

# METALLIC NANOPARTICLE CHAINS AS OPTICAL WAVEGUIDES

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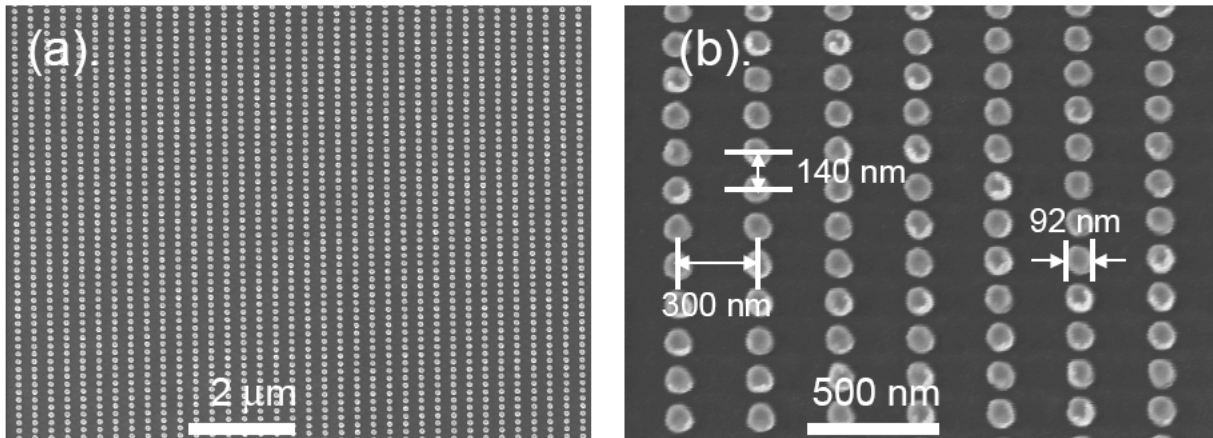
In collaboration with

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Moscow)

# Why plasmonic chains are of interest?

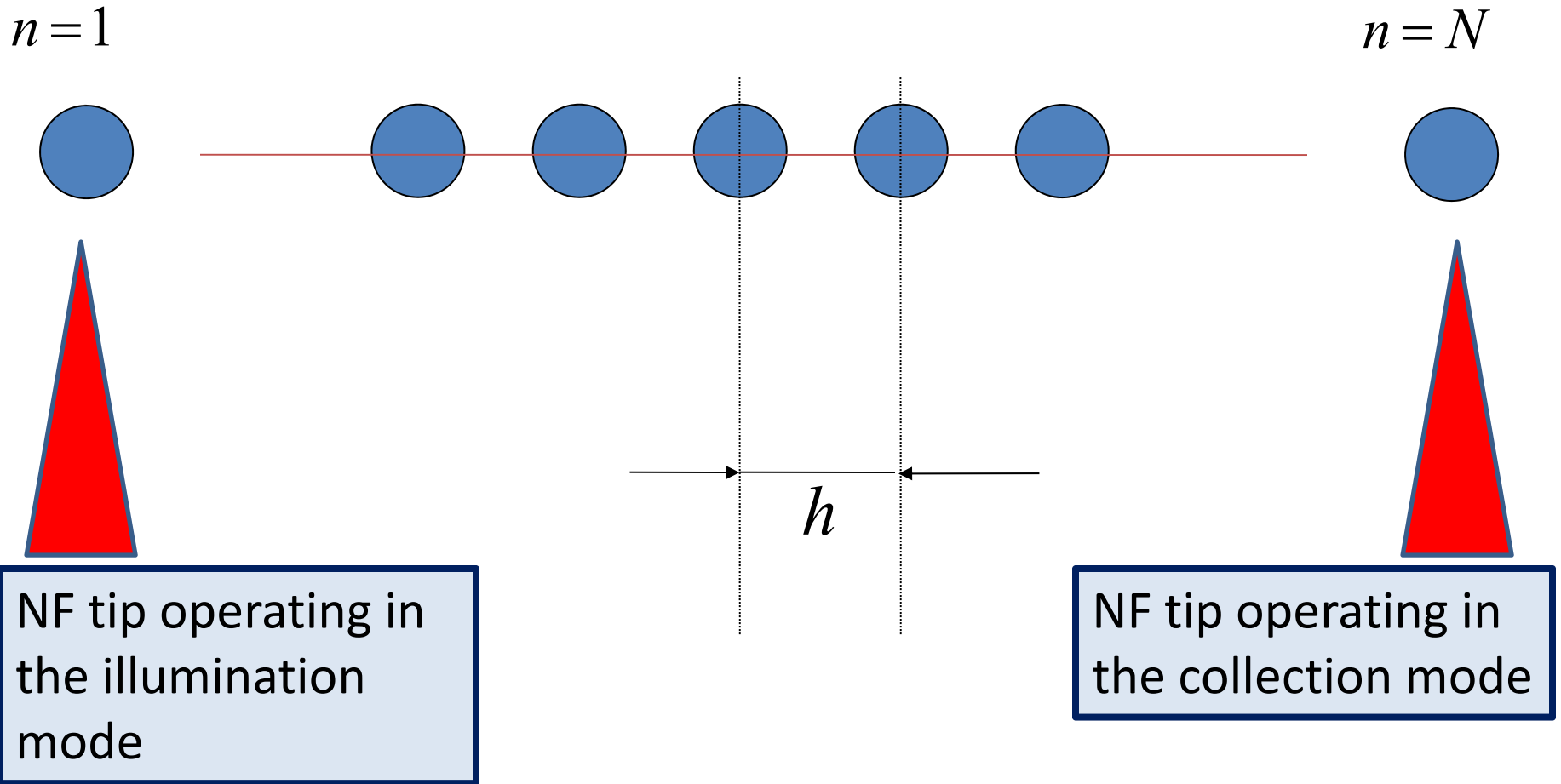
- Spectroscopy and sensing
- Waveguiding and optical elements
- Simple system with rich physics



From K.B.Crozier, E.Togan, E.Simsek, T.Yang, Opt.Ex. 15, 17482 (2007)

1. PHYSICAL MODEL
2. SPECTROSCOPY (NON-LORENTZIAN RESONANCES)
3. DISPERSION RELATIONS
4. PROPAGATION. STEADY STATE
5. PROPAGATION. TRANSIENT PHENOMENA
6. PROPAGATION LENGTH AND FIELD LOCALIZATION
7. CURVED CHAINS

# 1. Physical model



# A few choices

chains	Regular, linear, Infinite, quasistatic interactions	Substrate, host medium	More complex composition, disorder Curved chains	Far zone interaction, interference effects, localization	Non- receptical effects (e.g., in H-field)
Particles					
Spheres	XXXXXXXXXX	XXX	X	XXXXXX	X
More complicateds shape	XXXXXXXXXX	X	X	XX	
Dipole approx	XXXXXXXXXX	XXXX	XX	X	
Beyond DA	XXX	X		X	
Quantum FS effects	Single nanoparticle				

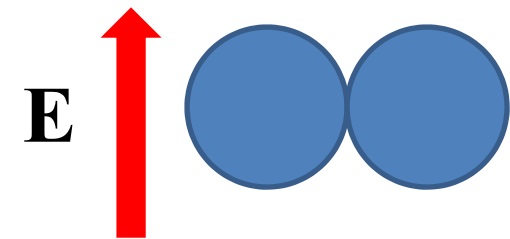
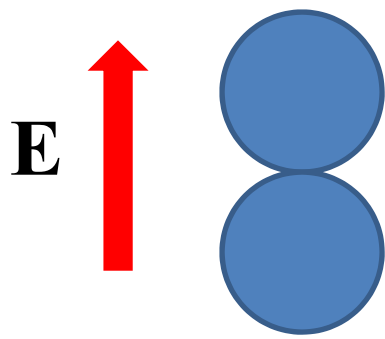
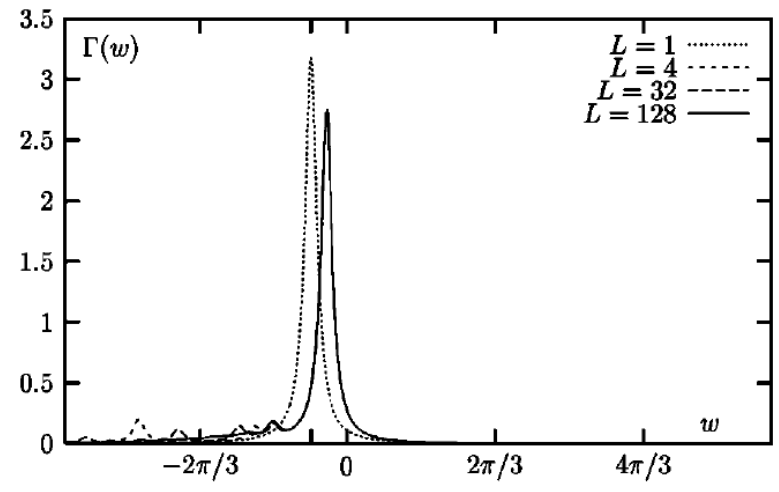
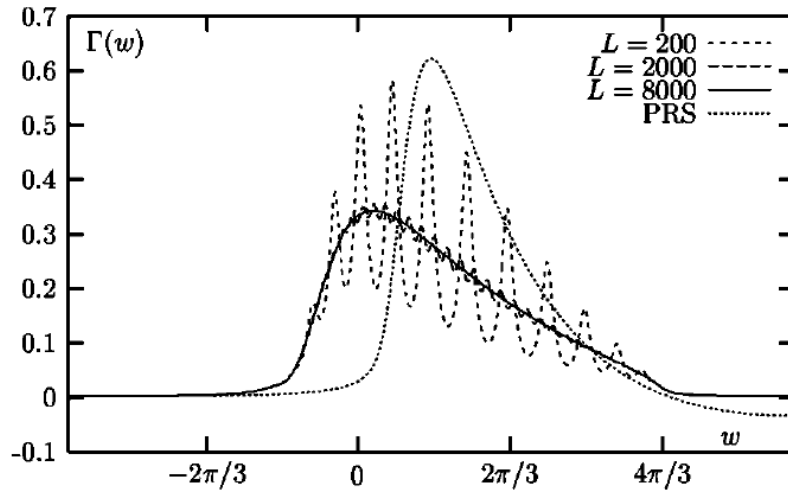
# Is the dipole approximation adequate?

