## Entropic forces, depletion forces

effective interactions

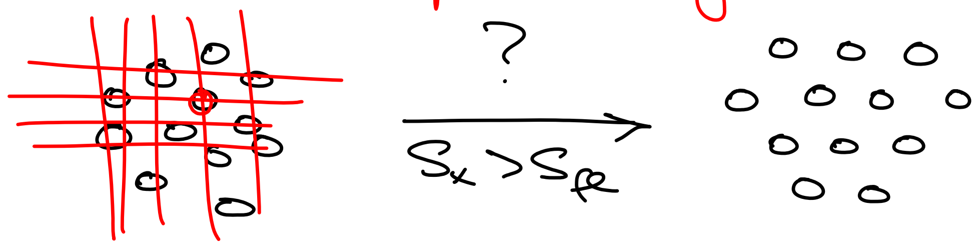
we will see 1) entropy leads to forces

2) entropy $\neq$ disorder

<u>example</u> : crystallization of hard spheres

$$F = \cancel{U} - TS$$

can hard spheres crystallize?




$F_{fl} = -TS_{fl}$ $\qquad$ $F_x = -TS_x$

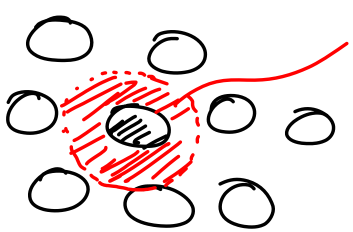
$x \mathrel{\hat{=}}$ crystal

a) configurational entropy $S^k$

$S^k \triangleq$ # configurations to arrange a set of hard spheres

$$\boxed{S^k_x < S^k_{fl}}$$

b) entropy of free volume $S^v$



accessible volume

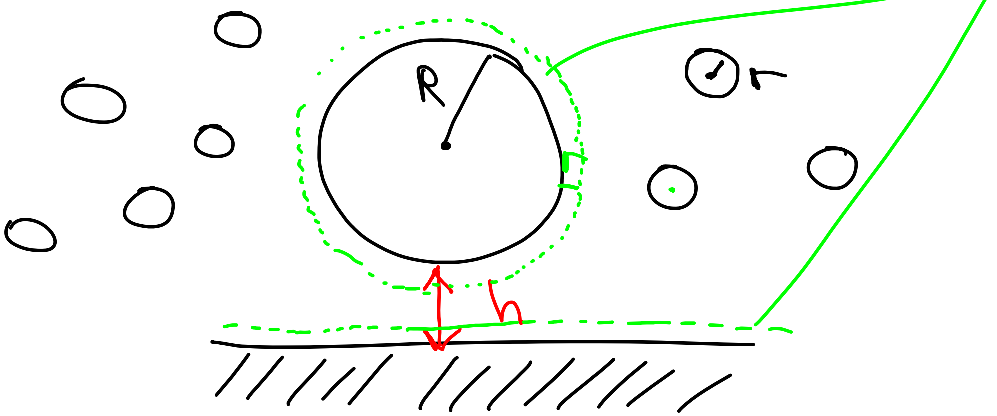
| random close packing | hex. close packing |
| --- | --- |
| rcp | hcp |
| 64% | 74% |
| $S^v_{fl} = 0$ | $S^v_x > 0$ |

$\phi \longrightarrow$

for $\phi > 49\%$ : $S^{v}_{x} + S^{k}_{x} > S^{v}_{fe} + S^{k}_{fe}$

$\longrightarrow$ spontan. crystallization

Qualitative description of entropic forces

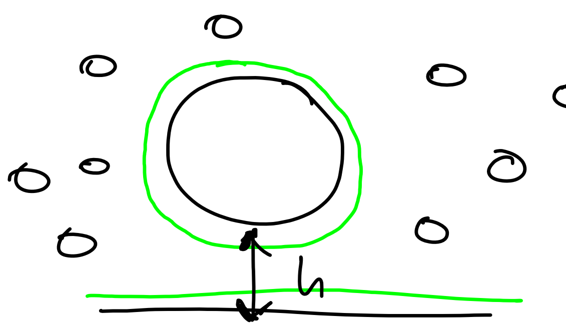



excluded volume
(forbidden for the small particle)
Centers of mass

$F(h) = ?$

a) <u>h large</u> (no overlapp between excluded volumes)

