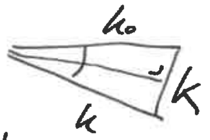
Soft Matter - Problem set 5

(19) a) $K = \frac{4\pi}{\lambda} \sin\left(\frac{\vartheta}{2}\right)$



$$\sin\left(\frac{\vartheta}{2}\right) = \frac{\frac{1}{2}|\vec{K}|}{|\vec{k}|} = \frac{K}{2k} = \frac{K\lambda}{4\pi} \quad \text{as } k = \frac{2\pi}{\lambda}$$

$$\Rightarrow K = \frac{4\pi}{\lambda} \sin\left(\frac{\vartheta}{2}\right)$$

b). $$P(k) = \left| \frac{\int_0^a \frac{\sin(kr)}{kr} 4\pi r^2 dr}{\int_0^a 4\pi r^2 dr} \right|^2$$

$$x = kr \rightarrow r = \frac{x}{k}$$

$$\frac{dr}{dx} = \frac{1}{k} \rightarrow dr = \frac{dx}{k}$$

numerator: $x = kr$, $dr = \frac{dx}{k}$

$$\rightarrow \int_0^a \frac{\sin x}{x} 4\pi \frac{x^2}{k^2} \frac{dx}{k} = \frac{4\pi}{k^3} \int_0^{ka} \underset{g}{x} \, \underset{f'}{\sin x} \, dx \qquad \int g f' dx = [fg] - \int f g' dx$$

$$= \frac{4\pi}{k^3} \left\{ \left[-x\cos x\right]_0^{ka} + \int_0^{ka} \cos x \, dx \right\} =$$

$$= \frac{4\pi}{k^3} \left\{ -ka\cos(ka) + \sin(ka) \right\}$$

denominator: $\int_0^a 4\pi r^2 dr = \frac{4}{3}\pi a^3 \quad (= V_p).$

$$\therefore P(k) = \left| \frac{\frac{4\pi}{k^3}\left\{-ka\cos(ka) + \sin(ka)\right\}}{\frac{4}{3}\pi a^3} \right|^2$$

$$= \left| 3\, \frac{\sin(ka) - ka\cos(ka)}{(ka)^3} \right|^2$$

c). 1st min $P(k)$: $ka = 4.49$, $k = \frac{4\pi}{\lambda} \sin\left(\frac{\vartheta}{2}\right)$

$a = 1 \cdot 10^{-6}$ ~~μ~~m
$\lambda = 532$ nm

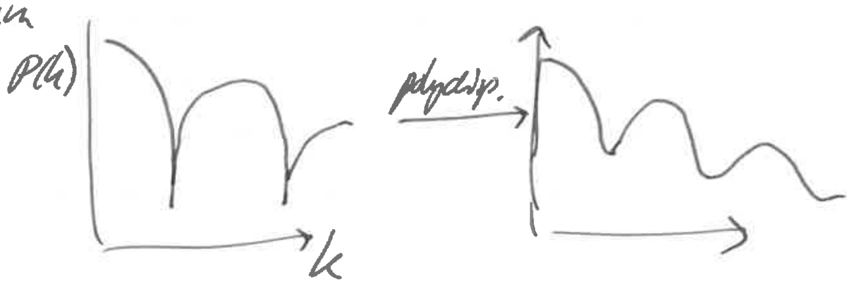
$\therefore \frac{4\pi}{\lambda} \sin\left(\frac{\vartheta}{2}\right) \cdot a = 4.49$

$$\vartheta = 2 \arcsin\left(\frac{4.49 \cdot \lambda}{4\pi a}\right) = 2 \arcsin\left(\frac{4.49 \cdot 532 \cdot 10^{-9}}{4\pi \cdot 1 \cdot 10^{-6}}\right)$$

$$= 0.38 \text{ rad} \mathrel{\hat{=}} 22^\circ \qquad \left(\frac{0.38}{\pi} \cdot 180\right).$$

as $ka = 4.49$ = constant, k will increase as a decreases, so the 1st minimum will shift to larger angles for smaller particles. e.g. $a = 0.5\,\mu$m $\vartheta = 0.78$ rad $\hat{=}\ 45°$

d). For polydisperse particles the minima "fill up" as every particle with a slightly different size will result in a slightly different location of the 1st minimum

