Physics 850: Soft Condensed Matter Physics, Fall04
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Lecture 4: Forces arising from Fluctuations

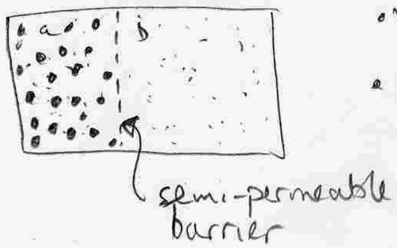
Fluctuations lead to measurable forces.

3 examples

1) osmotic pressure
2) "depletion"
3) entropic tension in a polymer.

At $T=0$, these effects vanish.

coming next time…



• Water molecules permeate the barrier

• Particles do not

Assume these are uncorrelated.

$$Q = \sum_{\substack{\text{all coordinates}\\ \text{all states}}} e^{-E_i/kT} = \sum e^{-\frac{E_{particles}}{kT} - \frac{E_{water}}{kT}} = \sum_{\substack{\text{particle}\\ \text{states } i}} e^{-E_i/kT} \times C$$

move to continuous variables

$$Q = \frac{1}{N!}\int_{-\infty}^{\infty} \frac{dx_1\, dy_1\, dz_1\, dp_{x1}\, dp_{y1}\, dp_{z1}}{h^3} \times \int d\vec{x}_2\, d\vec{p}_2 \cdots e^{-\frac{p_1^2+p_2^2+\cdots}{2mkT}}$$

use $\int_{-\infty}^{\infty} e^{-\alpha y^2}\, dy = \sqrt{\frac{\pi}{\alpha}}$

$$\to \frac{1}{N!} V^N \frac{\left(\sqrt{2\pi m k_B T}\right)^{3N}}{h^{3N}}$$

function of m, T, N not of V

in equil, $F = -k_BT\ln Q = -Nk_BT\ln V + Nk_BT\ln N - Nk_BT - Nk_BT\ln(\ )$

$$F = Nk_BT\ln\left(\frac{N}{V}\right) - Nk_BT + f(N,T)$$

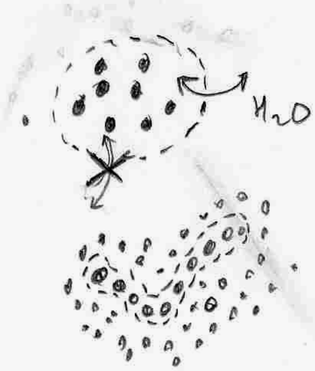
... Osmotic pressure.

Pressure $P = -\frac{\partial F}{\partial V}\Big)_{N,T}$

$F = -Nk_BT\ln\frac{V}{N} + \dots$

so $P = \frac{N}{V}k_BT = \underset{\uparrow \text{ concentration, } \frac{N}{V}}{C}\, k_BT$

<u>Example</u> lipid vesicles swell or burst by osmotic pressure



→ $P_{in} - P_{out} = (C_{in} - C_{out})k_BT$

→ if exterior is diluted, ΔP can be large, vesicle can burst.

→ if exterior is concentrated, $\Delta P < 0$ and H_2O is pushed out (vesicle collapses)

<u>Note</u>: $\cancel{P \neq -\frac{\partial E}{\partial V}\Big|_{N,T}}$

Must use <u>Free energy</u>, $F = E - TS$, to include osmotic/collision effects

Depletion Attraction

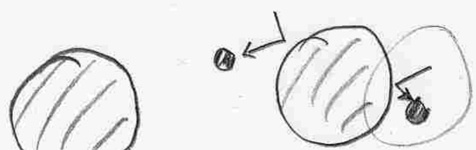
a.k.a "Excluded volume effect" or
"Macromolecular Crowding"

→ Asakura, Oosawa 1954

Two models (equivalent in ideal-gas limit)

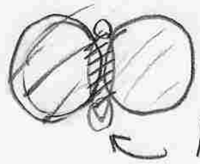
(1) Collision model ("Attraction through repulsion" - Vrij 1976)

a)