$V$




$$F = -T \cdot \underline{S}$$

consider small spheres as ideal gas and assume that total entropy is given by small spheres

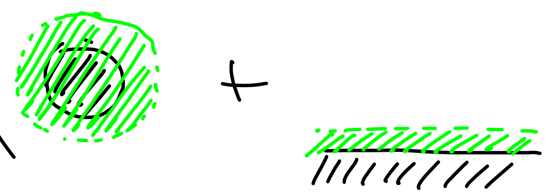
approx. valid when density of small spheres is small

<u>Asakura - Oosawa approx.</u>

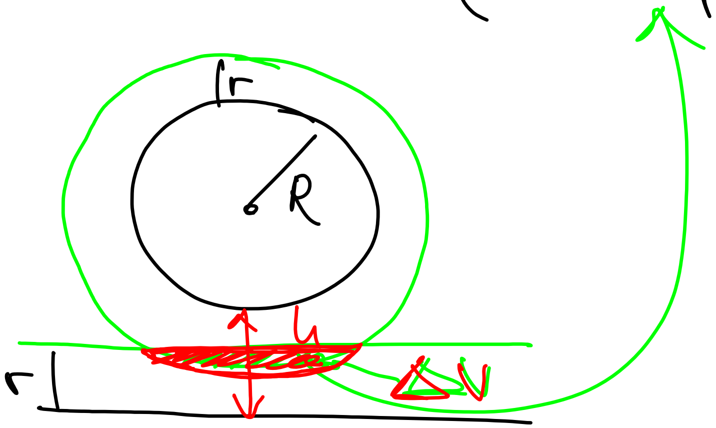
- small spheres interact with the large sphere and the wall
- no small - small interaction (id. gas)

(I) $= F = -N k_B T \cdot \ln V_0$

$\leftarrow$ volume accessible to small spheres

$V_0 = V - \Big($  $\Big) \approx V$ ( $V \gg$ excluded volume)

b) small h (overlapp of excl. volume)



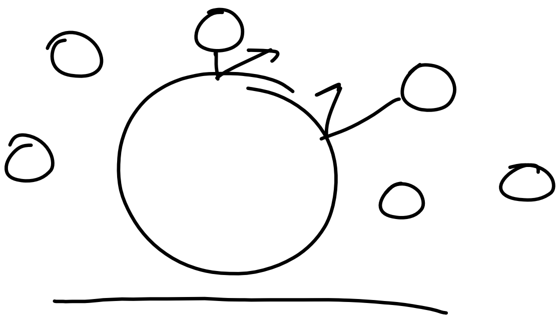

increase of volume accessible by small spheres to $V + \Delta V$

$$F = -N k_B T \cdot \ln(V + \Delta V)$$

$$\Delta F = -N k_B T \ln\left(\frac{V + \Delta V}{V}\right)$$

$\Rightarrow$ effective attraction between big sphere and wall due to entropic

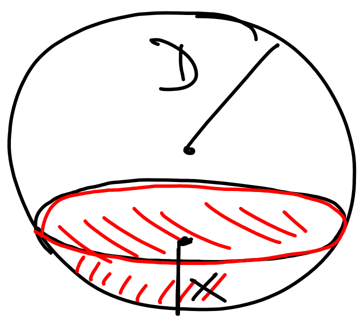
$\rightarrow$ entropic force



$\Delta V \ll V$ $\quad \ln\left(\frac{\Delta V + V}{V}\right) \sim \ln(1+x) \approx x - \frac{x^2}{2} + \dots$