## PRO:

1. It's simple!
2. It allows physical insight.
3. Captures interference phenomena well (DA is not the same as quasistatics).
4. Allows to deal with complex shapes as long as the polarizability is known.
5. Is not that inaccurate for moderate separations, especially for TE polarization.
6. After all, the mathematical shapes we use are approximations, often rough.

## CONTRA:

DA does break when the particles are close to touching, especially for polarization the TM polarization



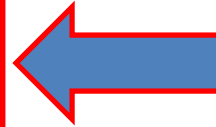
$$\sigma_e = 4\pi kV \operatorname{Im} \int \frac{\Gamma(w)dw}{z - w}$$

$$z = \frac{4\pi}{3} \frac{\epsilon + 2}{\epsilon - 1} \xrightarrow{\text{Drudean metals}} \frac{4\pi}{3} \frac{\omega_F^2 - \omega^2 - i\gamma\omega}{\omega_F^2}$$

From V.A.Markel, V.N.Pustovit, S.V.Karpov et al., PRB 70, 054202 (2004)

# The dipole approximation

$$\mathbf{d}_n = \alpha_n \left[ \mathbf{E}_n + \sum_{m \neq n} \hat{G}(k; \mathbf{r}_n, \mathbf{r}_m) \mathbf{d}_m \right]$$



The coupled-dipole equations in the frequency domain

$$k = \frac{\omega}{c}$$

$\mathbf{E}_n$  - external field

$\alpha_n$  - Polarizability of the  $n$ -th particle

$\hat{G}(k; \mathbf{r}_n, \mathbf{r}_m)$  - Frequency-domain Green's function

Green's function

$\mathbf{E}_n \propto \begin{cases} \delta_{n1} & \text{Near-field tip} \\ \exp(i\mathbf{k} \cdot \mathbf{r}_n) & \text{Plane wave} \end{cases}$



Spheres or spheroids,  $a \leq 10\text{nm}$

$$\frac{1}{\alpha} = \frac{4\pi}{\epsilon_h V} \left( \nu + \frac{\epsilon_h}{\epsilon_m - \epsilon_h} \right) - i \frac{2k^3}{3}$$

$\epsilon_h$  is the permittivity of the host medium (a transparent dielectric or vacuum)

$\epsilon_m = \epsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$  is the permittivity of metal (given by the Drude formula)

$V = \frac{4\pi abc}{3}$  is the volume of spheroid;  $k = \frac{\omega}{c}$

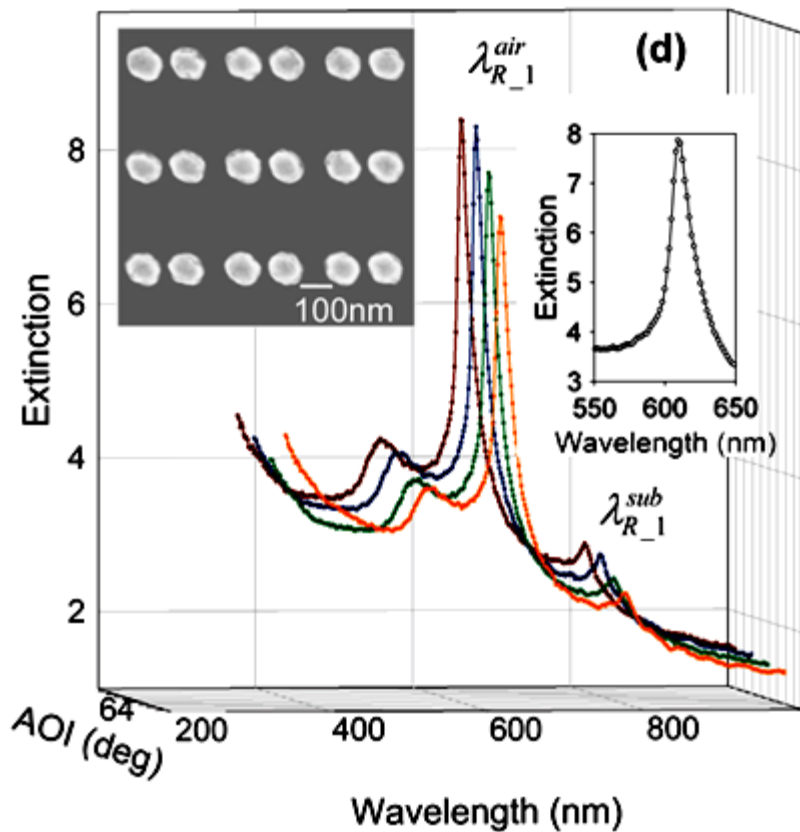
$\nu$  is the depolarization factor

Spheres  $a > 10\text{nm}$

$$\alpha = \frac{3i}{2k^3} \frac{m\psi_1(mkR)\psi_1'(kR) - \psi_1(kR)\psi_1'(mkR)}{m\psi_1(mkR)\xi_1'(kR) - \xi_1(kR)\psi_1'(mkR)}$$

Spheroids: similar approximations

## 2. SPECTROSCOPY (NARROW NON-LORENTZIAN RESONANCES)



EXPERIMENTAL SPECTRA

Gold

$h = 320\text{nm}$

p-polarization

$\theta = 62^\circ, 64^\circ, 66^\circ, 68^\circ$

- \* Incident plane wave
- \* Infinite, homogeneous periodic chain ( $\alpha_n = \alpha$ )

$$d_n = E_0 \frac{\exp(iqx_n)}{1/\alpha - h^{-3}S(\omega, q)}$$

$$q = k \cos \theta = \frac{\omega}{c} \cos \theta$$

The propagation constant

$$S(\omega, q) = h^3 \sum_{m \neq n} G(\omega; x_n, x_m) \exp(iqx_n)$$

The dipole sum ("self-energy")

$$S = S(k, q)$$

If  $kh = \xi$ ,  $qh = \eta$ , then

$$S_{\perp} = 2\xi^3 \sum_{n>0} \left[ \frac{1}{\xi n} + \frac{i}{(\xi n)^2} - \frac{1}{(\xi n)^3} \right] \exp(in\xi) \cos(n\eta)$$

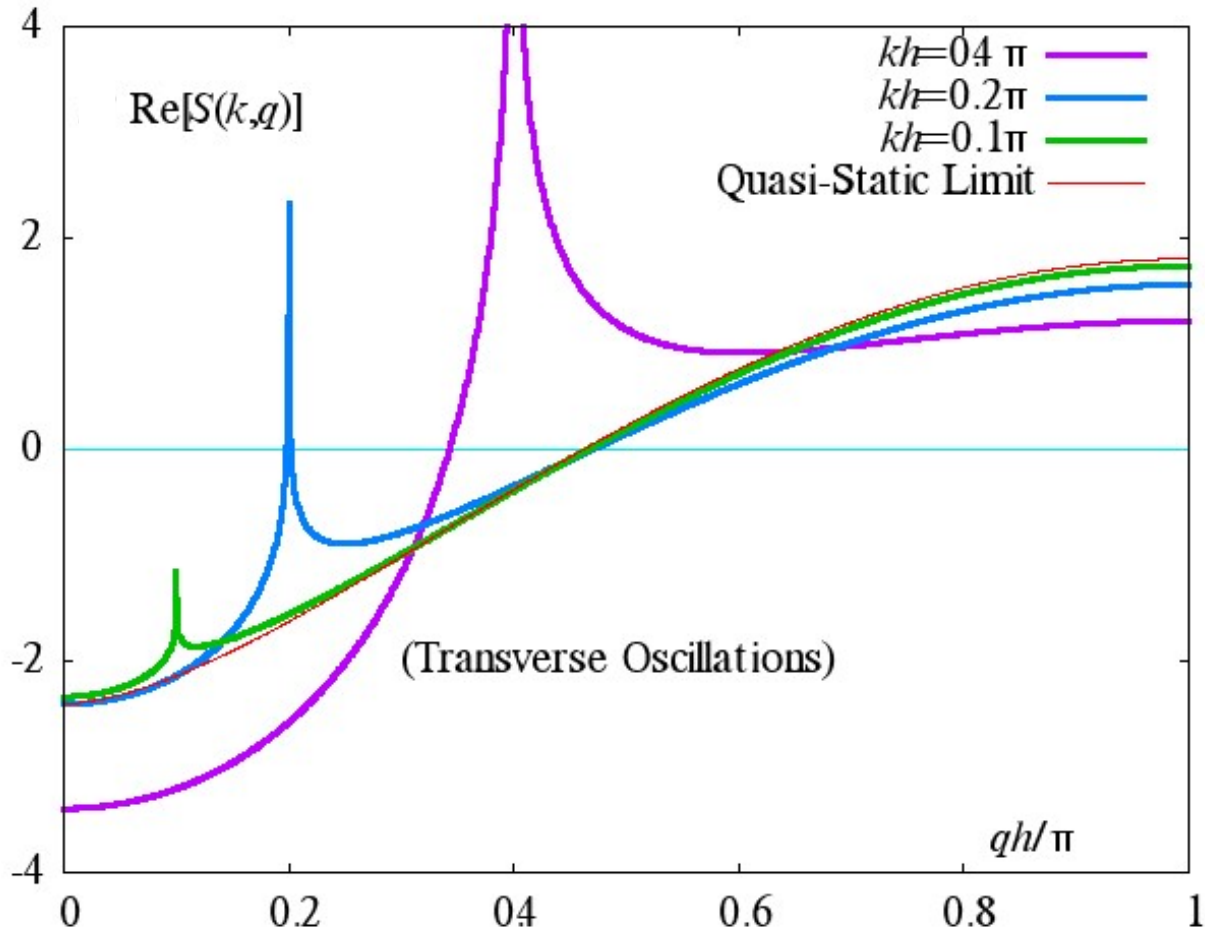
$$S_{\parallel} = 4\xi^3 \sum_{n>0} \left[ -\frac{i}{(\xi n)^2} + \frac{1}{(\xi n)^3} \right] \exp(in\xi) \cos(n\eta)$$

