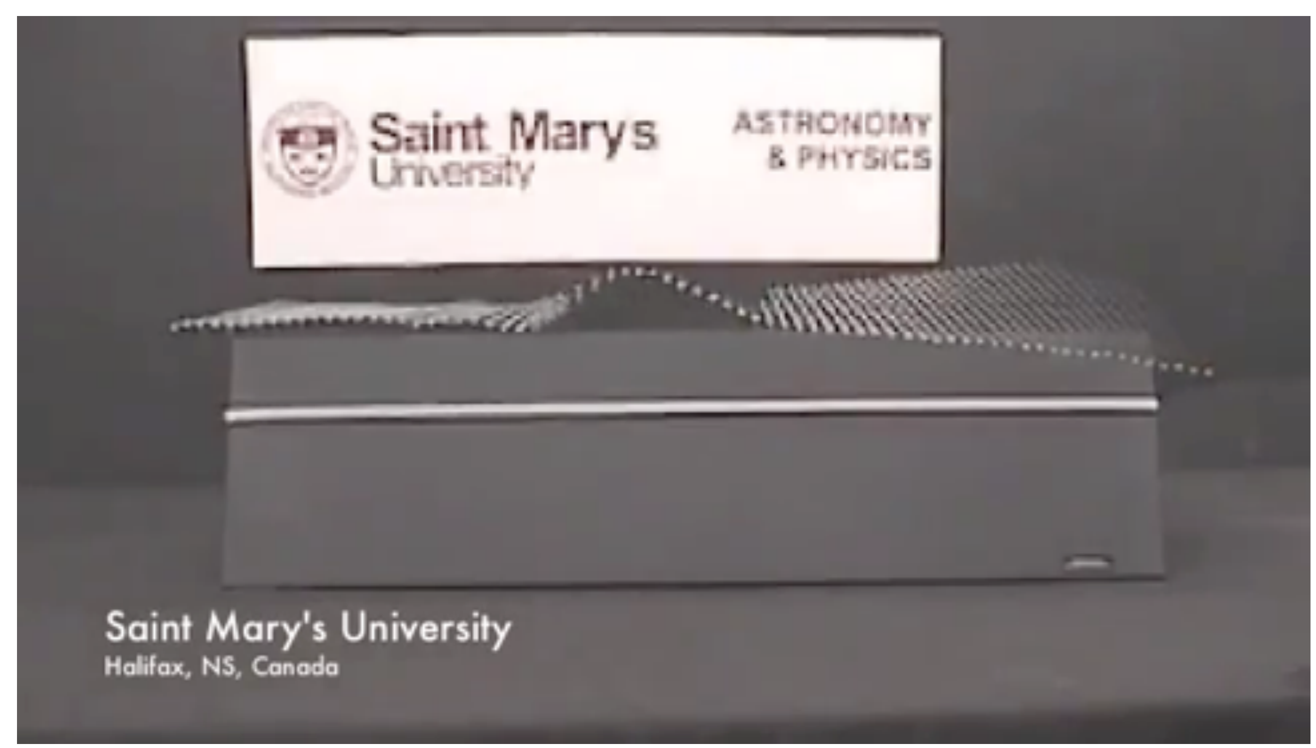
amplitude of transmitted electric field

$$\frac{E_t}{E_i} = \frac{2n_1}{n_1 + n_2}$$

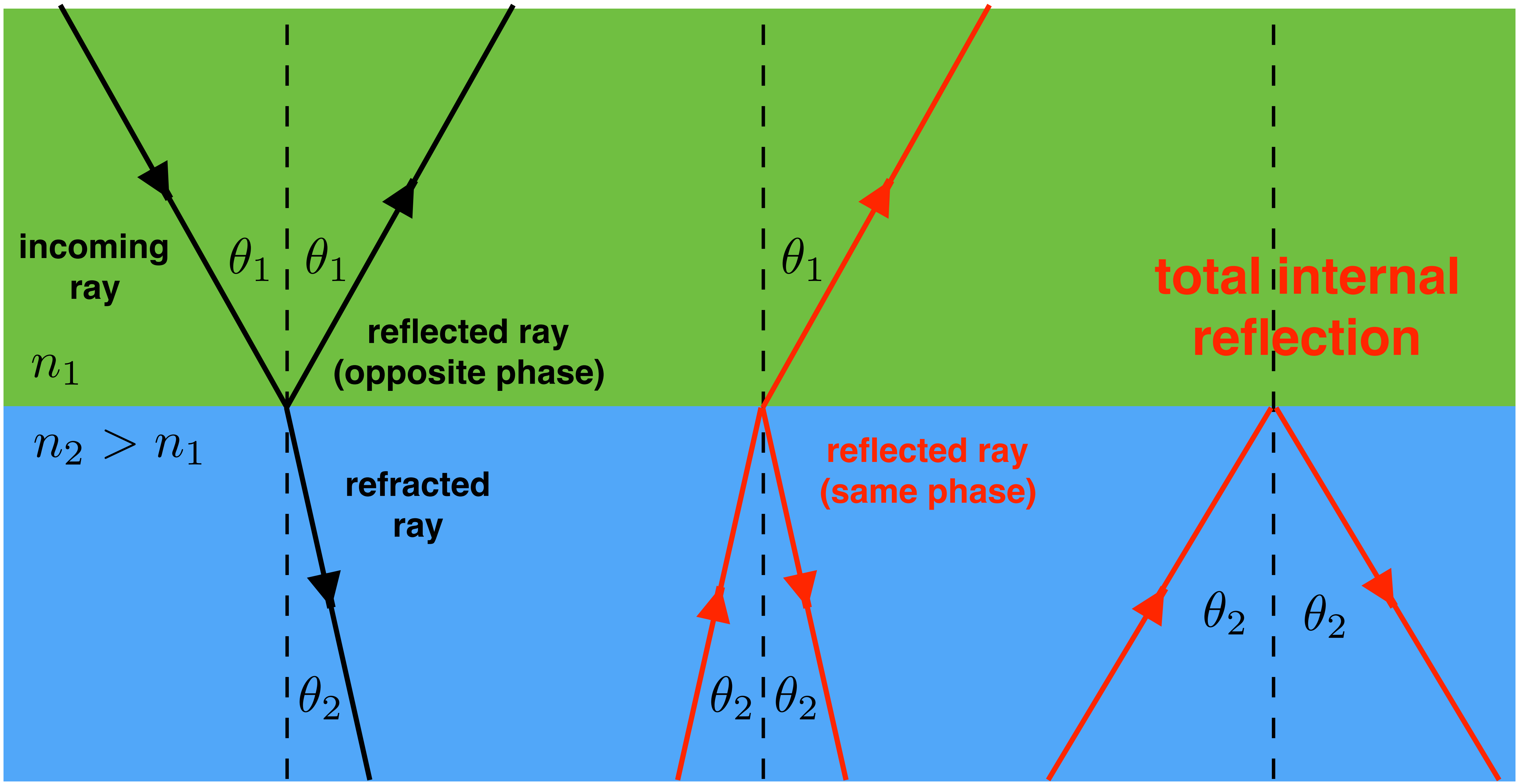
Reflection of elastic waves







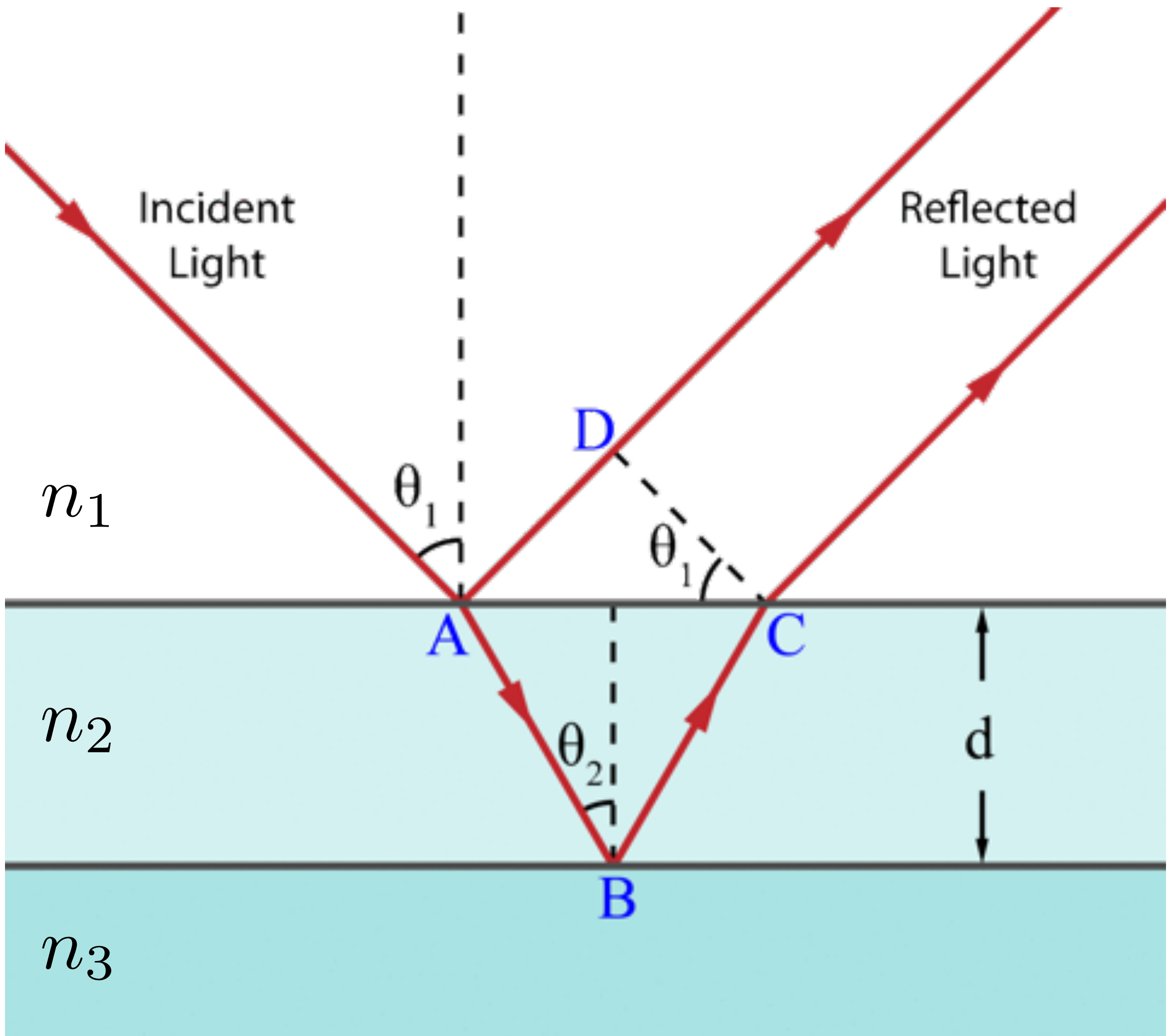
Refraction of light



Snell's law $\boxed{n_1 \sin\theta_1 = n_2 \sin\theta_2}$

Total internal reflection $\boxed{\theta_2 > \arcsin(n_1/n_2)}$