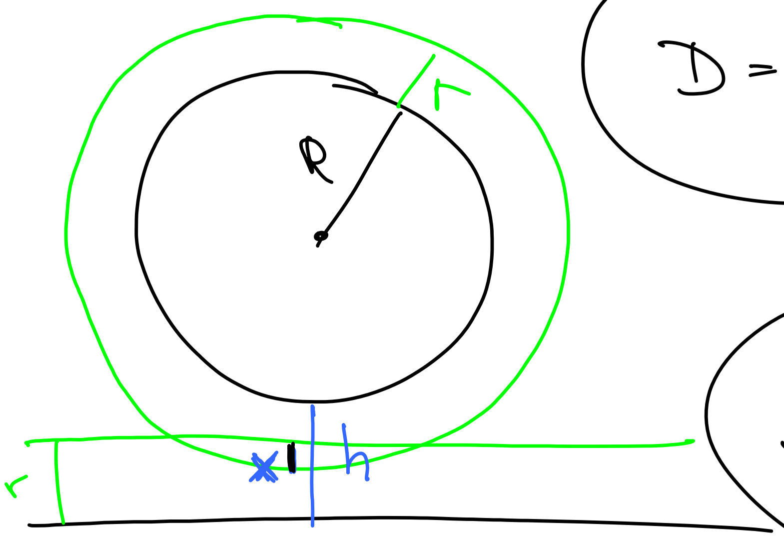
$$\Delta F = -\frac{N}{V} k_B T \, \Delta V$$