The " $\perp$ " dipole sum diverges logarithmically if

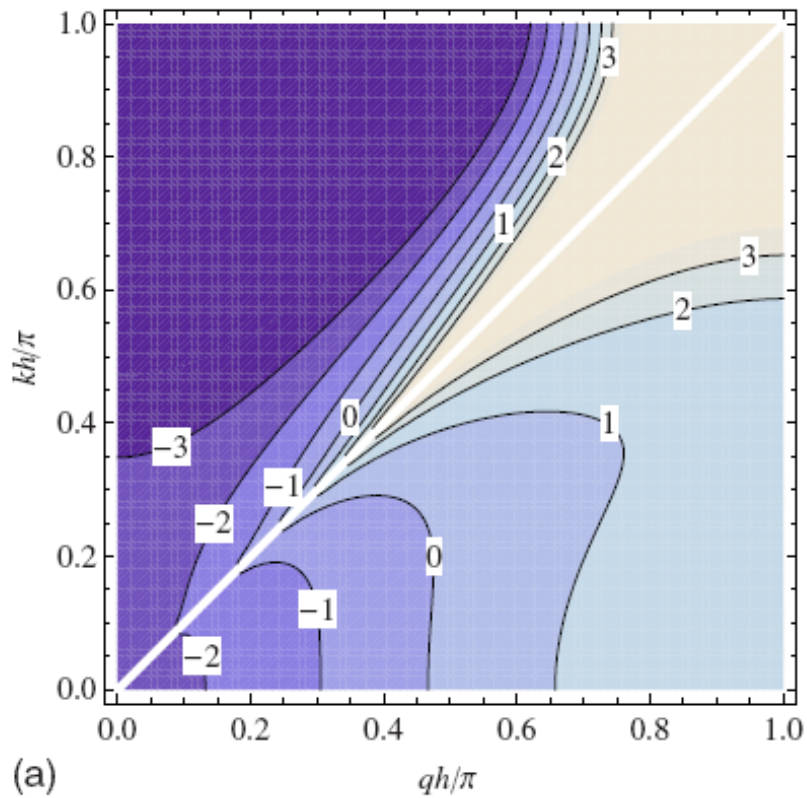
$$\xi \pm \eta = (k \pm q)h = 2\pi L$$

$L$  being an integer

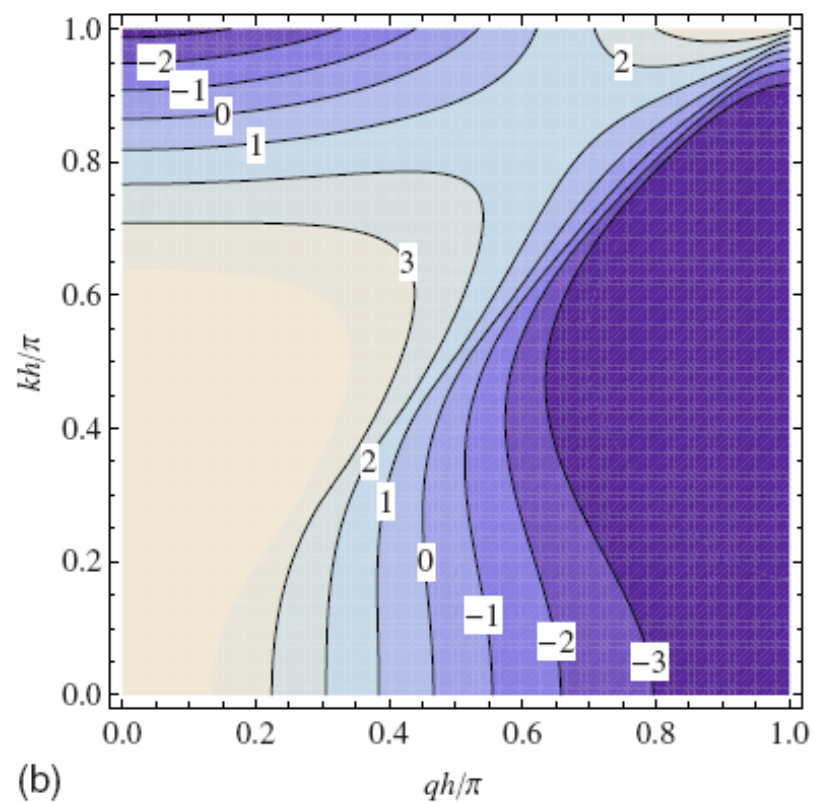
$\text{Re}S_{\perp}$  for some fixed values of frequency



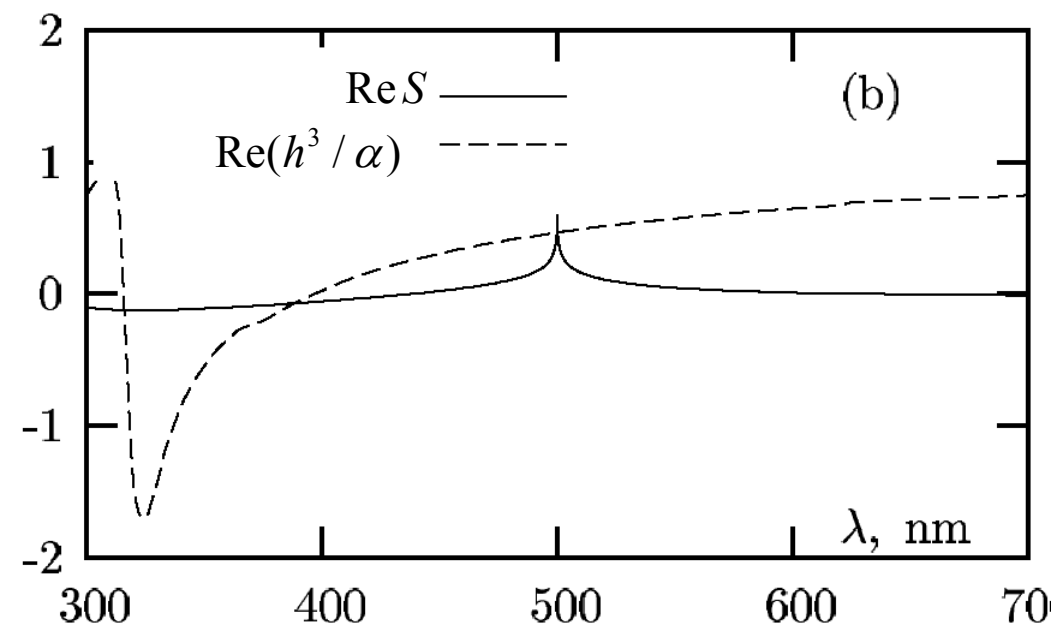
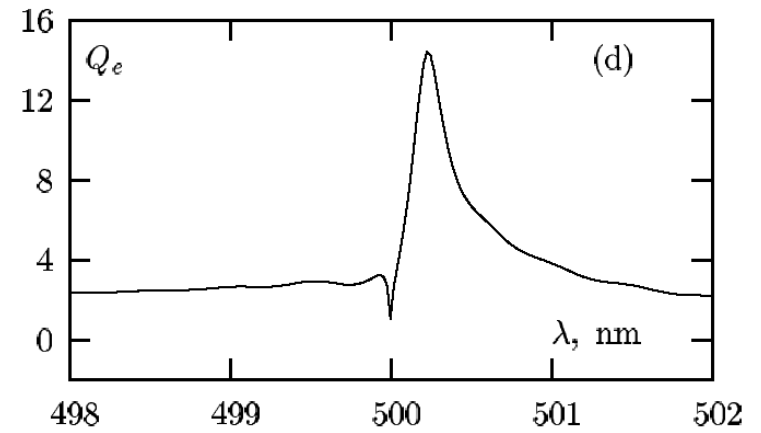
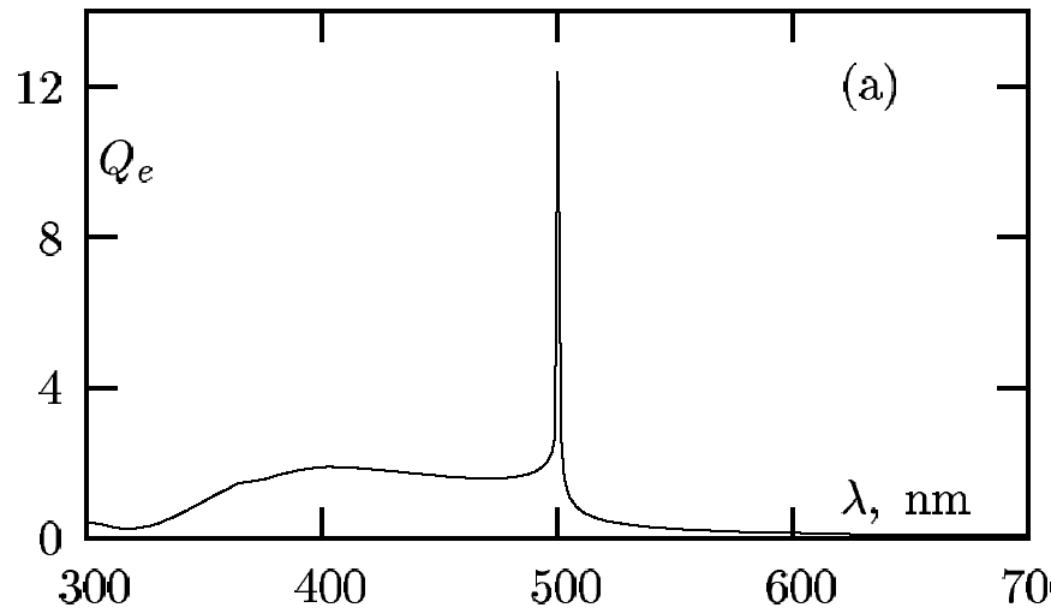
$$\text{Re}[S(kh, qh)]$$



