Steric Interactions

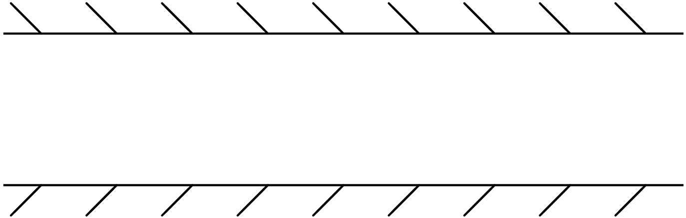
Tyler Shendruk

February 6, 2011

Polymer Brush

Consider:

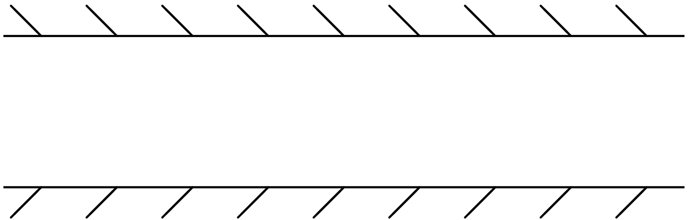
Consider two surfaces with polymers attached to the surfaces



Polymer Brush

Consider:

Consider two surfaces with polymers attached to the surfaces



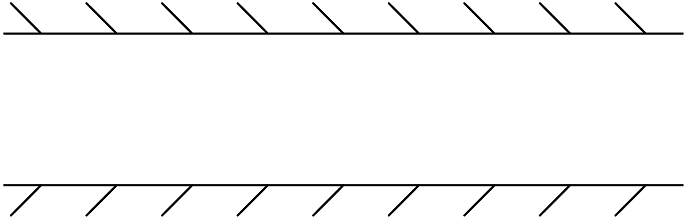
How do they interact?

- Mix?

Polymer Brush

Consider:

Consider two surfaces with polymers attached to the surfaces



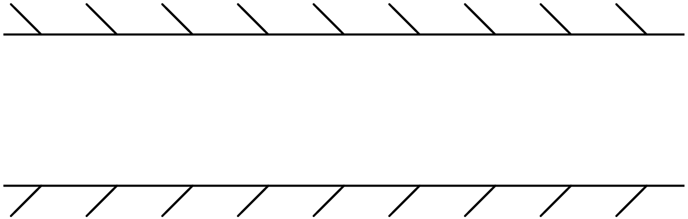
How do they interact?

- Mix?
- Interpenetrate?

Polymer Brush

Consider:

Consider two surfaces with polymers attached to the surfaces



How do they interact?

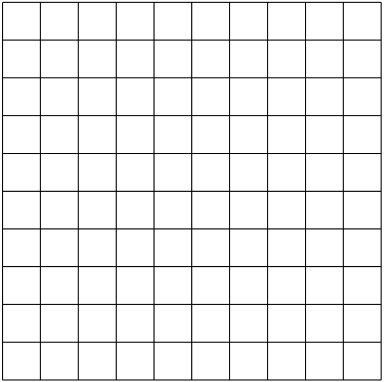
- Mix?
- Interpenetrate?
- Compress?

It depends.

Grid

Consider:

Consider a point particle on a grid.

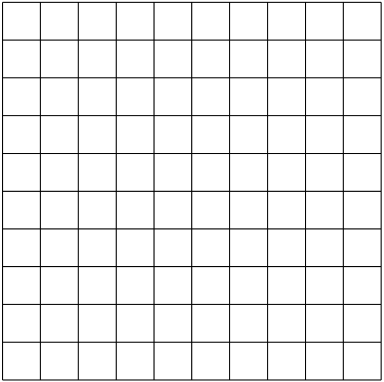


Entropy

Grid

Consider:

Consider a point particle on a grid.



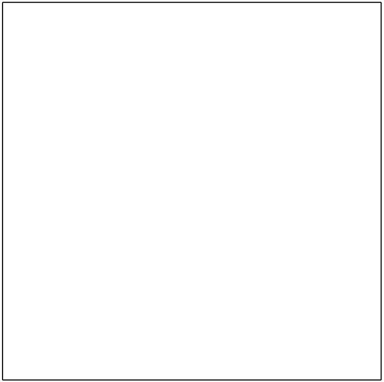
Entropy

$$S = k_B \ln$$

Point Particle

Consider:

Consider a point particle in a box.



