

1. Osmotic pressure & depletion forces -

Osmotic pressure effects arise whenever there are conc. gradients; example:



pure
water
 P_{out}

if $P_{in} = P_{out}$,
water flows ~~out~~ into
the cell, because
 $\mu_{in} < \mu_{out}$

(for the water) as the conc. of water in the cell, C_{in} ,
is $C_{in} < C_{out}$.

If the pressure inside can build up (e.g. plant cell),
since μ increases with P (because $\frac{\partial \mu}{\partial P} = \frac{V}{N_0} > 0$,
 V molar volume, N_0 Avogadro's number)
you can reach an equilibrium situation:

$$\mu_{in}(C_{in}, P_{in}) = \mu_{out}(C_{out}, P_{out}); \quad \Delta P = P_{in} - P_{out}$$

is the osmotic pressure.

At equilib.: $\mu_{in} = \mu_{out}$ (for the water!)

$$\mu = \mu(P, C) : \quad \mu = \frac{G(P, T, N)}{N}$$

use μ (or G) because it is the correct thermod. pot.
describing the equil. of a system at given P, T .

$$\frac{\partial \mu}{\partial P} = \frac{V}{N} = v \quad (\text{molecular volume})$$



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Liquid is roughly incompressible, so

$$\mu(P_2) - \mu(P_1) = \int_{P_1}^{P_2} dp \, v \approx v(P_2 - P_1)$$

i.e. $\mu(P) = vP + \text{const.}$

Also, if x is the mole fraction of the water

$$\left(x = \frac{\# \text{ moles of water}}{\text{tot. \# of moles}} \text{ in a given } V \right), \quad \boxed{\mu = \mu_0 + kT \ln x}$$

μ_0 chem. pot. of the pure component (at that P).

This just comes from the entropy of mixing (see later),
i.e. valid in the "ideal gas" approx.

So the chem. pot. of the water is :

$$\mu = \mu_0 + Pv + T \ln x_w$$

Equil.: $P_{in} v + T \ln x_w = P_{out} v \quad (\text{outside, } x_w = 1)$

$$\Rightarrow P_{in} - P_{out} = - \frac{T}{v} \ln x_w$$

Since $x_w + x_s = 1$, $x_s \ll 1$ (x_s mole fraction of salt)

$$\ln x_w = \ln(1 - x_s) \approx -x_s ;$$

$$x_s = \frac{N_s}{N_s + N_w} \approx \frac{N_s}{N_w} \Rightarrow \frac{x_s}{v} = \frac{N_s}{N_w} \frac{N}{V} \approx \frac{N_s}{V}$$

$$\Rightarrow \Delta P = P_{in} - P_{out} = T \frac{N_s}{V}$$

Chem. pot. and entropy of mixing =

consider ideal gas of N_1 molecules in V_1 ;

dilute it by adding N_2 ^{different} molecules , i.e. $N_1 \rightarrow N_1 + N_2$

then to keep p const. you have to increase the volume

$$V_1 \rightarrow V_1 + V_2 \quad \text{with} \quad \frac{N_1}{V_1} = \frac{N_1 + N_2}{V_1 + V_2} ;$$

since $S \propto \ln V$, e.g. for component 1 the change in S

$$\text{is : } \Delta S_1 = \ln \frac{V_1 + V_2}{V_1} = \ln \frac{N_1 + N_2}{N_1} = -\ln x_1$$

since $G = E + PV - TS$, E and p const.

$$\rightarrow \Delta G_1 = T \ln x_1$$



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The osmotic pressure $\Pi = \frac{N_s kT}{V}$ is a big effect!

Example = sea water ~ 0.3 M salt

So $\Delta p = \frac{0.3 \times 6 \times 10^{23}}{10^3} \times 4 \times 10^{-14} \text{ dynes/cm}^2$

$= 8 \times 10^6 \text{ dynes/cm}^2 = 80 \text{ N/cm}^2 \simeq 8 \text{ atm} !$

($\rightarrow 80 \text{ m of water} !$).