Orthogonal (TE) polarization



Parallel (TM) polarization

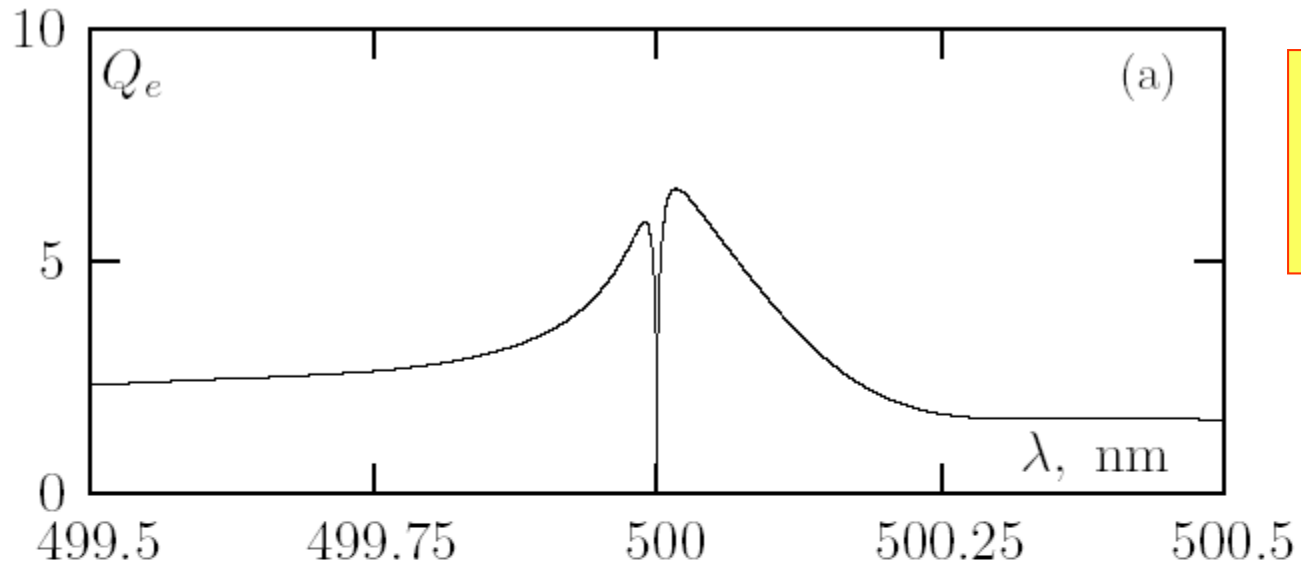


Experimental parameters for silver

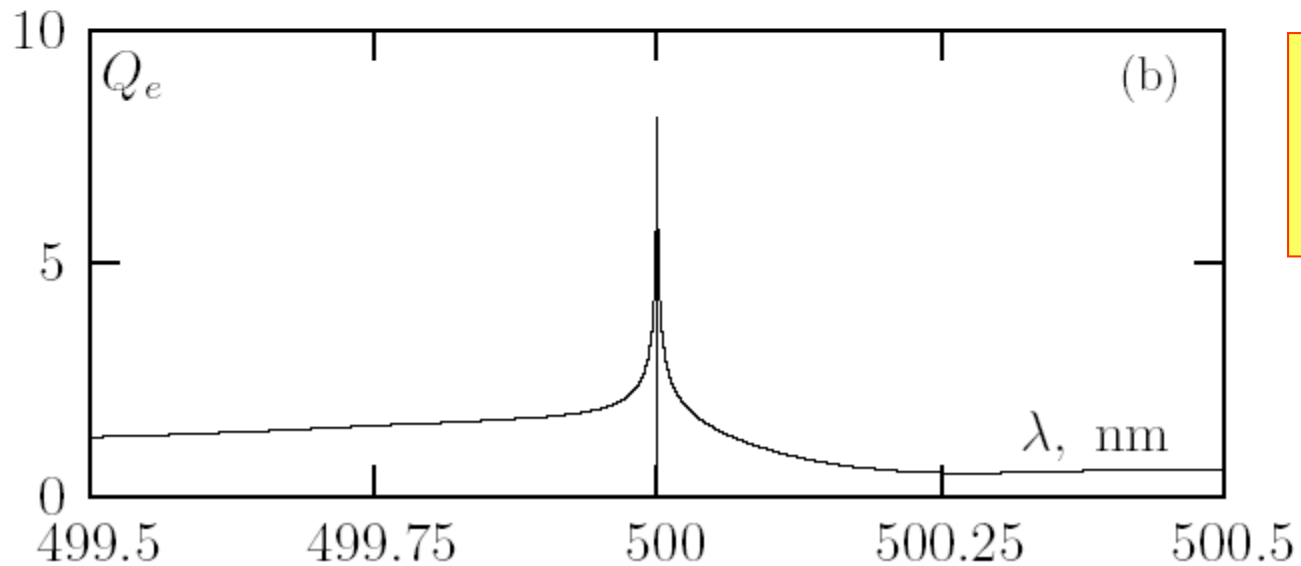
$a = 50\text{nm}$ ,  $h = 500\text{nm}$

$$\Delta\lambda = \frac{h}{2\pi} \exp\left[-\frac{C}{2(2\pi)^2} \left(\frac{h}{a}\right)^3\right]$$

$C \sim 1$



$a = 45\text{nm}$   
 $h = 500\text{nm}$



$a = 40\text{nm}$   
 $h = 500\text{nm}$



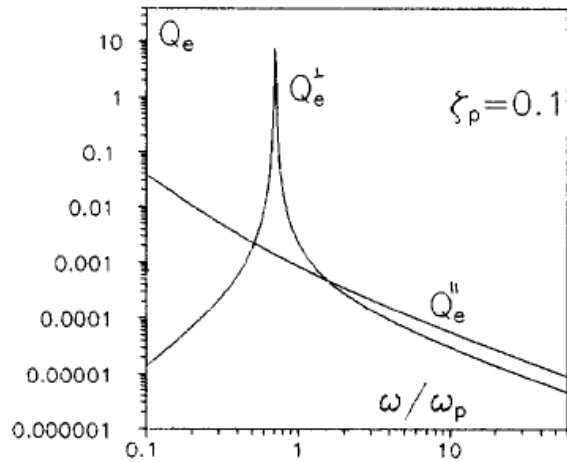
# Why is the resonance non-Lorentzian ?