$\Rightarrow$ 

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a). $\langle x(t')x(t)\rangle = \frac{k_BT}{k} e^{-|t'-t|/\tau}$ $\tau = \frac{\xi}{k}$

$MSD = \langle [x(t') - x(t)]^2 \rangle = \langle x^2(t') + x^2(t) - 2x(t')x(t)\rangle =$

$= \langle x^2(t')\rangle + \langle x^2(t)\rangle - 2\langle x(t')x(t)\rangle$

from auto-correlation function:

$\langle x^2(t')\rangle = \langle x^2(t)\rangle = \frac{k_BT}{k}$ [comes from equipartition $\frac{1}{2}kx^2 = \frac{1}{2}k_BT \rightarrow x^2 = \frac{k_BT}{k}$].

$\Rightarrow$ sub in: $MSD = \frac{k_BT}{k} + \frac{k_BT}{k} - 2\cdot\left(\frac{k_BT}{k} e^{-|t'-t|/\tau}\right)$

$\therefore MSD = \frac{2k_BT}{k}\left(1 - e^{-|t'-t|/\tau}\right) = \frac{2k_BT}{k}\left(1 - e^{-\Delta t/\tau}\right)$

$\Delta t = |t'-t|$.

b). $\underline{\Delta t \ll \tau}$: much faster than trapping ~~relat~~ relaxation time, so particle doesn't really feel confining effect of trap on this timescale

$e^{-\Delta t/\tau} \simeq 1 - \Delta t/\tau$ (Taylor-expansion for small Δt)

$\Rightarrow MSD = \frac{2k_BT}{k}\left(1 - \left(1 - \frac{\Delta t}{\tau}\right)\right) = \frac{2k_BT}{k}\frac{\Delta t}{\tau}$ $\left(\tau = \frac{\xi}{k}\right)$

$= \frac{2k_BT}{\xi}\Delta t$ $\rightarrow$ diffusive! (in 10), as expected.

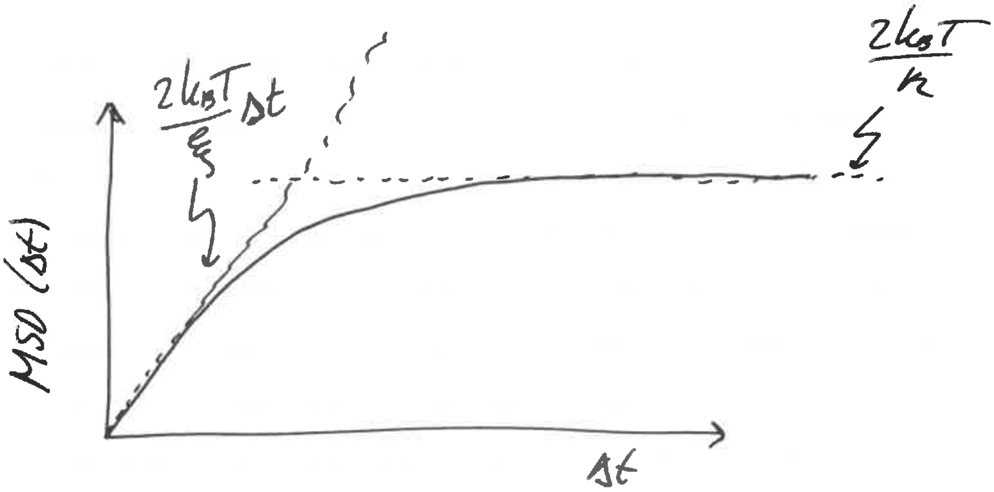
$\Delta t \gg \tau$: much longer than trapping relaxation time, so expect particle to really feel confining effect of optical trap.