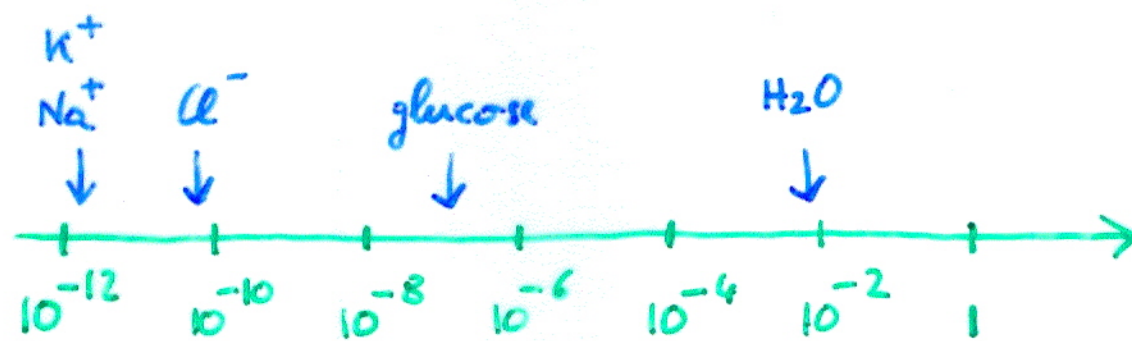
Examples : - the osmotic problem of the cell (transp.)

- depletion forces : Singh-Zocchi et al. measurement of the osmotic pressure contribution to the interaction potential for a sphere against a wall.



The osmotic problem of the cell :

the cell membrane is permeable to water but not to ions :



permeability λ (cm/s)

current : $j = \lambda \Delta C$ ΔC conc. diff.

inside the cell : charged metabolites + counterions
proteins + counterions

→ large osmotic pressure → cell bursts !

Remedy : $Na^+ - K^+$ pump

pumps Na^+ out of the cell and K^+ in

Energy comes from ATP hydrolysis -

30% of the cell's energy consumption is for the pump -

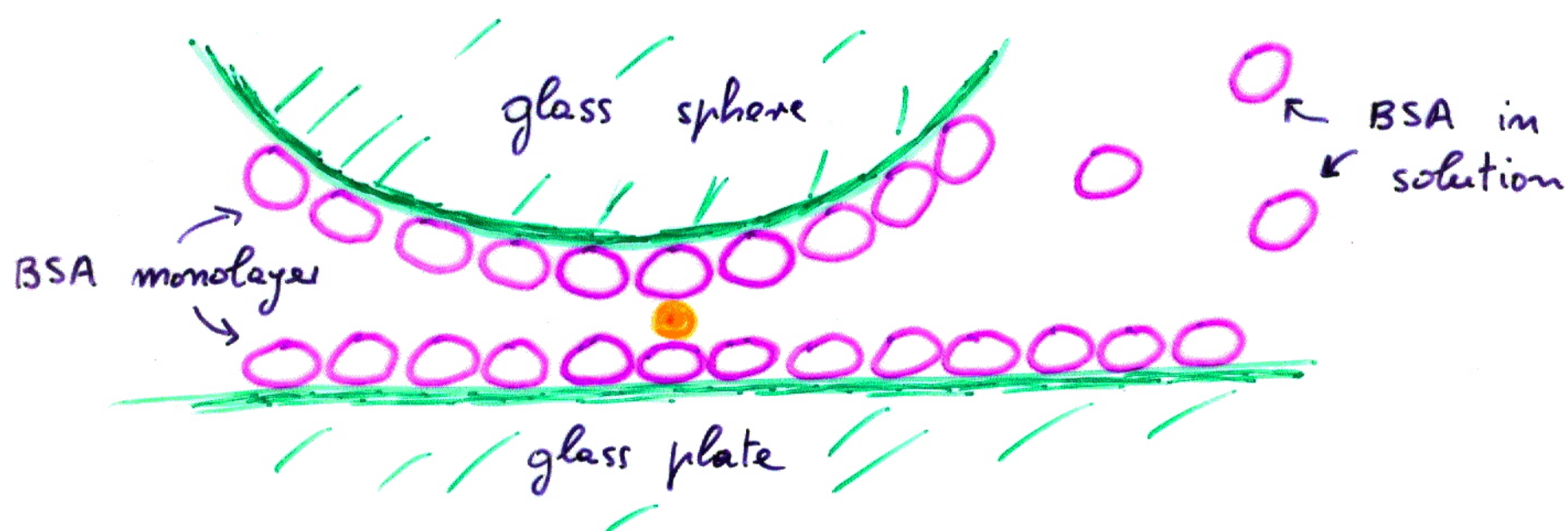
For every ATP consumed, $3 Na^+$ are pumped out
and $2 K^+$ in .