$$\Lambda(\omega) = \frac{f_n}{\omega - \omega_0 - \Sigma(\omega)}$$

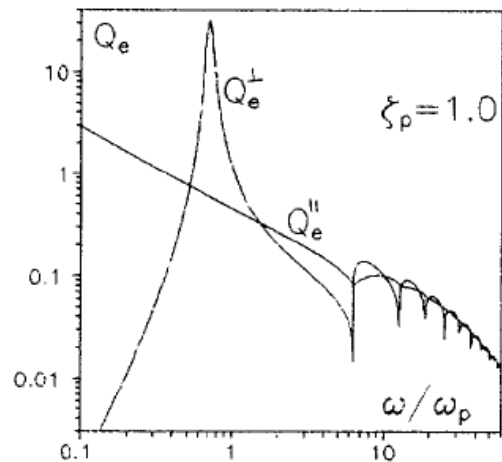
$$\Sigma(\omega) \approx \Sigma(\omega_0) + \left. \frac{\partial \Sigma}{\partial \omega} \right|_{\omega=\omega_0} (\omega - \omega_0)$$

(Quasiparticle pole approximation)

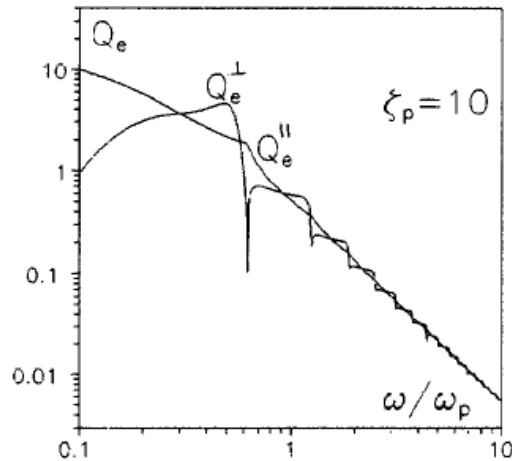
But  $\frac{\partial S}{\partial \omega}$  does not exist at  $\omega = \omega_0$  !



(a)



(b)



(c)

Narrow spectral features in extinction spectra of an infinite chain of Drudean spheres.

$\frac{\omega_p h}{c} = 0.1$  (a),  $\frac{\omega_p h}{c} = 1$  (b), and  $\frac{\omega_p h}{c} = 10$  (c).

" $\perp$ " - polarization orthogonal to the chain

" $\parallel$ " - polarization parallel to the chain

From V.A.Markel, J. Mod. Opt. 40, 2281 (1993).

# 3. DISPERSION RELATIONS

$$h^3 / \alpha(\omega) - S(\omega, q) = 0 \quad \Rightarrow \quad \omega = f(q) \quad [\text{Recall that } k = \omega / c]$$

Is it possible to find a solution such that  $\omega, q \in \mathbb{R}$ ?

Only if: (i)  $q > k = \omega / c$

(ii)  $\text{Im}(1/\alpha) = -2k^3 / 3$

Modes with  $q > k$  are called Surface Plasmon Polaritons (SPP)

# What is the role of losses (both radiative and absorptive)?

A few possible approaches:

- \* Take real  $\omega$  and seek complex  $q$
- \* Take real  $q$  and seek complex  $\omega$
- \* Solve eqn  $\text{Re}\left[h^3 / \alpha(\omega) - S(\omega, q)\right] = 0$  for  $\omega, q \in \mathbb{R}$

When losses are small, there is not much of a difference...

# What is the role of particle nonsphericity?

- Nanoparticle chains have been studied almost exclusively for the case of spherical particles
- However, nonsphericity can be expected to provide a useful additional parameter to control:
  - SPP dispersion curves
  - SPP bandwidth
  - Propagation distance

# Model for the polarizability, $\alpha$

$$\frac{1}{\alpha} = \frac{4\pi}{\varepsilon_h V} \left( \nu + \frac{\varepsilon_h}{\varepsilon_m - \varepsilon_h} \right) - i \frac{2k^3}{3}$$

$\varepsilon_h$  is the permittivity of the host medium (a transparent dielectric or vacuum)

$\varepsilon_m = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$  is the permittivity of metal (given by the Drude formula)

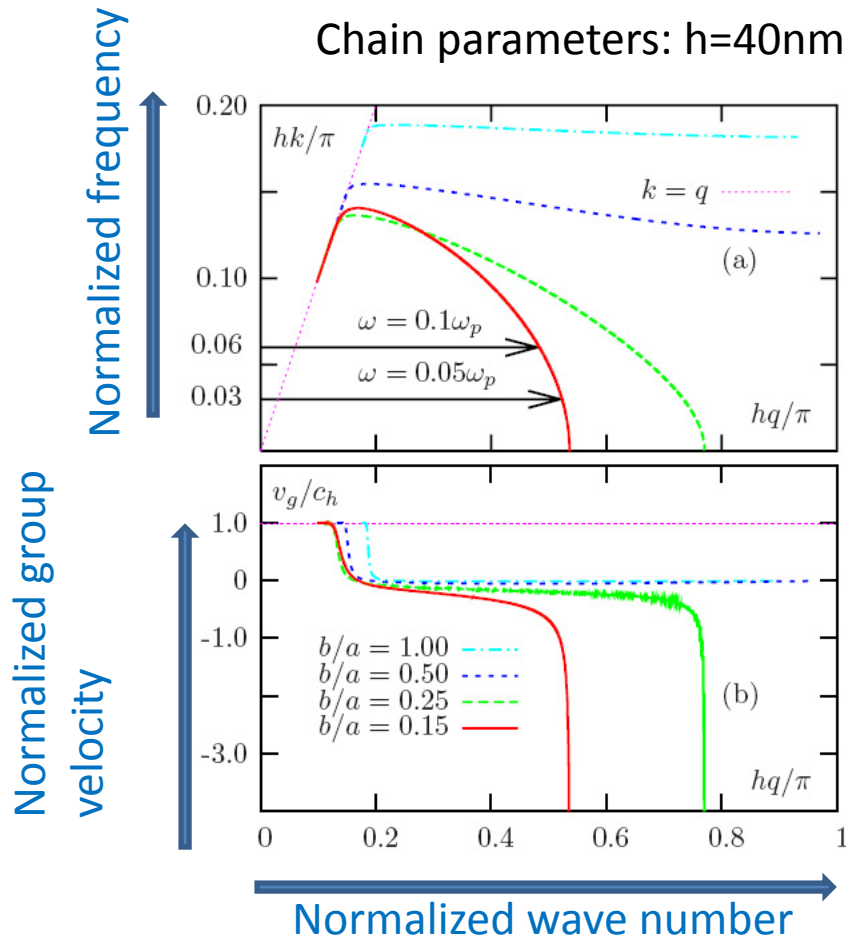
$V = \frac{4\pi abc}{3}$  is the volume of spheroid;