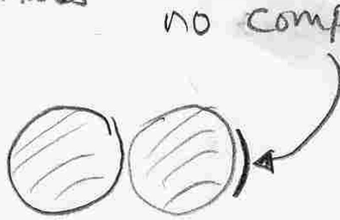
collision creates force.
$\langle \text{force} \rangle_{\text{area}} = 0$

b)



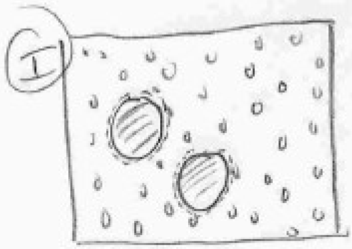
No particles here, so no outward force. Hence particles are squeezed together.

force = $P_{\text{particles}} \times$ Area over which there is no compensating pressure



... Depletion

b) "Entropic force" argument

I 

→ assume small particles overlap one another (ideal gas) but have steric repulsion from large sphere. E.g. polymers

 ← small particle.

→ $N_{small} \gg N_{large}$.

$$F = N_s k_0 T \ln \frac{N_s}{V_s} - N_s kT \quad \underbrace{+ N_L k_B T \ln \frac{N_L}{V_L} - N_L k_B T}_{\text{ignore, } N_L \ll N_s}$$

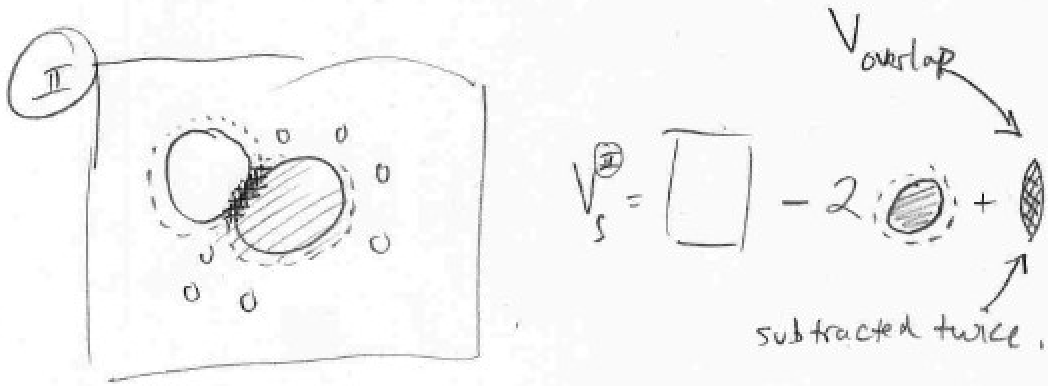
$$+ \text{mixing entropy} \quad \cancel{\sim N \ln \frac{N_L}{N_L + N_s}} \qquad \cancel{+ f(T, N_L, N_s)}$$

small

V_s = vol. accessible to centers of small particles

$V_s^{(I)} =$ 

(divide up the small spheres' degrees of freedom into rotations about the center of mass of each sphere and translations of the center of mass. Rotational DOF are not affected by the positions of the large spheres. The number of translation DOF depends only on accessible volume.



So $V_s \uparrow$ when Large particles *approach one another.*

$$F_{II} - F_I$$

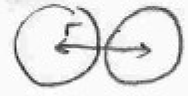
$$\Delta F = -N_s k_B T \ln (V_s^{(II)}) - (-N_s k_B T \ln V_s^{(I)})$$

$$= N_s k_B T \ln \frac{V_s^{(I)}}{V_s^{(II)}} = N_s k_B T \ln \frac{V_s^{I}}{(V_s^{I} + V_{overlap})}$$

$$= -N_s k_B T \ln \underbrace{\left(1 + \frac{V_{overlap}}{V_s^{I}}\right)}_{\simeq \frac{V_{overlap}}{V_s^{I}}}$$

$$= -\underbrace{\frac{N_s}{V_s^{I}}}_{\equiv C_s} k_B T \cdot \underbrace{V_{overlap}}_{= \frac{\pi}{6}(2R_L + 2R_s - r)^2 (2R_L + 2R_s + \frac{r}{2})}$$