→ Resultant ion
conc. :

	inside the cell (mM)	outside
Na^+	10	150
K^+	140	5
Cl^-	10	100

Modification of the interaction potential due to the osmotic pressure of macromolecules in solution

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$$P = \frac{N}{V} kT$$

P : osmotic pressure
 N/V : concentration

Example : BSA 1 mg/ml $\approx 10^{-5}$ M

$$\rightarrow P \approx 200 \text{ dynes/cm}^2$$

Attractive force $F = \pi P \{ R^2 - [h - (R - 2a)]^2 \}$ for $0 \leq h \leq 2a$
and $F = 0$ for $h > 2a$

E.g. $F(h=0) \approx P 4\pi a R$

$$F(h=0) \approx 4 \text{ pN} \left\{ \begin{array}{l} a = 5 \text{ nm} \\ R = 3 \text{ } \mu\text{m} \\ P = 200 \text{ dynes/cm}^2 \end{array} \right.$$

Thermal motion in a potential well (DLVO potential)

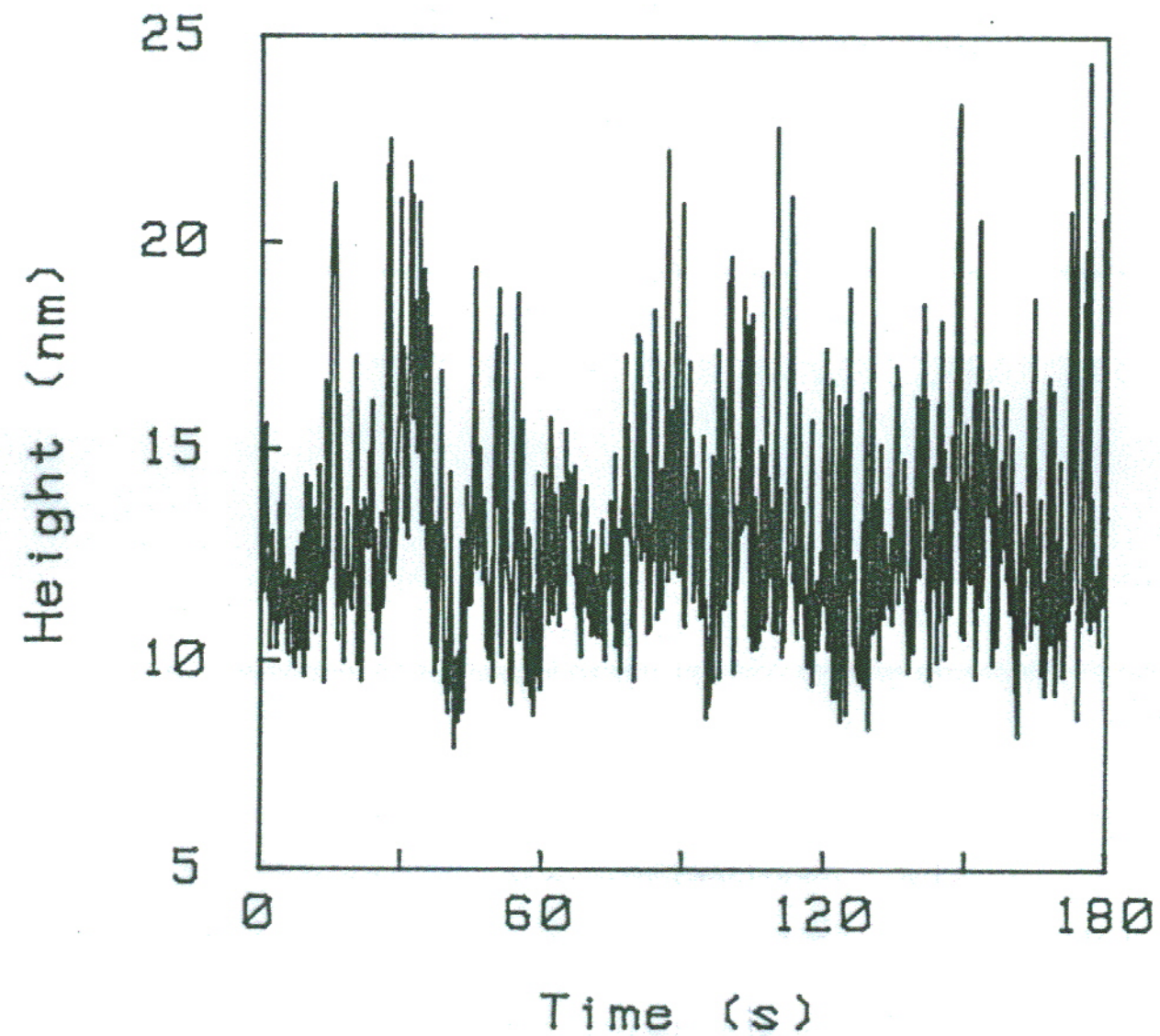
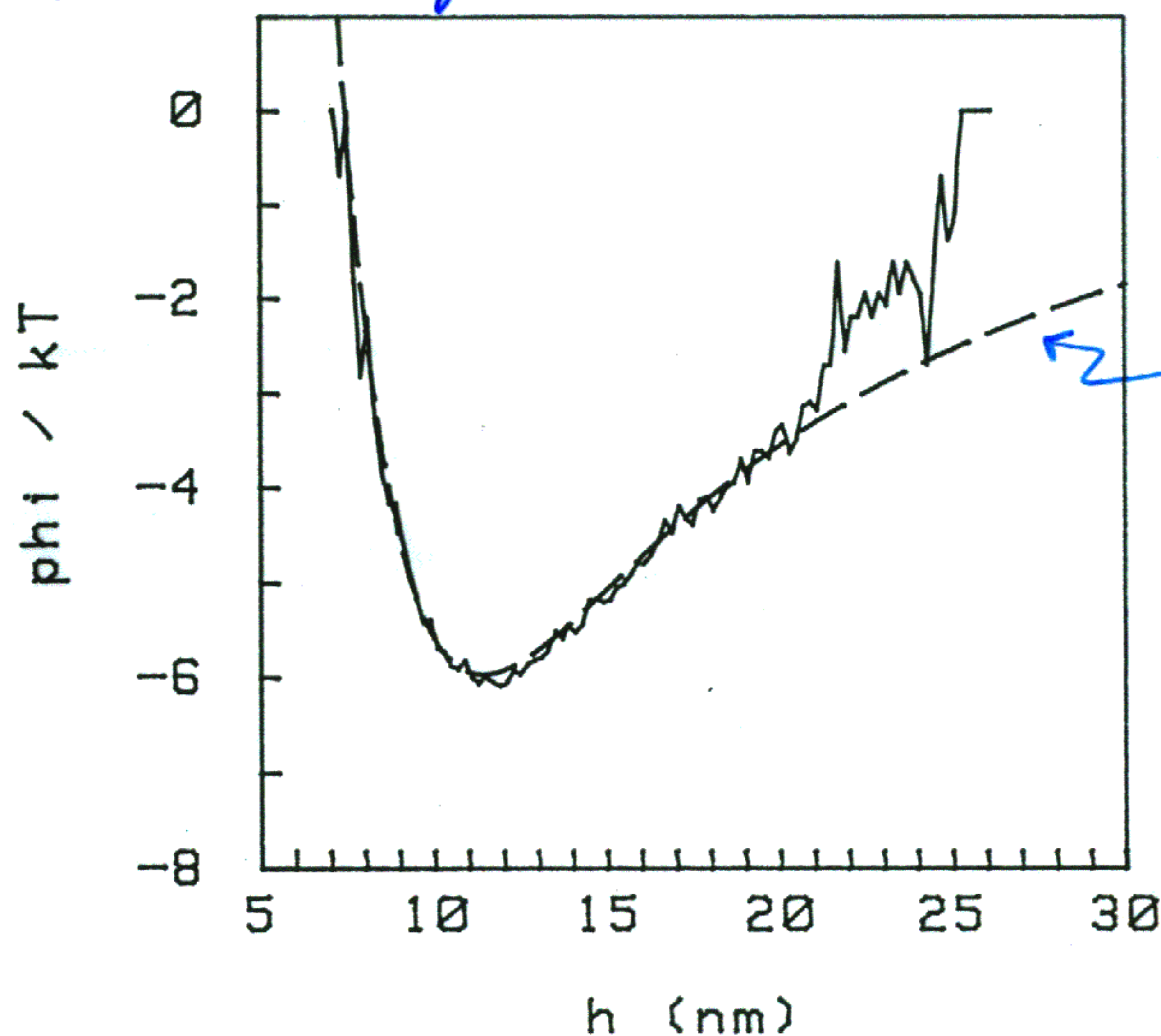