$$k = \frac{\omega}{c}$$

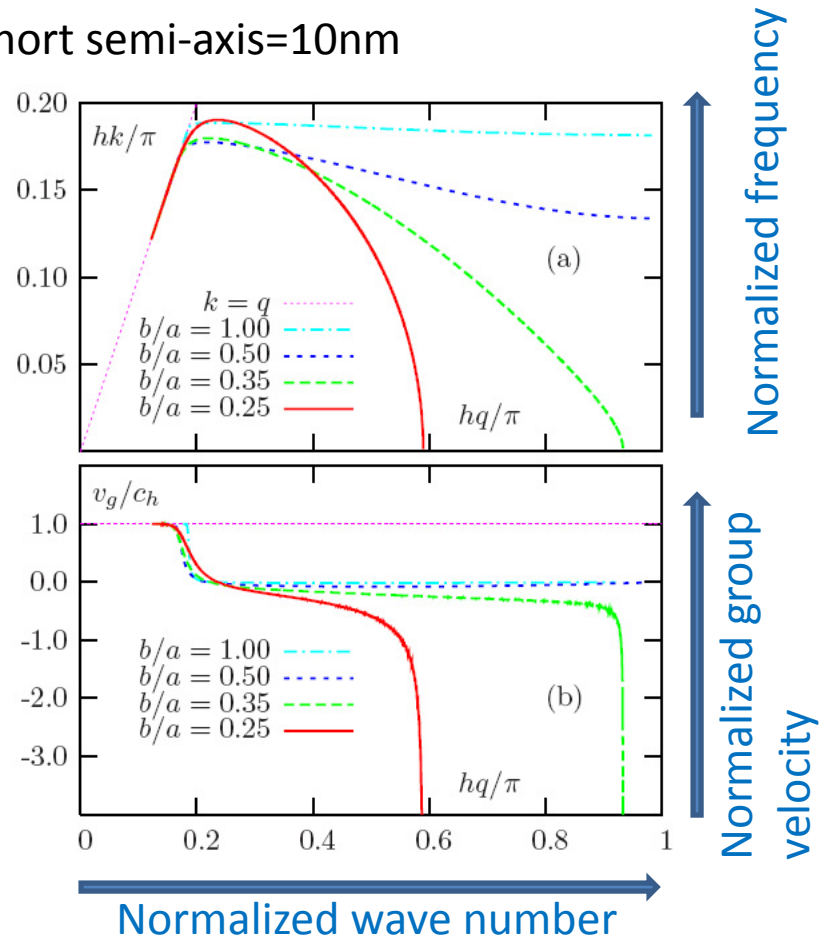
$\nu$  is the depolarization factor

# Dispersion curves and group velocities for transversely polarized SPPs and different aspect ratios $a/b$ of spheroids

Chain parameters:  $h=40\text{nm}$ , short semi-axis= $10\text{nm}$



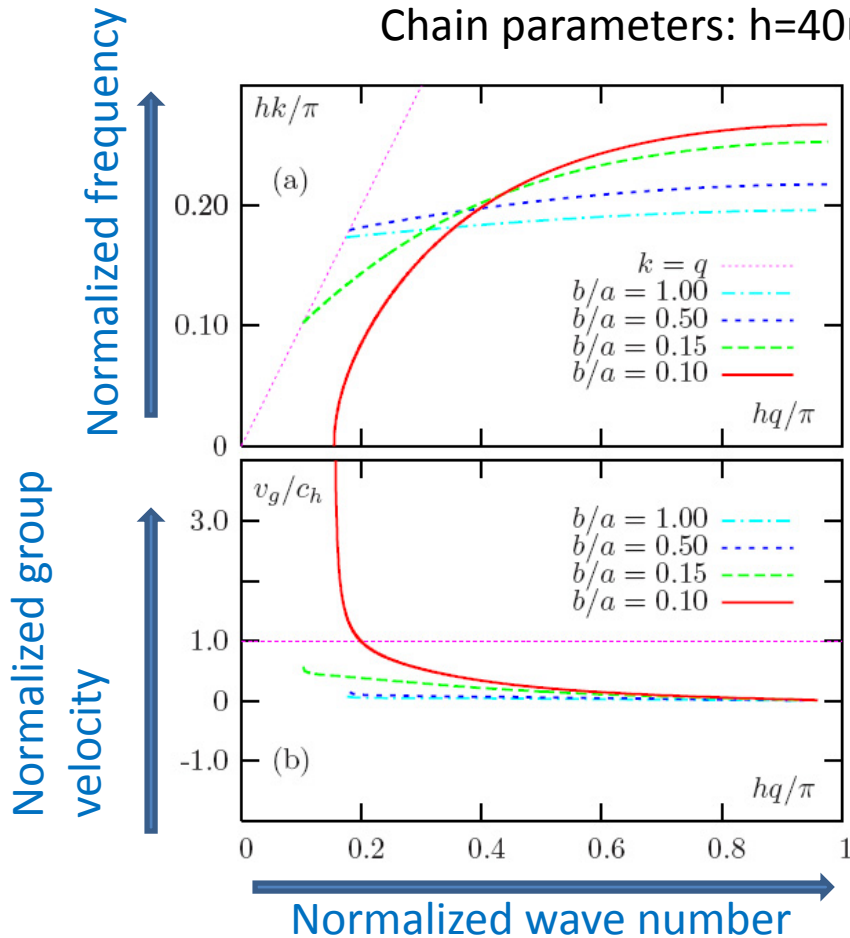
Prolate spheroids whose axis of symmetry is perpendicular to the chain



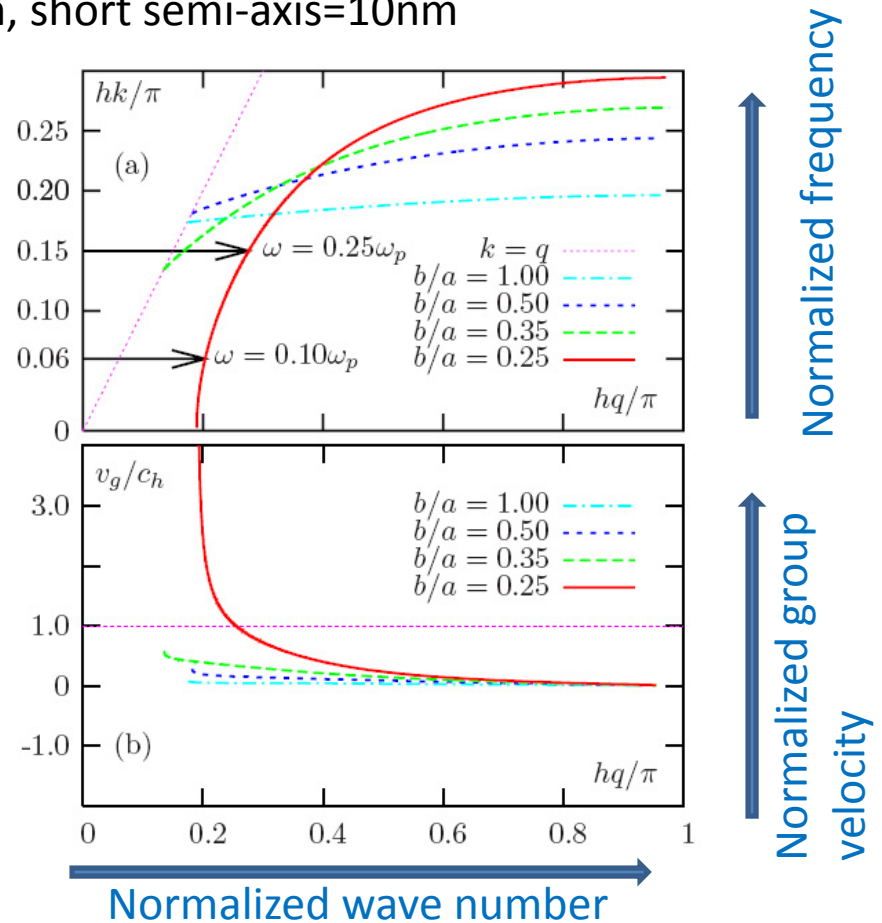
Oblate spheroids whose axis of symmetry is parallel to the chain

# Dispersion curves and group velocities for longitudinally polarized SPPs and different aspect ratios $a/b$ of spheroids

Chain parameters:  $h=40\text{nm}$ , short semi-axis= $10\text{nm}$

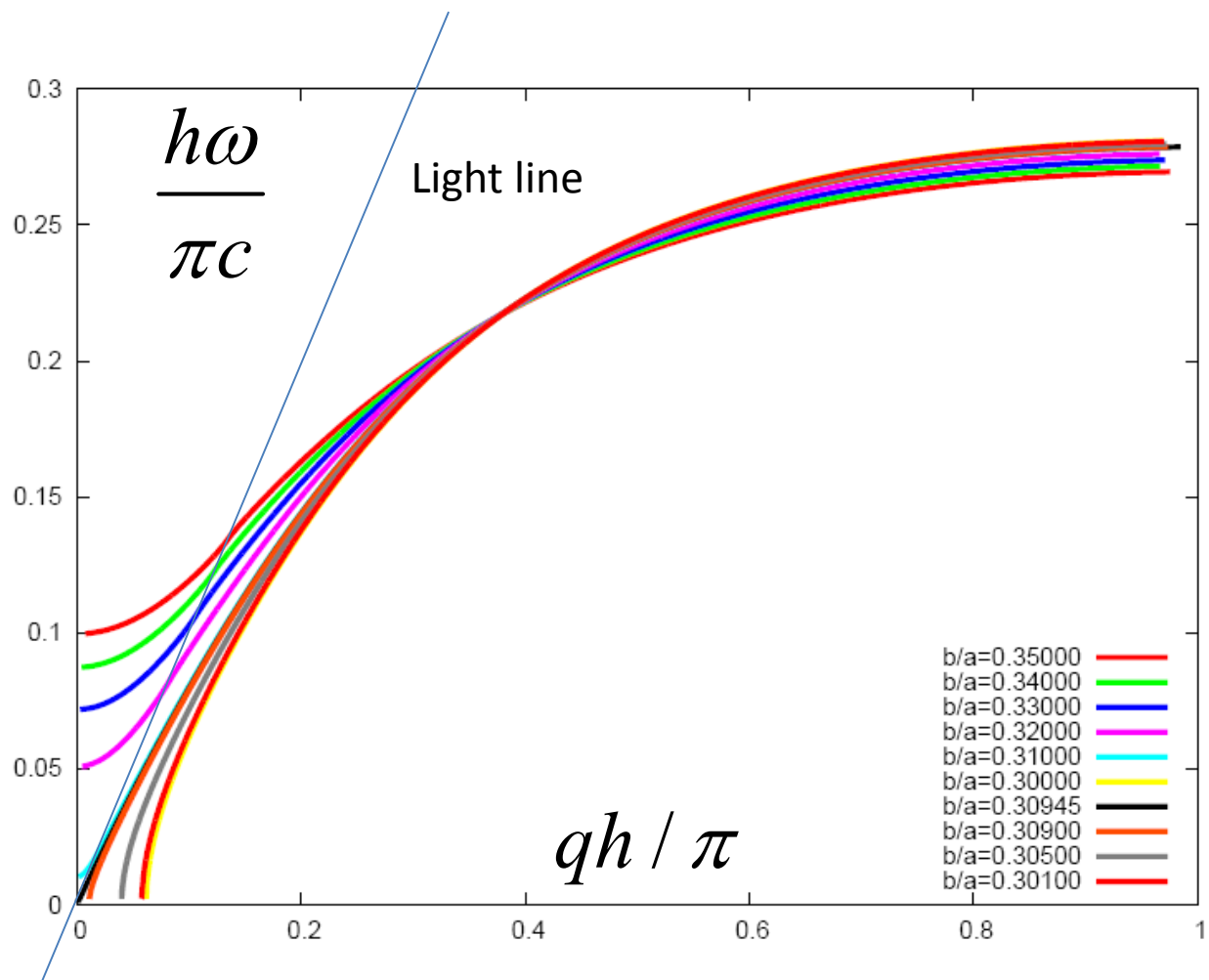
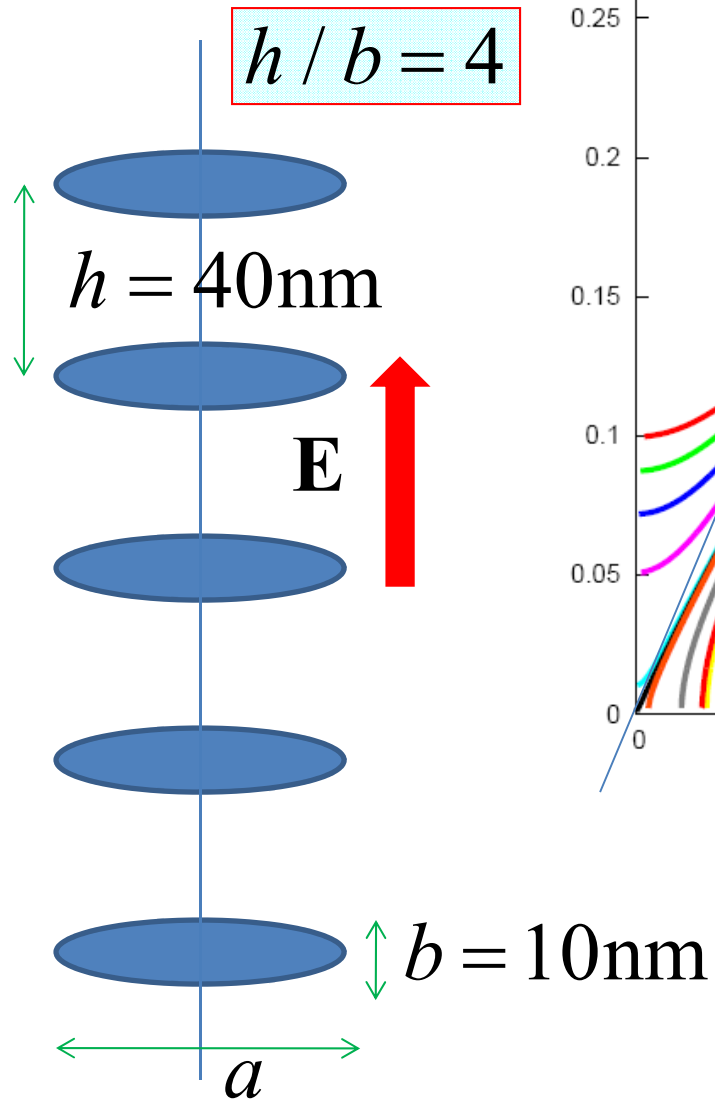