$e^{-\Delta t/\tau} \approx 0$ in this limit $\rightarrow$ ~~MSD~~

$MSD = \frac{2k_BT}{k}\left(1 - \cancelto{0}{e^{-\Delta t/\tau}}\right) = \frac{2k_BT}{k}$ $\rightarrow$ plateau!

so confined in trap as expected

c).



d). MSD for $\Delta t \gg \tau \Rightarrow \frac{2k_BT}{k} = MSD_{plateau}$

$T = 298\,K$

$k = 34.95 \cdot 10^{-15}/10^{-9}\ N/m$ $\qquad k_B = \frac{MSD_{pl.} \cdot k}{2T}$

$MSD\ plateau = 231 \cdot 10^{-18}\ m^2$

$$\therefore \quad k_B = \frac{231 \cdot 10^{-18} \cdot 34.95 \cdot 10^{-6}}{2 \cdot 298} = 1.35 \cdot 10^{-23}\ JK^{-1}$$

$N_{Av} = \frac{R}{k_B} = \frac{8.314}{1.35 \cdot 10^{-23}} = 6.14 \cdot 10^{23}$ (not bad!) $\qquad$ (c.f. $k_B = 1.38 \cdot 10^{-23}\ JK^{-1}$: pretty good!)

another method would be from $\Delta t \ll \tau \rightarrow$ initial slope $= \frac{2k_BT}{\xi}$ (diffusive)

→ downsides: • need accurate measure for
- size (radius) particle (R)
- viscosity solvent (η) $\Big\}\ \xi = 6\pi\eta R$

• difficult to measure accurately the initial slope of MSD vs Δt.

not required: let's try from data given in MSD slide lecture

→ initial slope $\approx 400 \cdot 10^{-18}/10^{-3} = 400 \cdot 10^{-15}\ m^2/s$

→ $R = 1 \cdot 10^{-6}\ \mu m$

→ $\eta = 0.89 \cdot 10^{-3}\ Pa \cdot s$

$$k_B = \frac{400 \cdot 10^{-15} \cdot 6\pi \cdot 0.89 \cdot 10^{-3} \cdot 1 \cdot 10^{-6}}{2 \cdot 298} = 1.13 \cdot 10^{-23}\ JK^{-1}$$

(not bad though)

(2)

a). $P(k) = \left| \dfrac{\int_0^a \frac{\sin(kr)}{kr} 4\pi r^2 dr}{\int_0^a 4\pi r^2 dr} \right|^2$

small k: $\dfrac{\sin(kr)}{kr} \simeq 1 - \frac{1}{6}k^2r^2 + \ldots$

combine →

$$P(k) = \left| \frac{\int_0^a r^2(1-\frac{1}{6}k^2r^2+\ldots)dr}{\int_0^a r^2 dr} \right|^2 = \left| 1 - \frac{1}{6}k^2 \frac{\int_0^a r^4 dr}{\int_0^a r^2 dr} \right|^2$$

$$= 1 - \frac{1}{3}k^2 \frac{\int_0^a r^4 dr}{\int_0^a r^2 dr} + O(k^4)$$

↳ terms of order k^4 (or higher).

b). ~~$O(k^4)$ → neglect~~ ignore & $R_g^2 = \int_0^a r^4 dr \Big/ \int_0^a r^2 dr$

$P(k) = 1 - \frac{1}{3}k^2 R_G^2$

$= \exp(-\frac{1}{3}k^2 R_G^2)$ → Guinier's law

as for small k: $e^{-x} \simeq 1-x$

$\therefore \exp(-\frac{1}{3}k^2R_G^2) \simeq 1 - \frac{1}{3}k^2R_G^2 = P(k)$ for small k.