Interference on thin films



difference between optical path lengths of the two reflected rays

$$OPD = n_2\left(\overline{AB} + \overline{BC}\right) - n_1\overline{AD}$$

$$OPD = 2n_2 d\cos(\theta_2)$$

no additional phase difference due to reflections

$n_1 < n_2 < n_3$ $\qquad$ $n_1 > n_2 > n_3$

constructive interference

$$OPD = m\lambda$$

destructive interference

$$OPD = (m + 1/2)\lambda$$

$$m = 0, \pm1, \pm2, \ldots$$

additional π phase difference due to reflections

$n_1 < n_2 > n_3$ $\qquad$ $n_1 > n_2 < n_3$

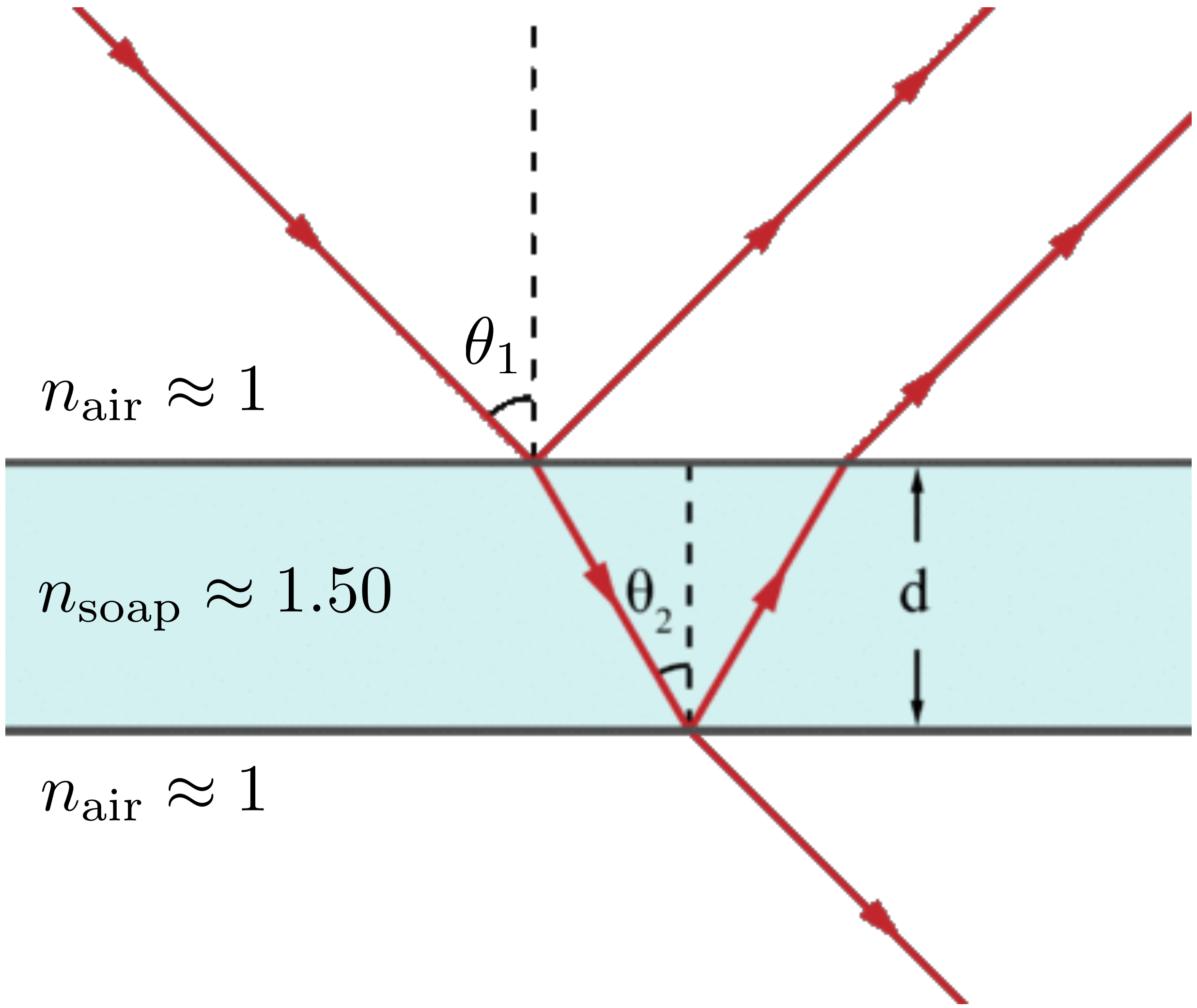
constructive interference

$$OPD = (m + 1/2)\lambda$$

destructive interference

$$OPD = m\lambda$$

Interference on soap bubbles



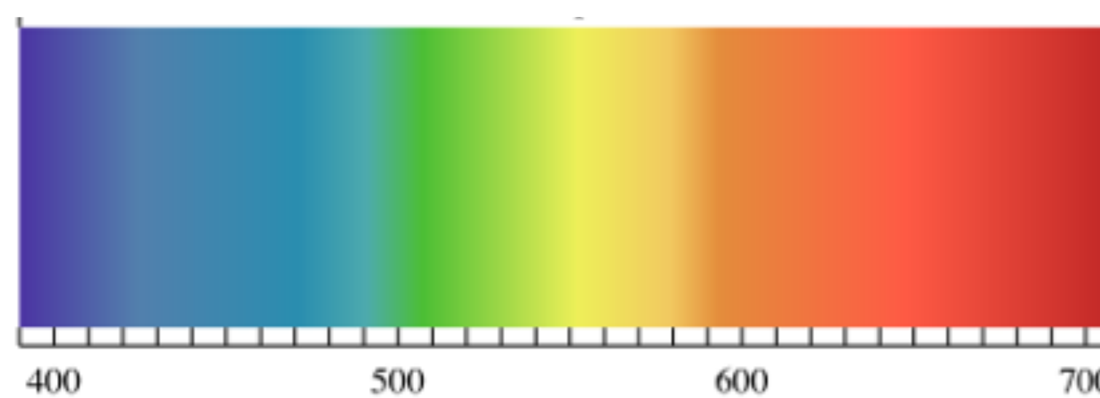
soap bubble