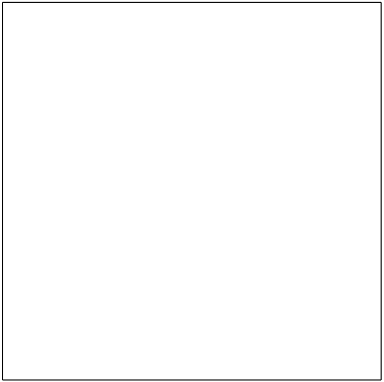
Entropy

$$S = k_{\text{B}} \ln$$

Excluded Edges

Consider:

Consider a finite particle in a box.



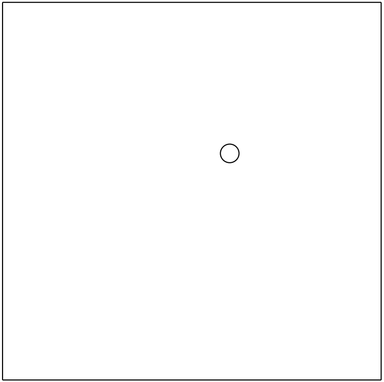
Entropy

$$S = k_{\mathrm{B}} \ln$$

Excluded Region

Consider:

Consider adding a fixed finite particle.



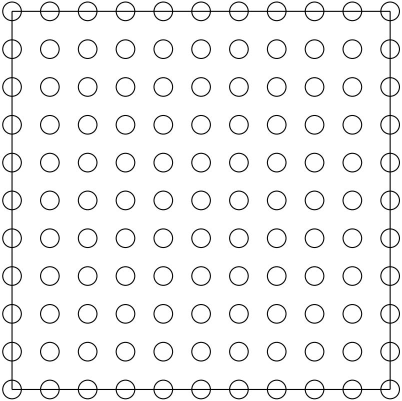
Entropy

$$S = k_B \ln$$

Reduced Space

Consider:

Consider adding many fixed finite particles.



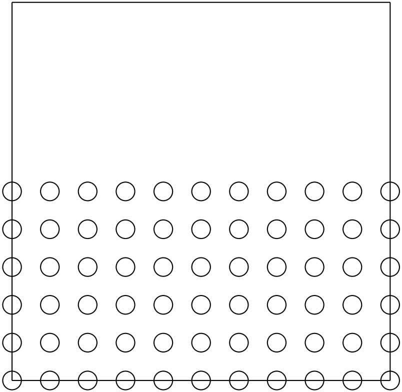
Entropy

$$S = k_B \ln$$

Half Space

Consider:

Consider half the space has particles and half do not.



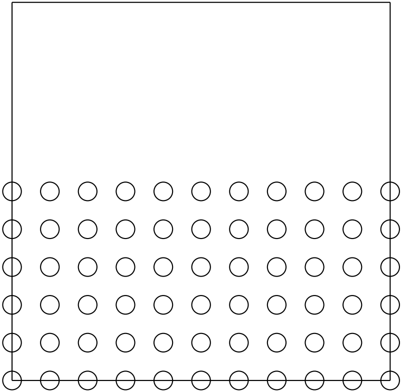
Entropy

$$S_{\mathrm{above}} = k_{\mathrm{B}} \ln$$
$$S_{\mathrm{below}} = k_{\mathrm{B}} \ln$$

Half Space

Consider:

Consider half the space has particles and half do not.



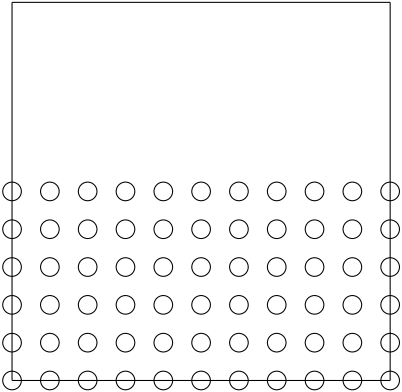
Entropy

$$S_{\text{above}} = k_B \ln V_{\text{above}}$$
$$S_{\text{below}} = k_B \ln V_{\text{below}}$$

Half Space

Consider:

Consider half the space has particles and half do not.