Prolate spheroids whose axis of symmetry is perpendicular to the chain

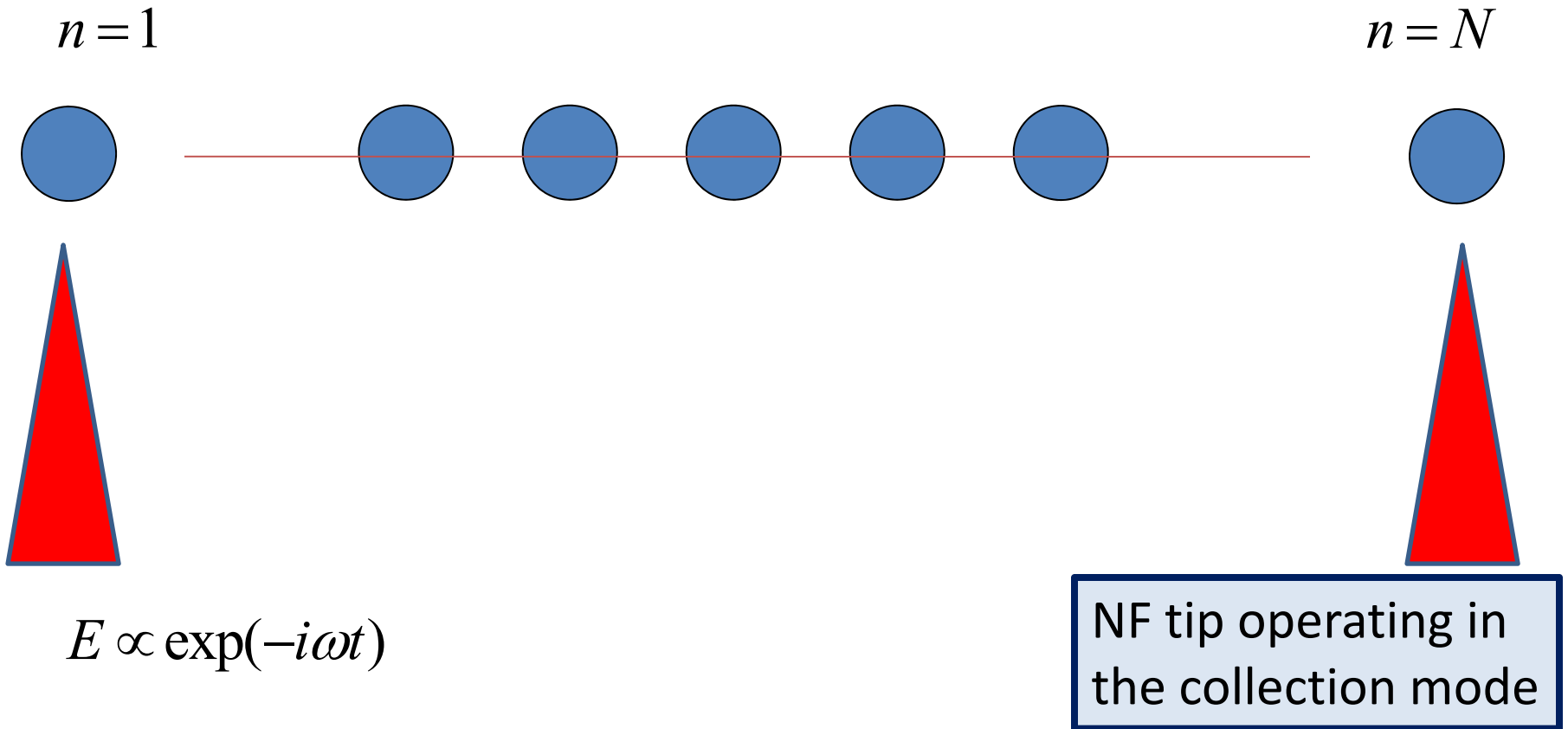


Oblate spheroids whose axis of symmetry is parallel to the chain





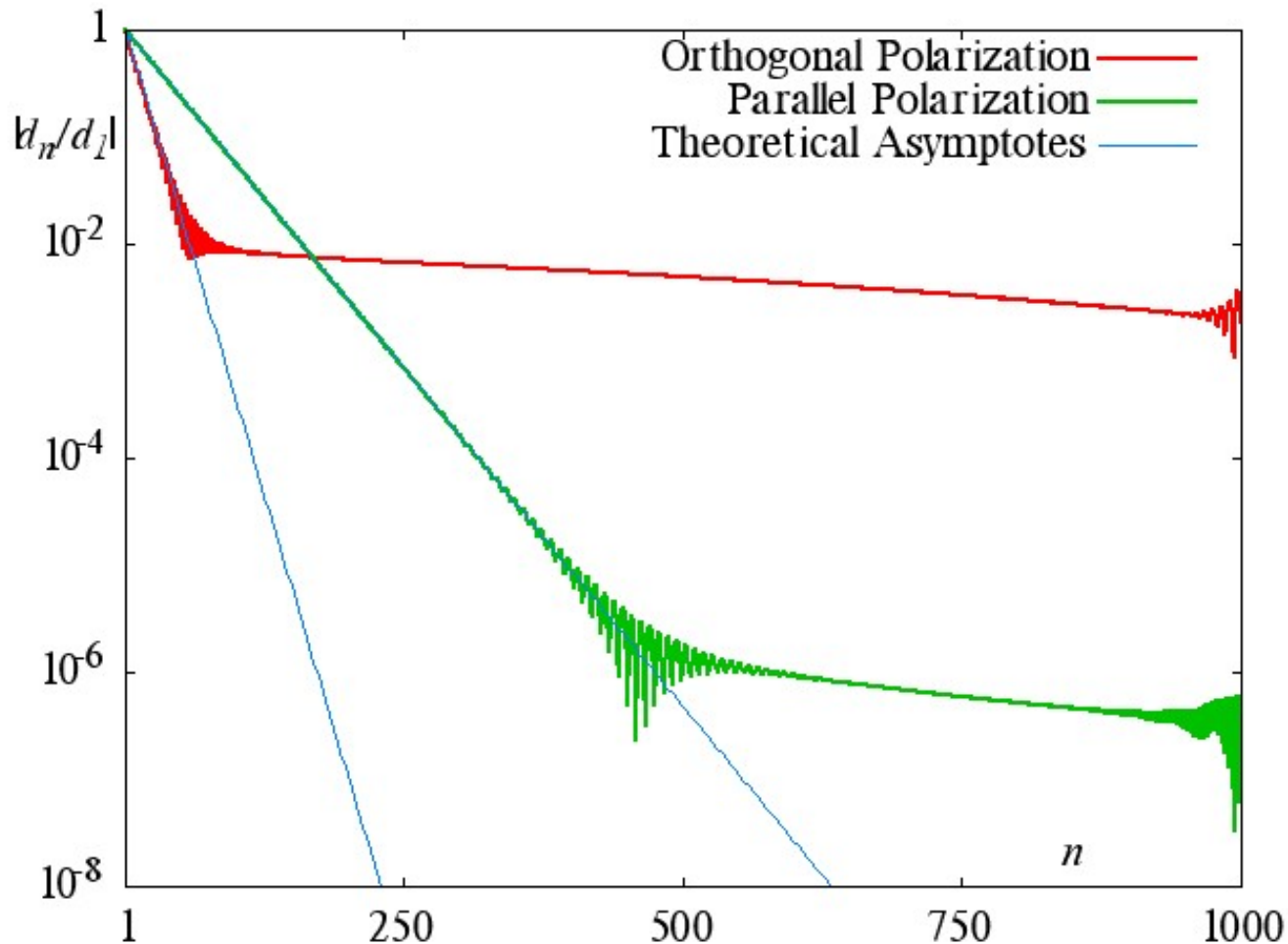
# 4. PROPAGATION. STEADY STATE



- \* Incident plane wave
- \* Infinite, homogeneous periodic chain ( $\alpha_n = \alpha$ )
- \* First particle in the chain illuminated by an external source (e.g., NSOM tip)