if $2R_L < r < 2R_L + 2R_s$



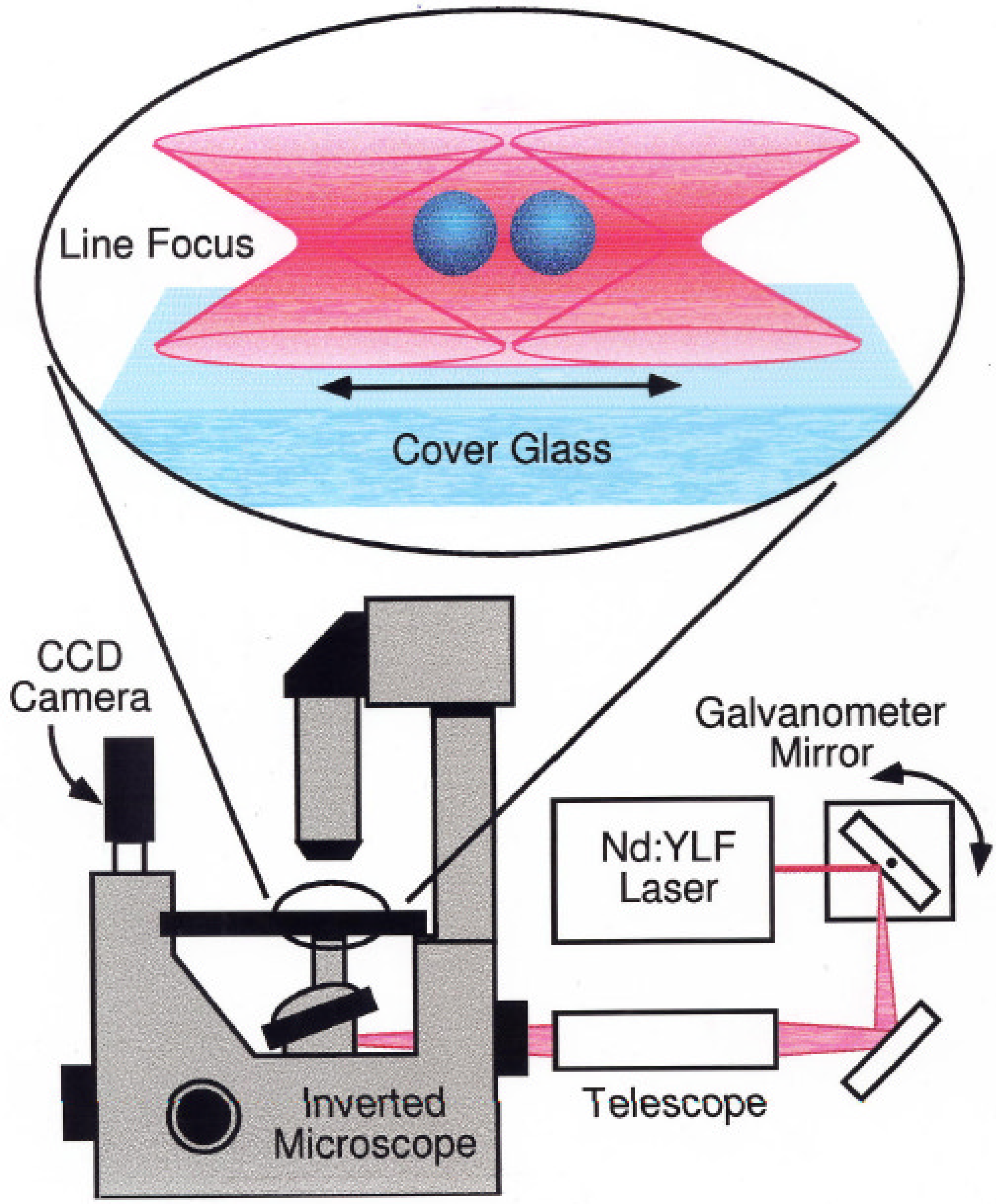
at contact $(r = 2R_L)$

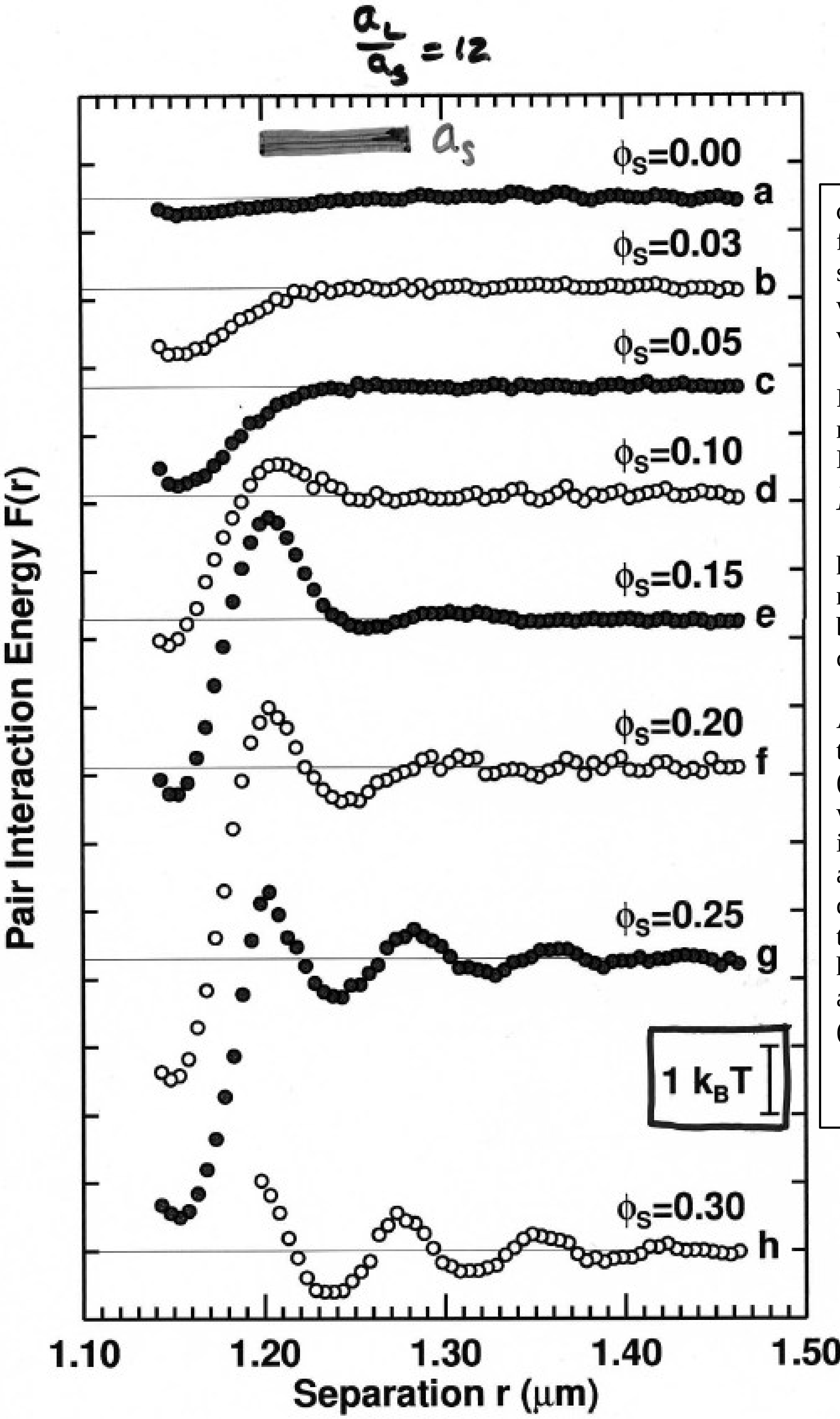
$$\Delta F = -\frac{3}{2} \phi_s k_B T \cdot \frac{R_L}{R_s} + \text{small correction} \quad \text{(in ideal gas approx.)}$$

volume fraction of small, $\phi_s = \frac{N_s \frac{4}{3}\pi R_s^3}{V}$

Crocker, Matteo, Dinsmore, Yodh, ~~to appear in~~ PRL (1999).