Entropy

$$S_{\text{above}} = k_B \ln\left(\frac{V}{2}\right)$$

$$S_{\text{below}} = k_B \ln\left(\frac{V}{2} - Vc\right)$$

Some Thermodynamics

Thermodynamics

ΔS Entropy Difference

$\downarrow$

Some Thermodynamics

Thermodynamics

ΔS Entropy Difference

$\downarrow$

ΔF Free Energy Difference

$\downarrow$

Some Thermodynamics

Thermodynamics

ΔS Entropy Difference

$\downarrow$

ΔF Free Energy Difference

$\downarrow$

$\Delta \mu$ Chemical Potential Difference

$\downarrow$

Some Thermodynamics

Thermodynamics

ΔS Entropy Difference

$\downarrow$

ΔF Free Energy Difference

$\downarrow$

$\Delta \mu$ Chemical Potential Difference

$\downarrow$

Π Osmotic Pressure

Osmotic Pressure

Form

Guess a form for the osmotic pressure:

$$\Pi =$$

Osmotic Pressure

Form

Guess a form for the osmotic pressure:

$$\Pi =$$

- Should the osmotic pressure depend on the temperature?

Osmotic Pressure

Form

Guess a form for the osmotic pressure:

$$\Pi =$$

- Should the osmotic pressure depend on the temperature?
- Should it depend on the concentration?

Osmotic Pressure

Form

Guess a form for the osmotic pressure:

$$\Pi =$$

- Should the osmotic pressure depend on the temperature?
- Should it depend on the concentration?
- Should it be proportional to first order?

Osmotic Pressure

Form

Guess a form for the osmotic pressure:

$$\Pi =$$

- Should the osmotic pressure depend on the temperature?
- Should it depend on the concentration?
- Should it be proportional to first order?
- Should there be higher orders?

Osmotic Pressure

Form

$$\frac{\Pi}{k_B T} = \frac{c}{M} + B_2 c^2 + B_3 c^3 + \dots$$

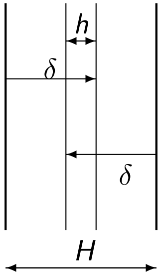
Bs are virial coefficients whose values we don't really care about.

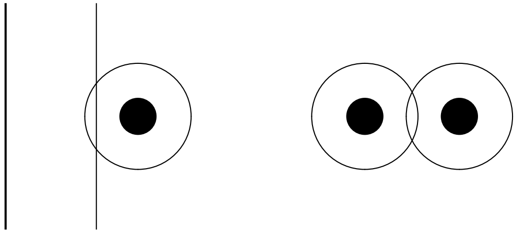
Interaction Energy

Interaction Energy

The osmotic pressure is a force per unit area so the interaction energy of two overlapping brushes is the integral of the force *i.e.*

$$U_{\text{brush}} = -\int_{2\delta}^{H} \Pi_e A dx$$





Interaction Energy

Final Questions

- What's Π_e?

Interaction Energy

Final Questions

- What's Π_e?

$$\Pi_e = -\Pi_{\text{overlap}} + \Pi_{\text{separate}_1} + \Pi_{\text{separate}_2} = 2\Pi_{\text{separate}} - \Pi_{\text{overlap}}$$
$$= 2\Pi(c) - \Pi(2c)$$

Interaction Energy

Final Questions

- What's Π_e?

$$\Pi_e = -\Pi_{\text{overlap}} + \Pi_{\text{separate}_1} + \Pi_{\text{separate}_2} = 2\Pi_{\text{separate}} - \Pi_{\text{overlap}}$$
$$= 2\Pi(c) - \Pi(2c)$$

Let $\Pi(c) \approx c/M + \ldots$ then

$$\Pi_e =$$

Interaction Energy

Final Questions

- What's Π_e?

$$\Pi_e = -\Pi_{\text{overlap}} + \Pi_{\text{separate}_1} + \Pi_{\text{separate}_2} = 2\Pi_{\text{separate}} - \Pi_{\text{overlap}}$$
$$= 2\Pi(c) - \Pi(2c)$$

Let $\Pi(c) \approx c/M + B_2 c^2 + \ldots$ then

$$\Pi_e =$$

Interaction Energy

Final Questions

- What's Π_e?

$$\Pi_e = 2k_{\mathrm{B}}TB_2c^2$$

- How to deal with the integral?