constructive interference for different colors happens at different angles

$$2dn_{\text{soap}}\cos(\theta_2) = (m + 1/2)\lambda$$

$$m = 0, \pm 1, \pm 2, \ldots$$

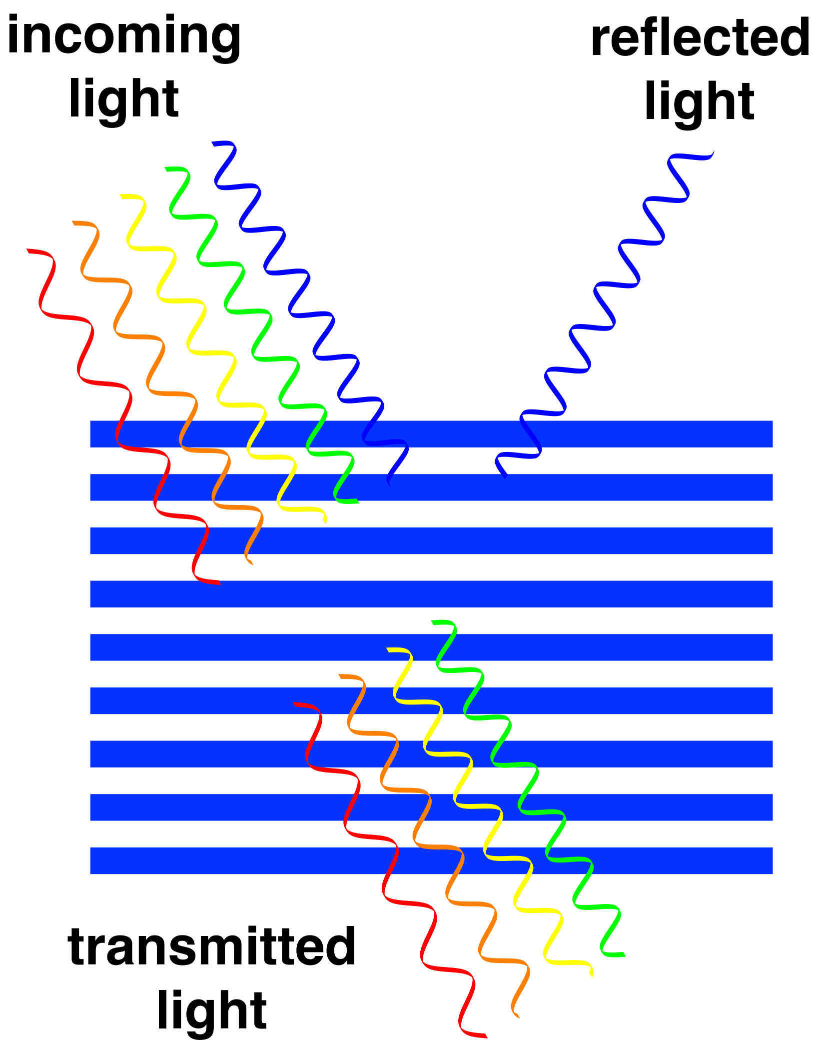
visible spectrum

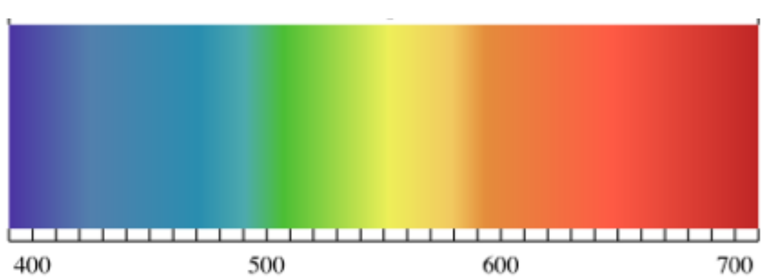


wavelength $\lambda[\text{nm}]$

Single structural color

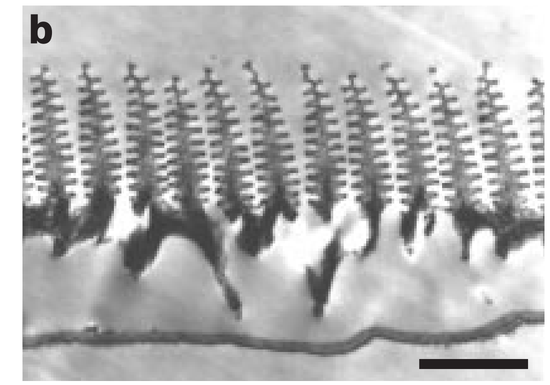
Single reflected color on structures with uniform spacing