Fig. 1

Sphere attached by a single biotin-avidin
6 μm diam. glass sphere contact



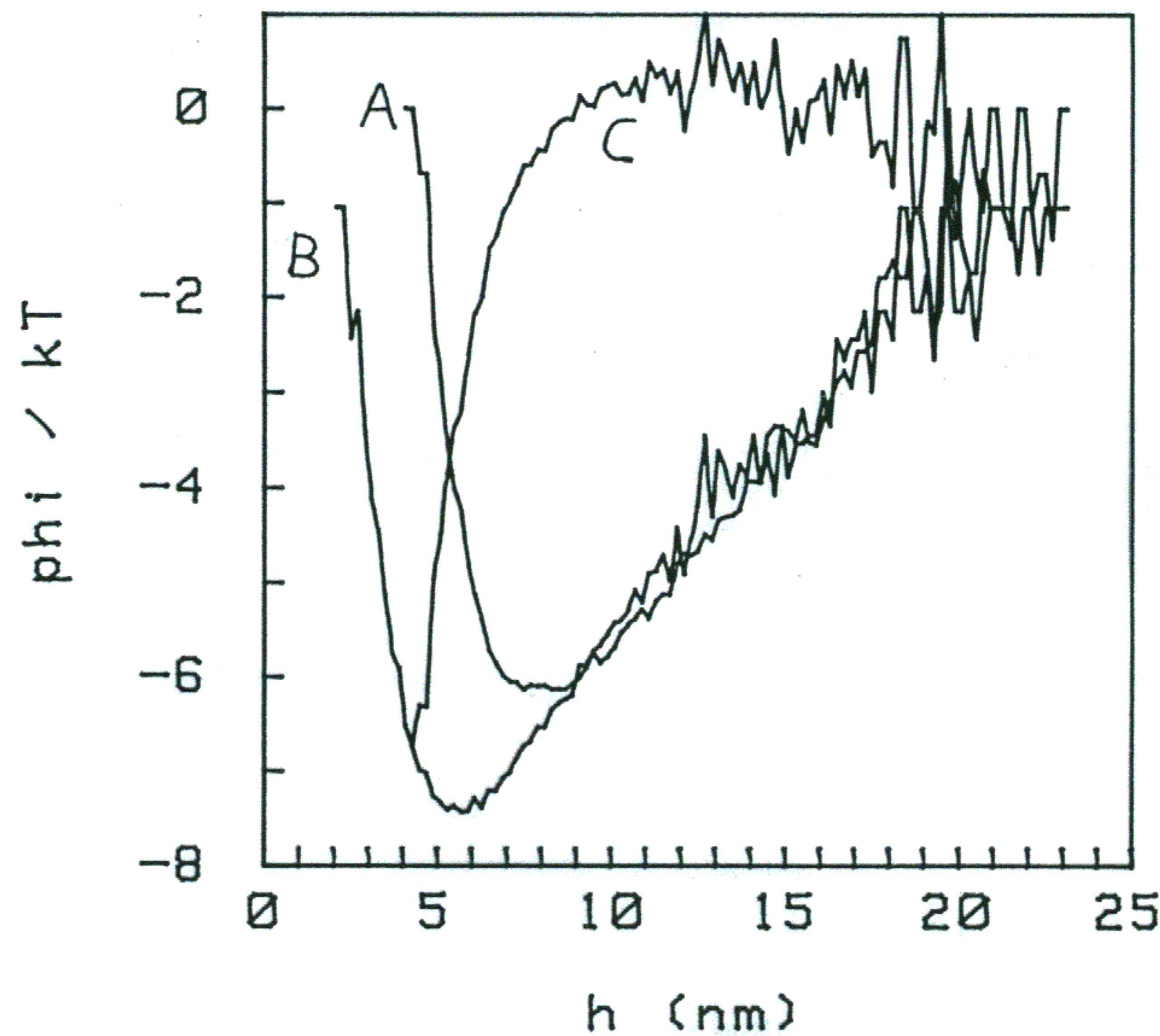
DLVO potential

$$\phi = Ae^{-h/\delta} - \frac{B}{h} + \phi_0$$

→ Hamaker constant
 $\approx 1.0 \times 10^{-14}$ ergs

(for glass-water-glass:
 $\sim 3 \times 10^{-14}$ ergs)