Calculate $\Delta V(h)$




$$\boxed{\Delta V(x) = \frac{1}{3}\pi x^2 (3D - x)}$$

$x = D \quad \frac{1}{3}\pi D^2 (2D) \quad \frac{2}{3}\pi D^3$ ✓




$D = R + r$

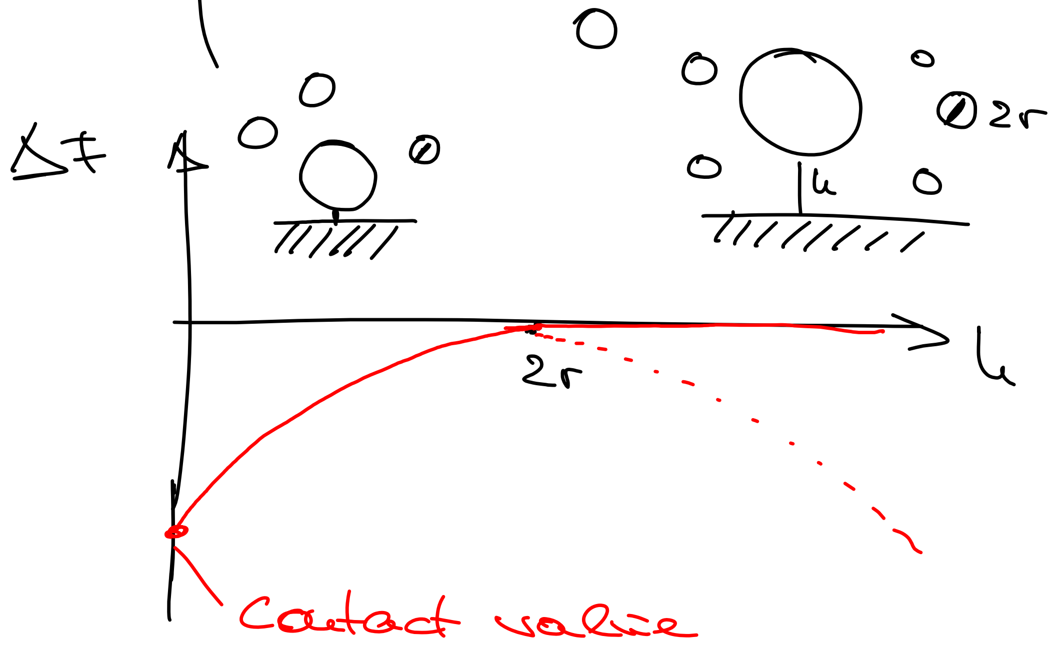
$x = 2r - h$

$$\Delta V = \frac{1}{3}\pi(2r-h)^2\left(3(R+r)-(2r-h)\right)$$

$$= \frac{1}{3}\pi(4r^2+h^2-4rh)(3R+r+h)$$

$$= \pi\left(4Rr^2+\frac{4}{3}r^3+\frac{1}{3}h^3+(R-r)h^2-4Rrh\right.$$

$$\Delta F = \begin{cases} -\dfrac{N}{V} k_B T \pi \left(4Rr^2 + \dfrac{4}{3} r^3 + \cdots \right) & 0 < h < 2r \\ & h \geq 2r \end{cases}$$

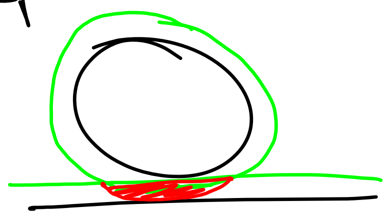



$$\Delta F = -\frac{N}{V} k_B T \pi \left(4Rr^2 + \frac{4}{3} r^3\right)$$

- attractive
- range is $2r$
- Strength $\propto \frac{N}{V}$

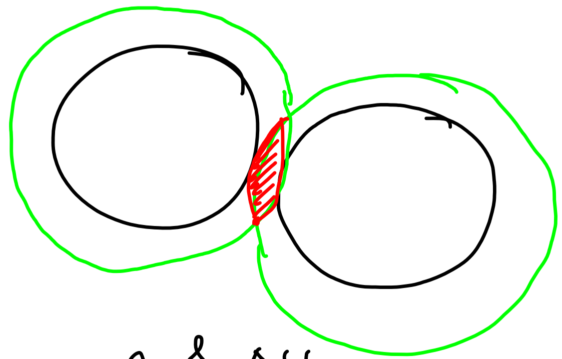
## Other examples

a) Sphere-wall



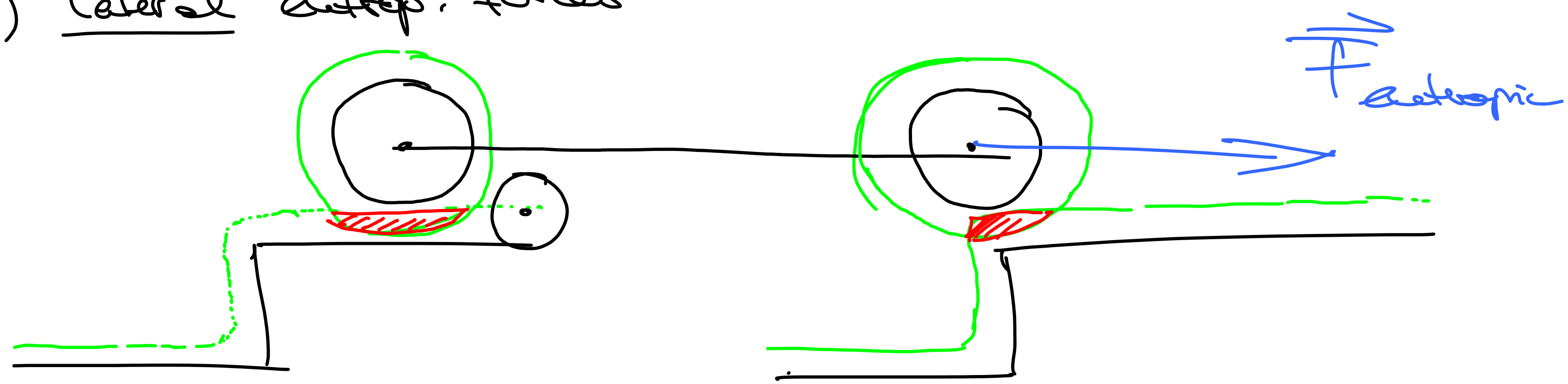
$\Delta U$

b)



$\sim \frac{1}{2} \Delta U$

c) <u>lateral</u> entrop. forces



d) particles in vesicle