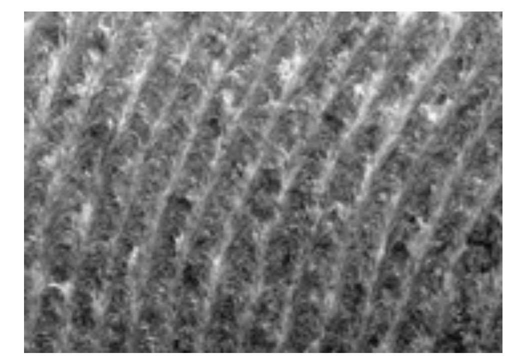
wavelength $\lambda[\mathrm{nm}]$

Morpho butterfly



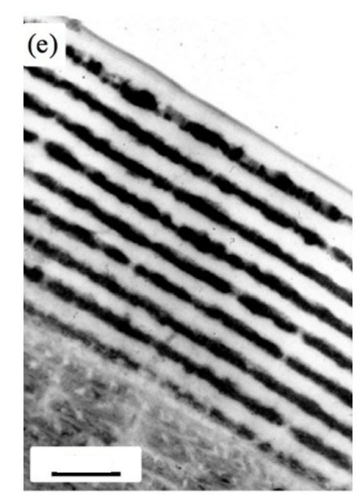
$1.7\mu\mathrm{m}$

Marble berry



$250\mathrm{nm}$

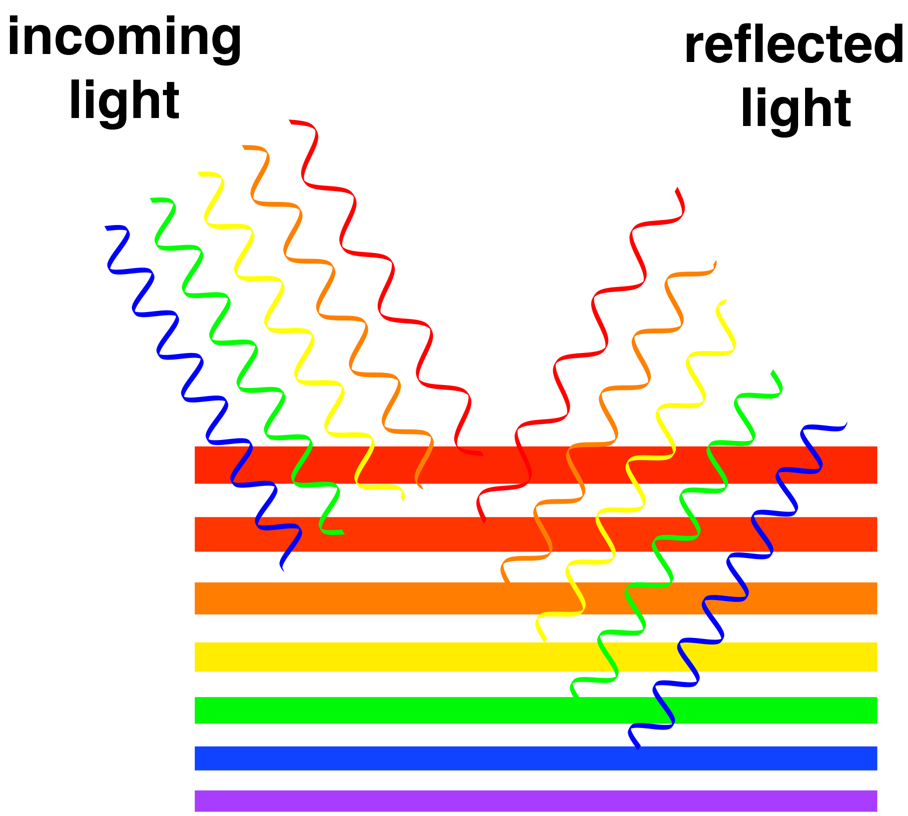
Chrysochroa raja bettle

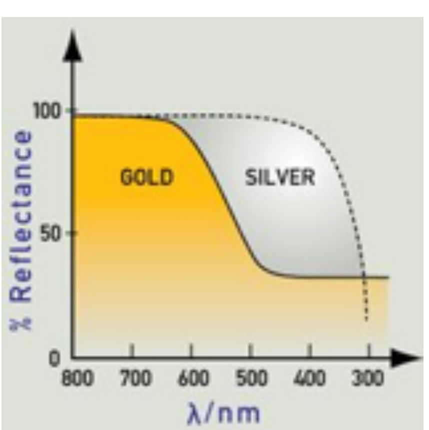


$1\mu\mathrm{m}$

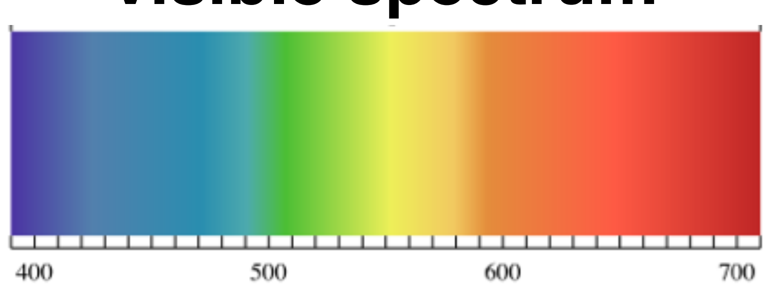