Interaction Energy

Final Questions

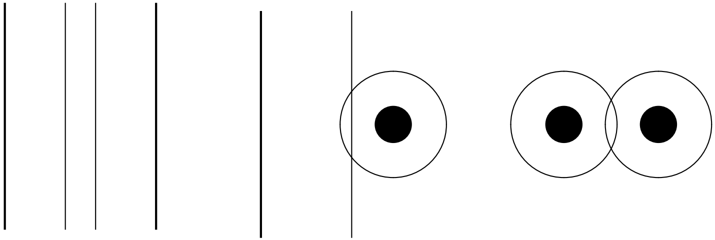
- What's Π_e?

$$\Pi_e = 2k_B T B_2 c^2$$

- How to deal with the integral?
  If we assume $c \neq c(x)$ (poor assumption) then

$$U_{brush} = -\int_{2\delta}^{H} \Pi_e A dx$$
$$= \Pi_e V_0$$

Volume

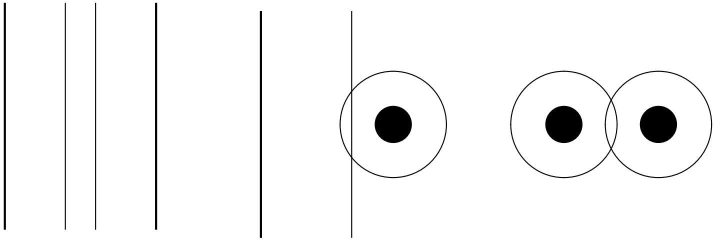


$$V_0 = hA$$

$$V_0 = \frac{\pi h^2}{3}\left[3R - h\right]$$

$$V_0 = 2\frac{\pi h^2}{3}\left[3R - h\right]$$

Volume



$$V_0 = hA$$

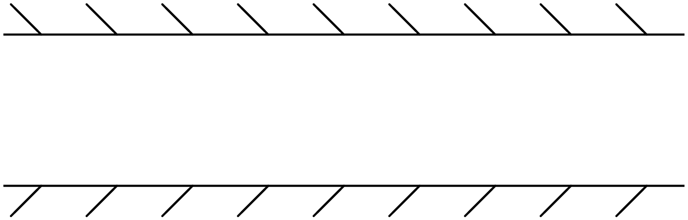
$$V_0 = \frac{\pi h^2}{3}\left[3R - h\right] \qquad V_0 = 2\frac{\pi h^2}{3}\left[3R - h\right]$$

where

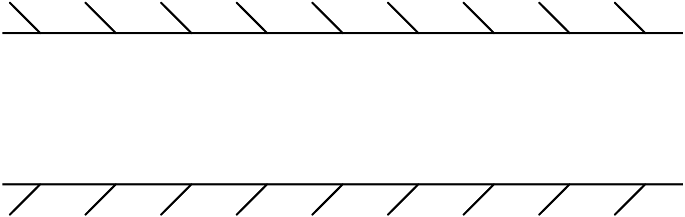
$$h = (2\delta - H)$$

$$R = r + \delta$$

Springs



Springs



Free Energy

When chains are densely grafted their free energy is

$$F = F_{\text{int}} + F_{\text{el}}$$

F_{int} is the excluded volume interaction (osmotic) energy of seeing other while F_{el} is the elastic energy of being stretched.

Equalibrium

Equalibrium

$$H \approx \sigma^{(1-\nu)/2\nu} b^{1/\nu} N$$
$$F_0 \approx H\sqrt{\sigma}$$

Free Energy Cost of Compression

Interact

For dense brushes the osmotic pressure is too high and the brushes can't overlap. They can only compress.

Compression

$$F = F_{\text{int}} + F_{\text{el}}$$
$$\approx F_0 \left[\left(\frac{H}{h} \right)^{1/(3\nu - 1)} + \left(\frac{h}{H} \right)^{(1-4\nu)/(1-3\nu)} \right].$$