A direct measurement of the depletion interaction between two PMMA colloidal spheres in solution with many spheres of much smaller size ($R_L/R_S = 12$). Laser tweezers are used to restrict the large spheres to a line so that their center-to-center distance can be accurately measured. If the particles could move out of the plane, then only the projection of their separation onto the plane could be measured.





ϕ_S is the volume fraction of small spheres. The small dip with $\phi_S = 0$ is probably van der Waals.

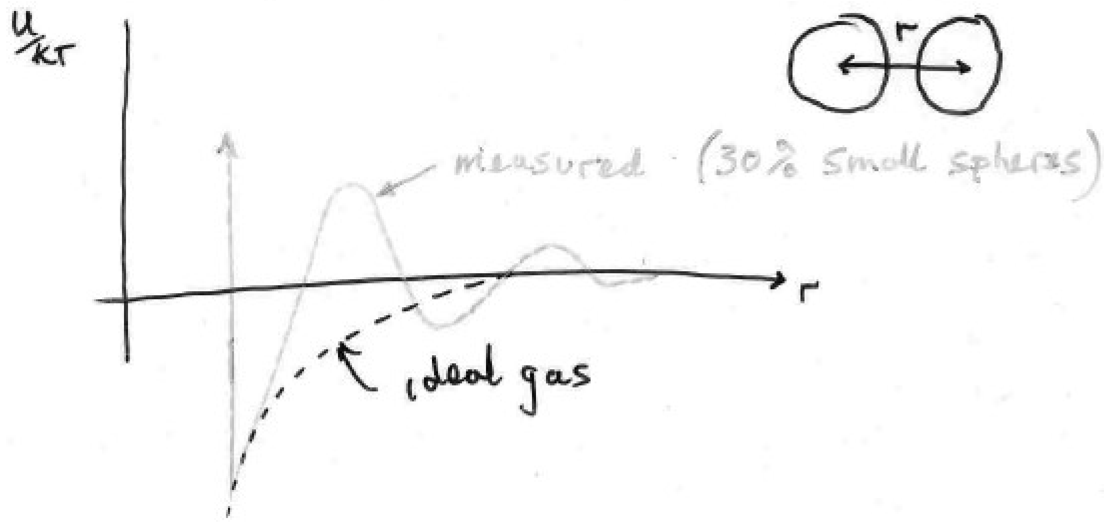
Free energy F is measured using the Boltzmann relation:

$$P(r) \propto e^{-F(r)/k_B T}$$

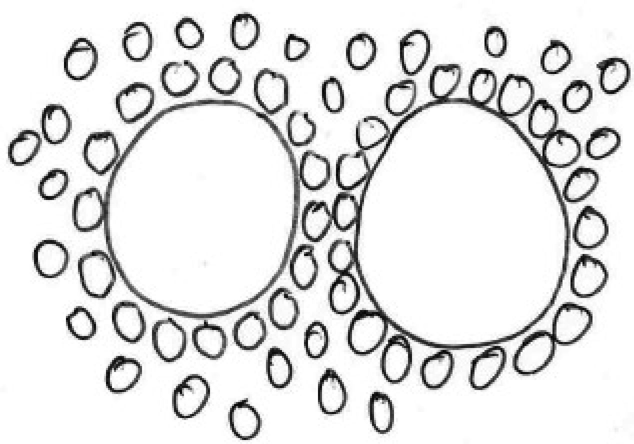
P(r) is measured by histogramming the measured separations r between large-sphere centers.