Silver and gold structural colors

Many colors reflected on structures with varying spacing





visible spectrum

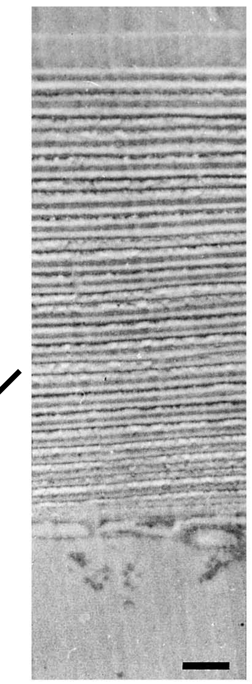


wavelength $\lambda[\mathrm{nm}]$

chirped structure

Chrysina limbata beetle

Chrysina aurigans beetle



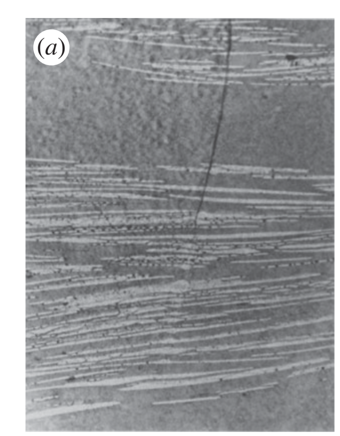
$1\mu\mathrm{m}$

thicker

thinner

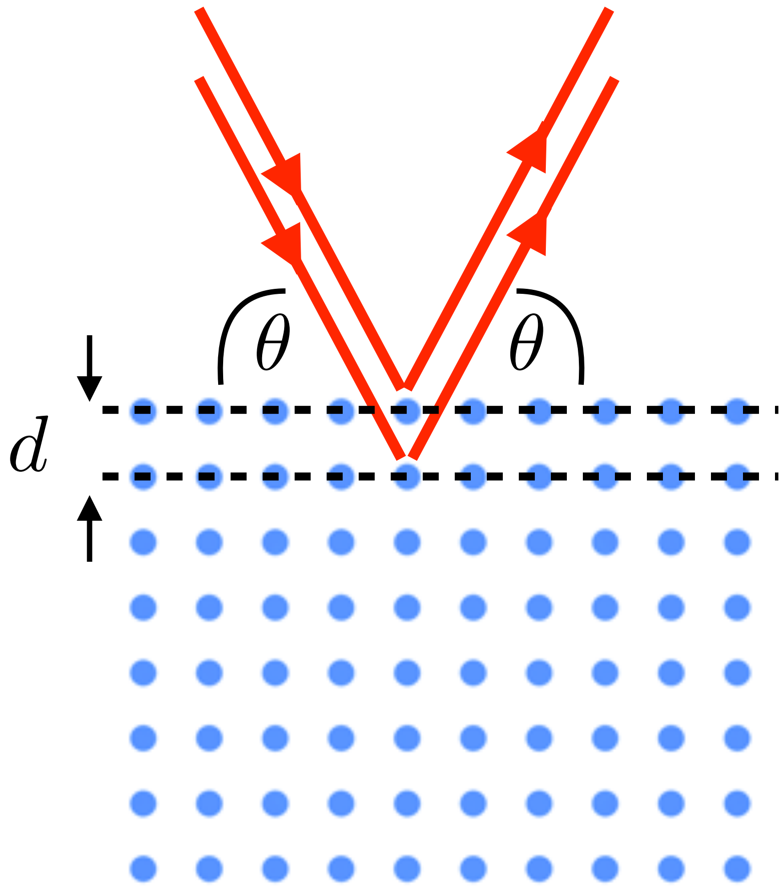