c). $R_G^2 = \dfrac{\int_0^a r^4 dr}{\int_0^a r^2 dr} = \dfrac{\left[\frac{1}{5}r^5\right]_0^a}{\left[\frac{1}{3}r^3\right]_0^a} = \dfrac{3}{5}\dfrac{a^5}{a^3} = \dfrac{3}{5}a^2$

$R_G = \sqrt{\frac{3}{5}}\,a.$

d). $P(k) = \exp\left(-\frac{1}{3} k^2 R_G^2\right)$

$$R_G^2 = \frac{3}{5} a^2$$

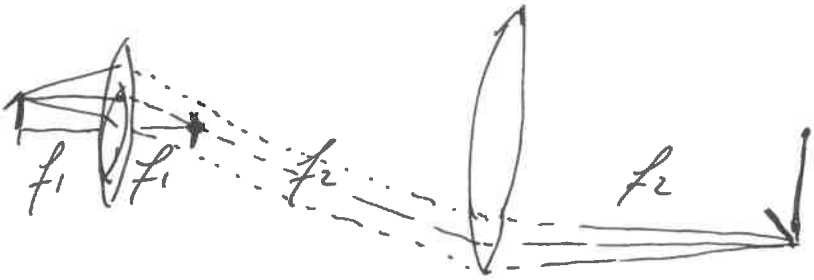
$$\therefore \; P(k) = \exp\left(-\frac{1}{3} k^2 \cdot \frac{3}{5} a^2\right) = \exp\left(-\frac{1}{5} k^2 a^2\right)$$

$\Rightarrow$ so $\ln P(k) = -\frac{1}{5} (ka)^2$

and, hence, a plot of $\ln P(k)$ vs $(ka)^2$ will have a slope of $-1/5$ in the small-k limit.

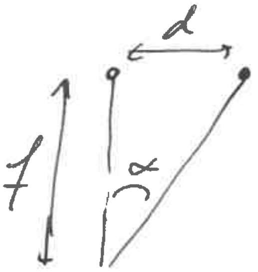
(22)

a) see @ the end.
→ Just a rough sketch here:



b). $\rho_{min} = \frac{1}{2} k D \sin\alpha = C \qquad C = 3.8317$

from panel (a)



$$\sin\alpha = \frac{d}{\sqrt{d^2+f^2}} \approx \frac{d}{f}$$

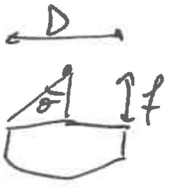
↑ $f \gg d$

also: $k = \frac{2\pi}{\lambda} \implies \frac{1}{2} k \cdot D \cdot \sin\alpha = C$

$$\frac{1}{\cancel{2}} \cdot \frac{\cancel{2}\pi}{\lambda} \cdot D \cdot \frac{d}{f} = C$$

$$d = \frac{C \cdot f \cdot \lambda}{\pi \cdot D} = \frac{3.8317}{\pi} \cdot \frac{f\lambda}{D} = 1.22 \frac{f\lambda}{D}.$$

c). $NA = n\sin\vartheta = \sin\vartheta$ ($n=1$).
↳ air



(panel c)

$$\sin\vartheta = \frac{D/2}{\sqrt{\frac{D^2}{4}+f^2}} \approx \frac{D}{2f} \quad (f \gg D).$$