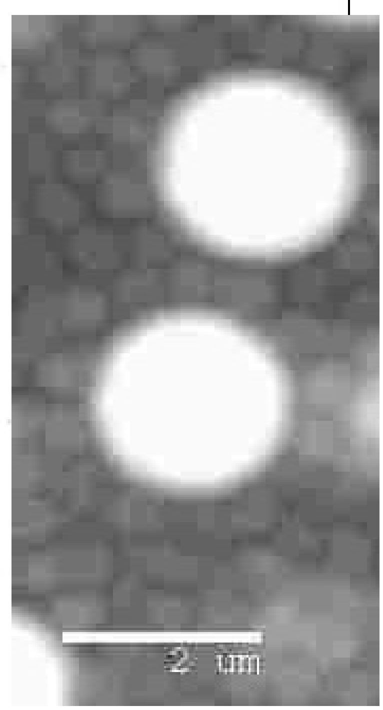
An intriguing result is that the minimum (contact value) of *F* is well described by the ideal-gas approximation that was discussed, even though the small particles are hard spheres and have a large concentration (ϕ_S as large as 0.3).

This slide explains why there is a depletion barrier when $\phi_S > 0.05$ (when the small particles are hard spheres. The small particles tend to form a shell around the large spheres. In order for the larger spheres to move closer together, the shell of small spheres must be expelled, which costs entropy. In short, the large spheres prefer to be separated by 0, 1, 2, … layers of small spheres. Not by 0.5, 1.5, 2.5…. layers. When the small particles are random-coil polymers (which better approximate an idea gas), this structuring is not seen and the attraction is monotonically attractive, as in the ideal-gas model.



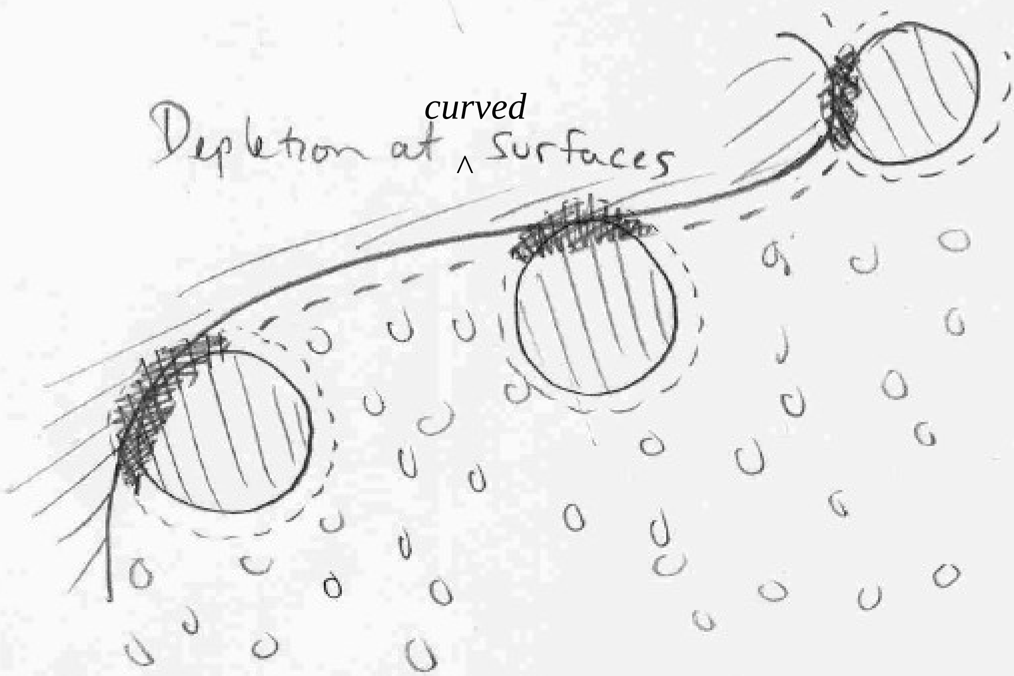
Crocker et al, PRL





confocal microscope image of binary hard-sphere mixture (Dinsmore and Weitz).