disordered layer spacing

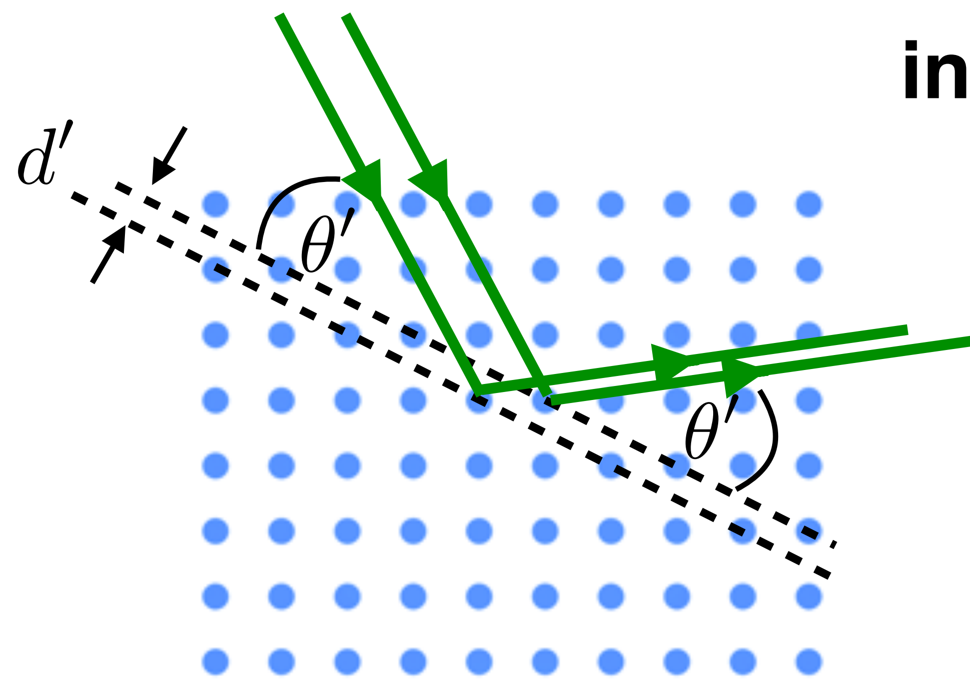
bleak fish



$1\mu\mathrm{m}$

Bragg scattering on crystal layers



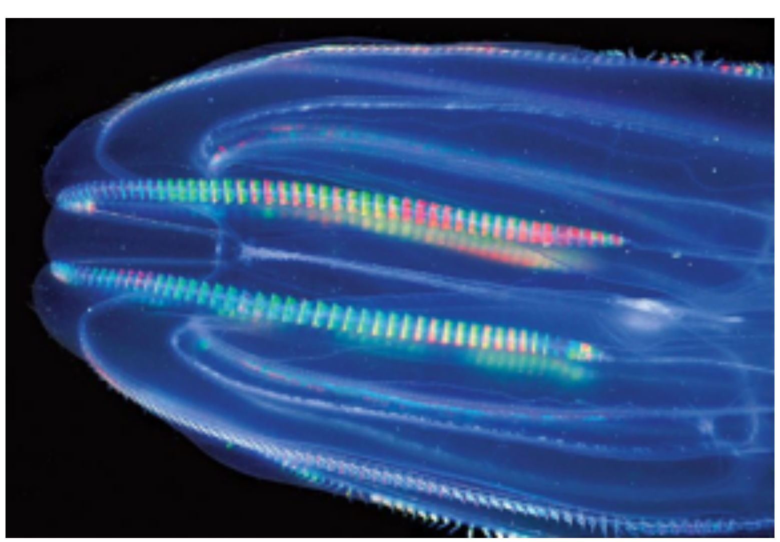


constructive interference condition

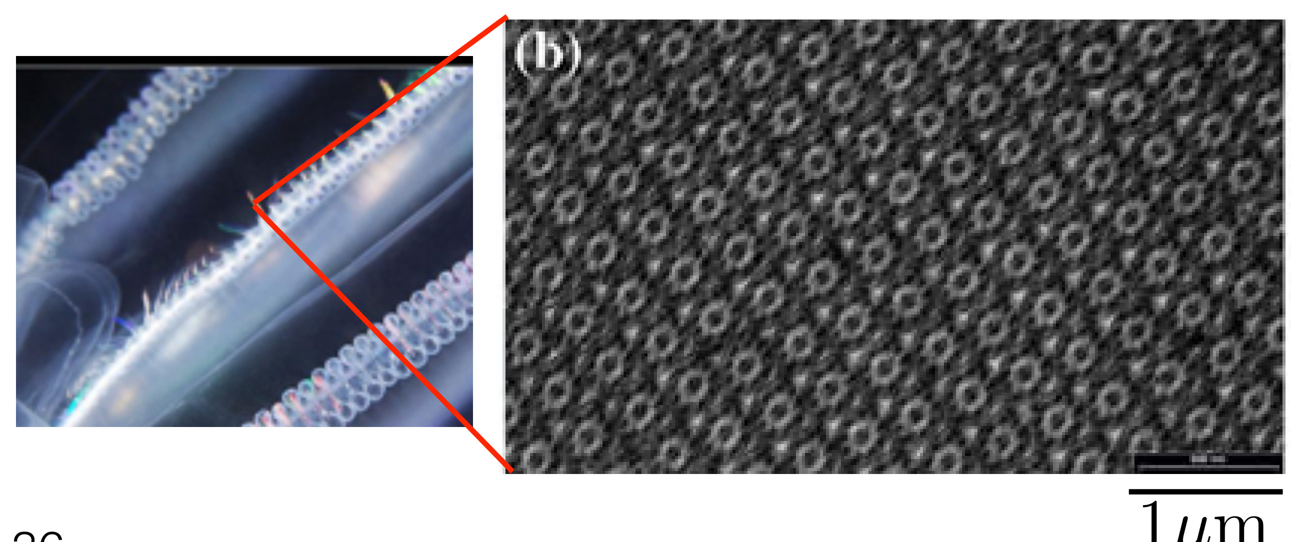
$$\boxed{\begin{aligned} 2d\sin\theta &= m\lambda \\ 2d'\sin\theta' &= m\lambda' \end{aligned}}$$