Depletion interaction between a sphere
and a plane caused by albumin in solution



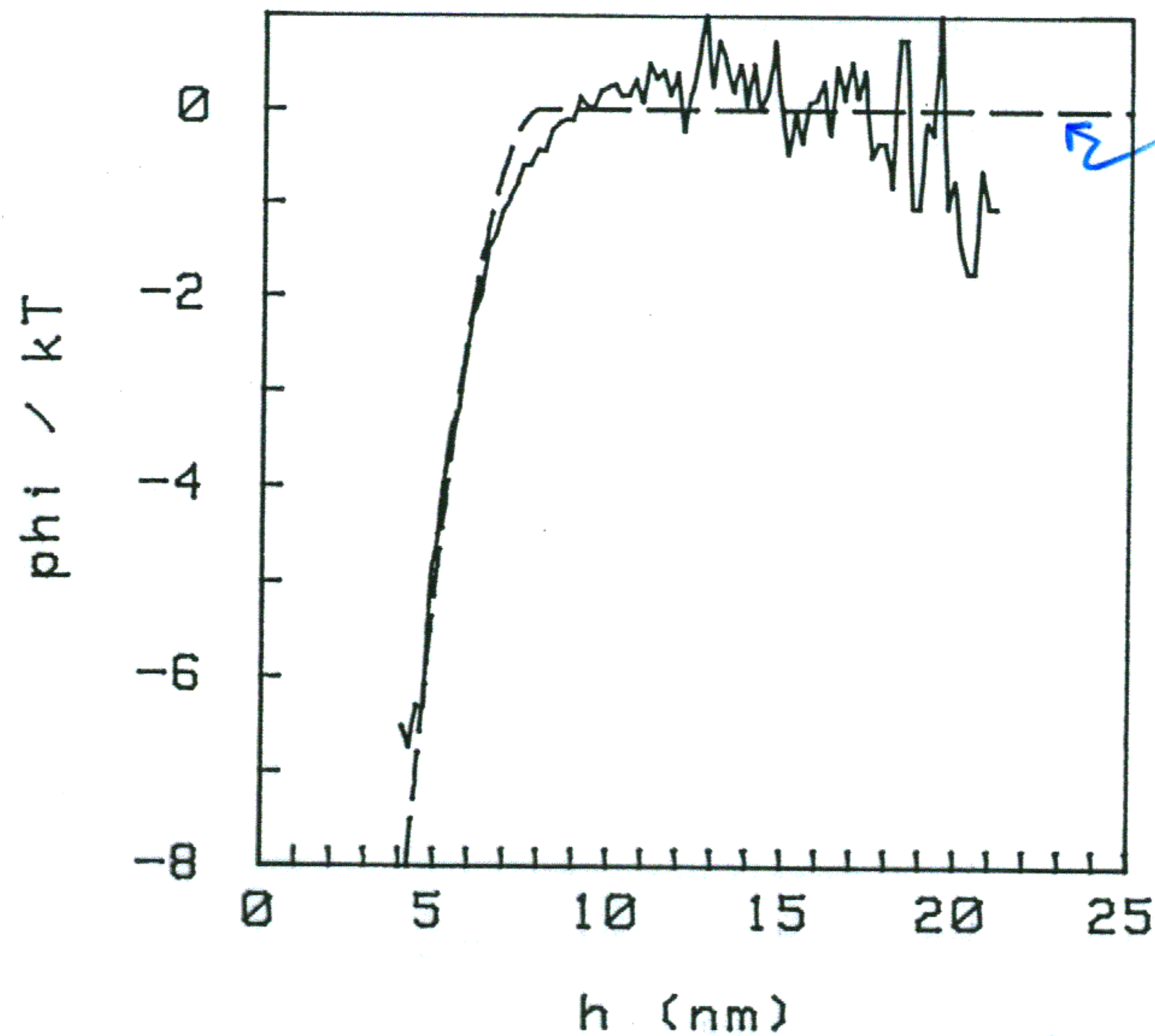
ϕ_A : without albumin

ϕ_B : with albumin
5 mg/ml in solution

$$\phi_C = \phi_B - \phi_A$$

osmotic part of the
potential

The depletion interaction



$$\phi_{\text{osmo}} = \begin{cases} P\pi \left[R^2 h - \frac{1}{3}(h+R-2a)^3 \right] - \phi_i & \text{for } h < 2a \\ 0 & \text{for } h > 2a \end{cases}$$

$$a = 4.0 \text{ nm}$$

$$P = 2.5 \times 10^3 \text{ dynes/cm}^2$$