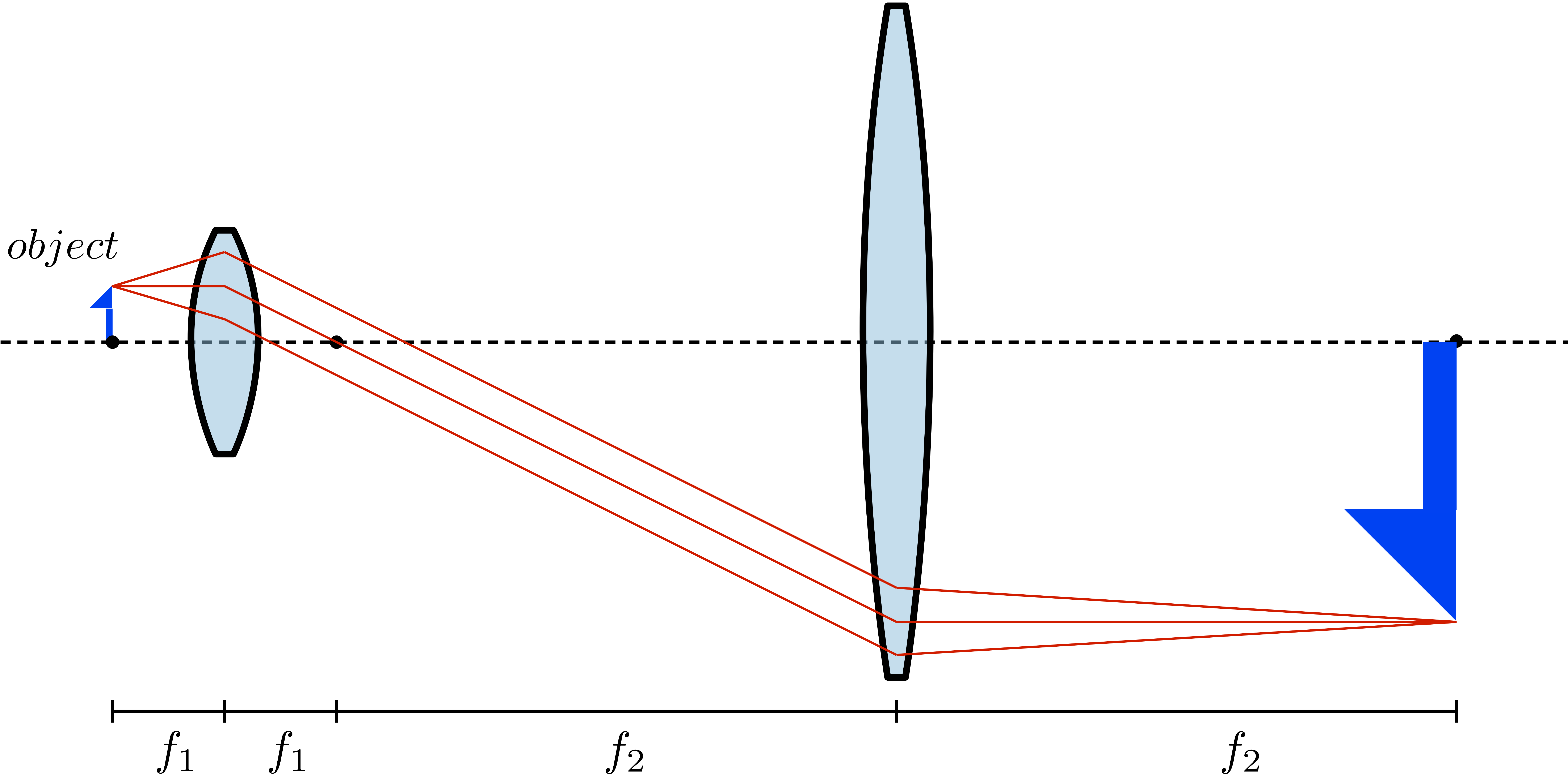
$\rightarrow D = 2f\sin\vartheta$

⇒ sub ~~in~~ answer ~~of~~ b):

$$d = 1.22\frac{f\lambda}{D} = \frac{1.22 \cdot f\lambda}{2f\sin\vartheta} = \frac{1.22\lambda}{2\sin\vartheta} = \frac{1.22}{2}\frac{\lambda}{NA} \simeq \frac{\lambda}{2NA}.$$

d). $NA = 1.42$
$\lambda = 532 \cdot 10^{-9}\,m \qquad d = \frac{532 \cdot 10^{-9}}{2 \cdot 1.42} = 187$ nm.

so can easily resolve μm-sized colloids, but small particles & micelles, or polymers etc → below diffraction limit.



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f_1
f_1
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