Depletion at curved surfaces



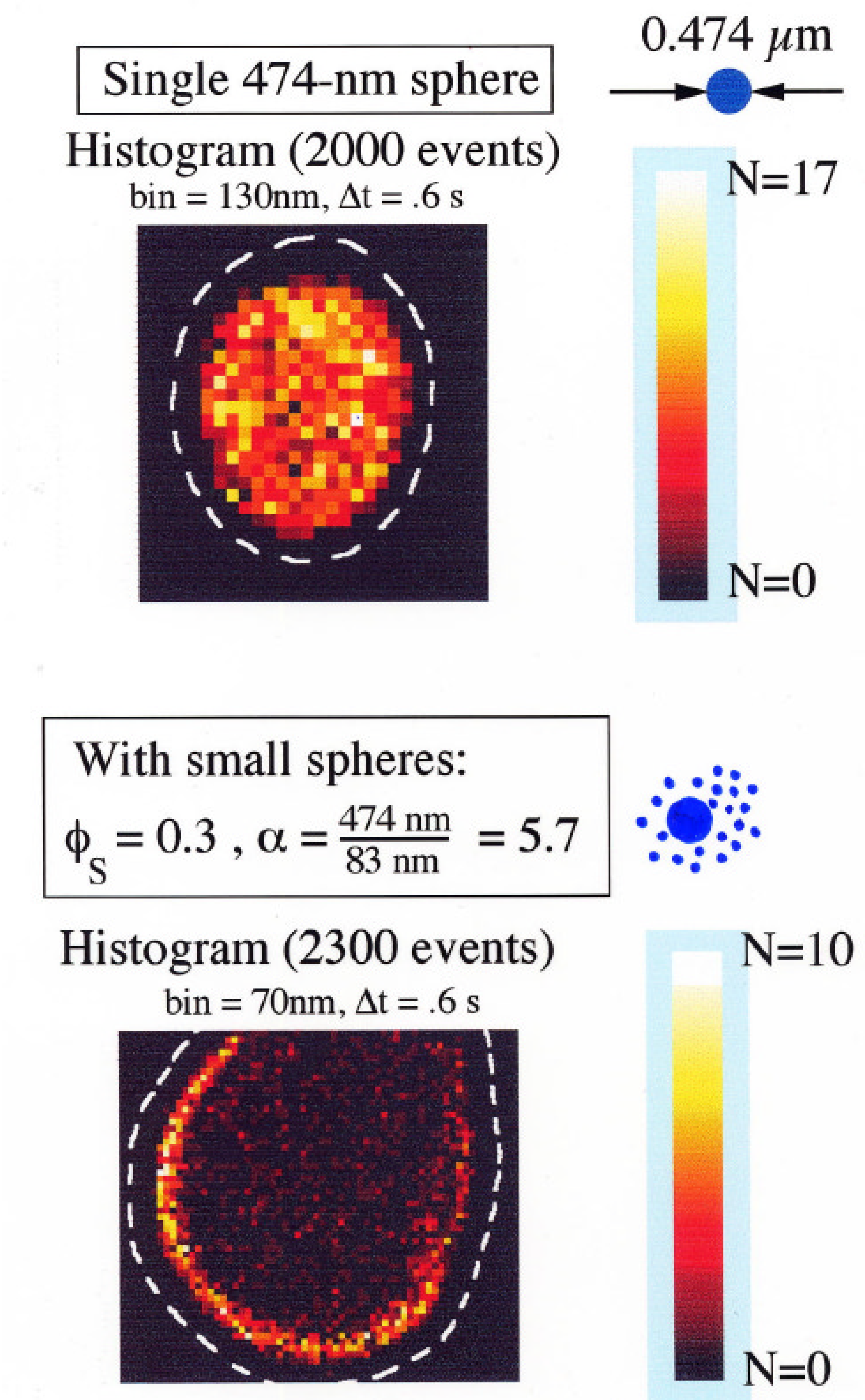
$$\Delta F_{\text{sphere-wall}} = 2\,\Delta F_{\text{sphere-sphere}}$$

(Derjaguin)

In general, $|\Delta F| \uparrow$ as surface becomes more concave.

Large sphere moves along the wall.

Depletion forces also push larger particles to flat surfaces and *along* surface of varying curvature. Here the addition of small particles means that the large particle is more often found near the concave sections of the vesicle wall. These measurements were made using an optical microscope and simply observing the position of the large sphere many many times.



Dinsmore et al PRL 80, 409 ('98)