$$m = 0, \pm 1, \pm 2, \ldots$$

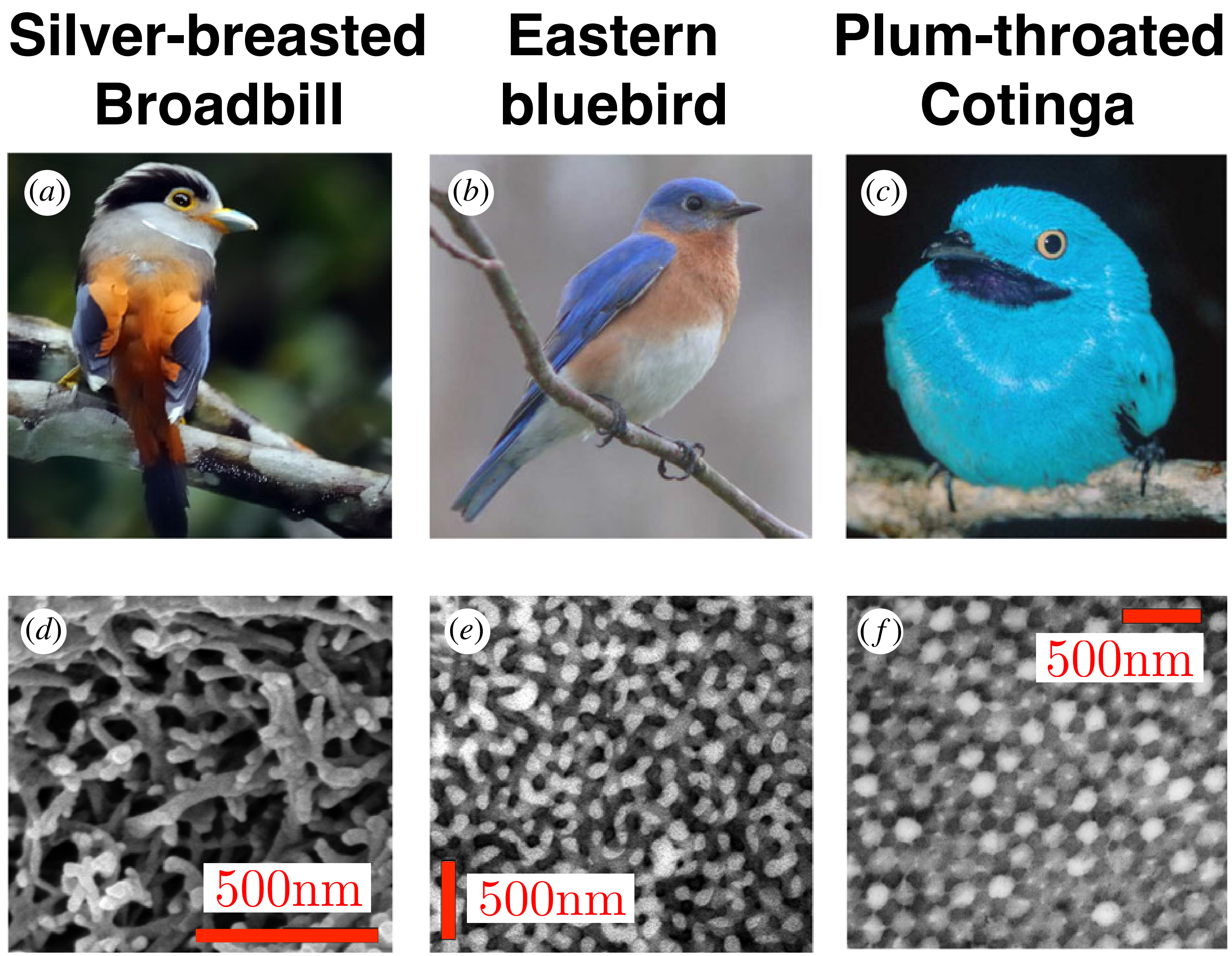
Comb jelly



Beating cilia are changing crystal orientation



Scattering on disordered structures



Disordered structures that are locally order and have a characteristic length scale.

This length scale determines what light wavelengths are preferentially scattered.

This gives rise to blue colors in birds above.

Noise barriers around the Amsterdam airport

Sound from airplanes that are landing and taking off is reflected from artificial barriers into the atmosphere.