$$d_n = E_0 \int_{-\pi/h}^{\pi/h} \frac{\exp(iqx_n)}{1/\alpha - h^{-3}S(\omega, q)} \frac{dq}{2\pi}$$

# Simulation for a finite chain of $N=1000$ identical nanospheres



Parameters:

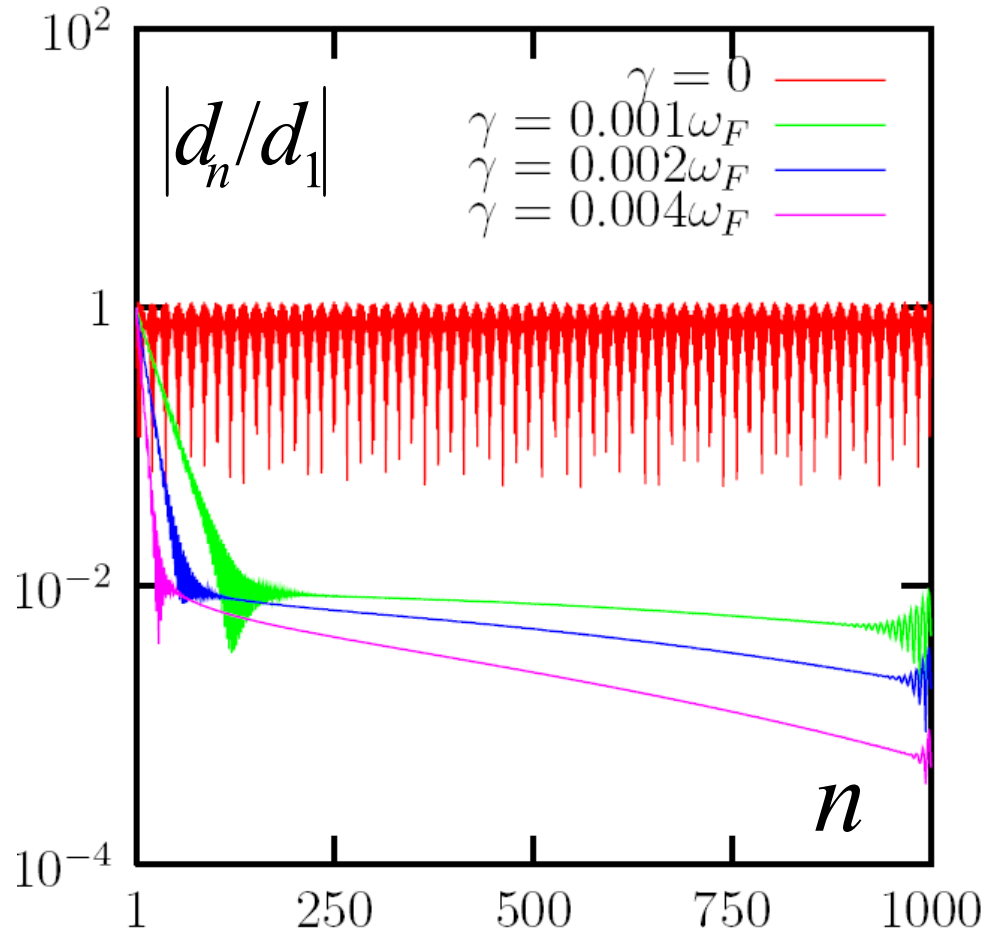
$$\omega = \omega_F$$

$$\frac{\gamma}{\omega_F} = 0.002$$

$$\lambda = \frac{2\pi c}{\omega} = 10h$$

$$h = 4a$$

# Effect of Ohmic Losses



Parameters:

$$\omega = \omega_F$$

$\frac{\gamma}{\omega_F}$  varies

$$\lambda = \frac{2\pi c}{\omega} = 10h$$

$$h = 4a$$

# Effects of disorder

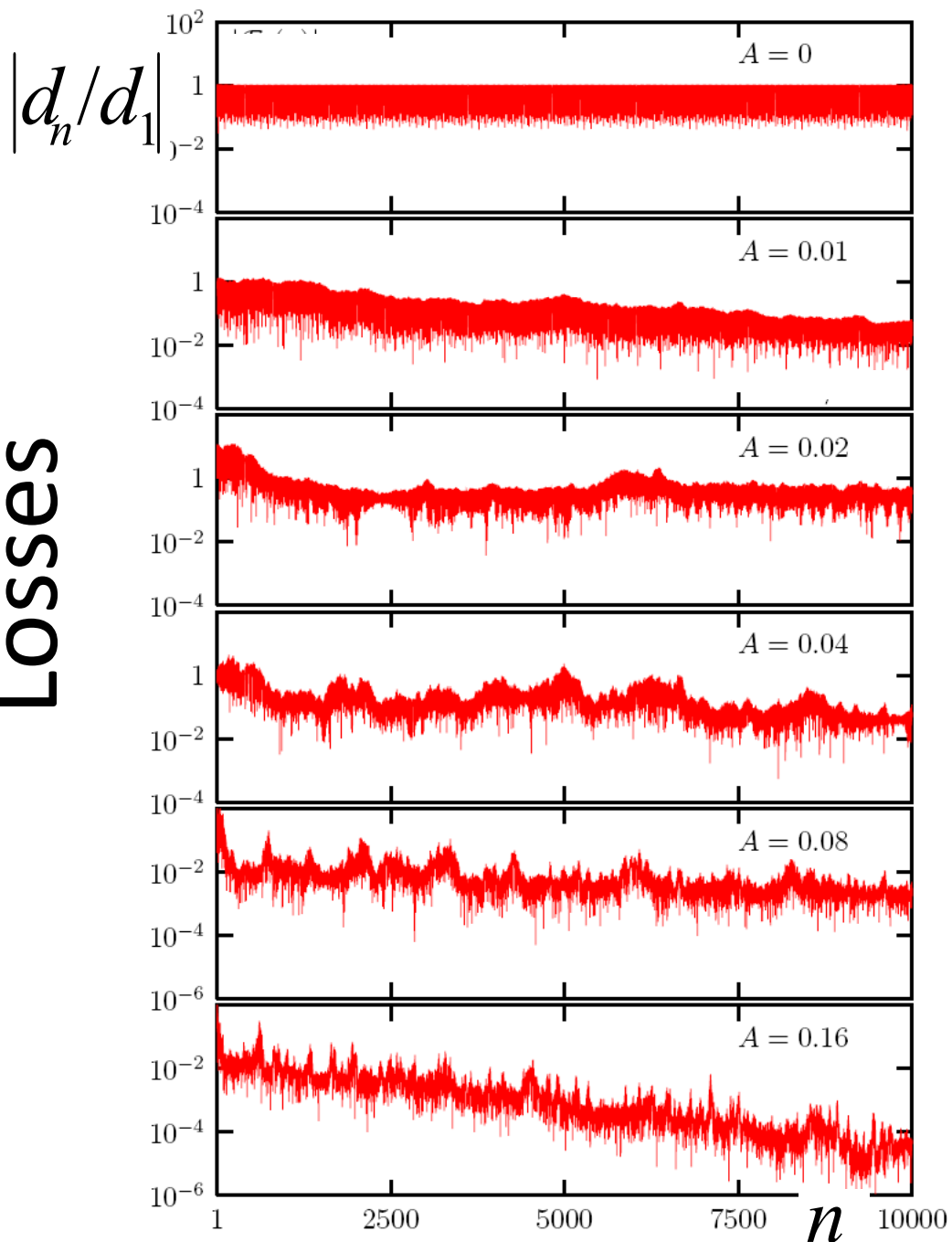
- Off-diagonal disorder (disorder in the nanoparticle positions)

We assume here that the position of the  $n$ -th particle is evenly distributed in the interval  $[h(n-A), h(n+A)]$ ,  $A \ll 1$

- Diagonal disorder  
[A more subtle effect, not considered in this talk; see Phys.Rev.B **75**, 085426 (2007)]

# Off-Diagonal Disorder in the Absence of Ohmic Losses

Losses



Parameters:

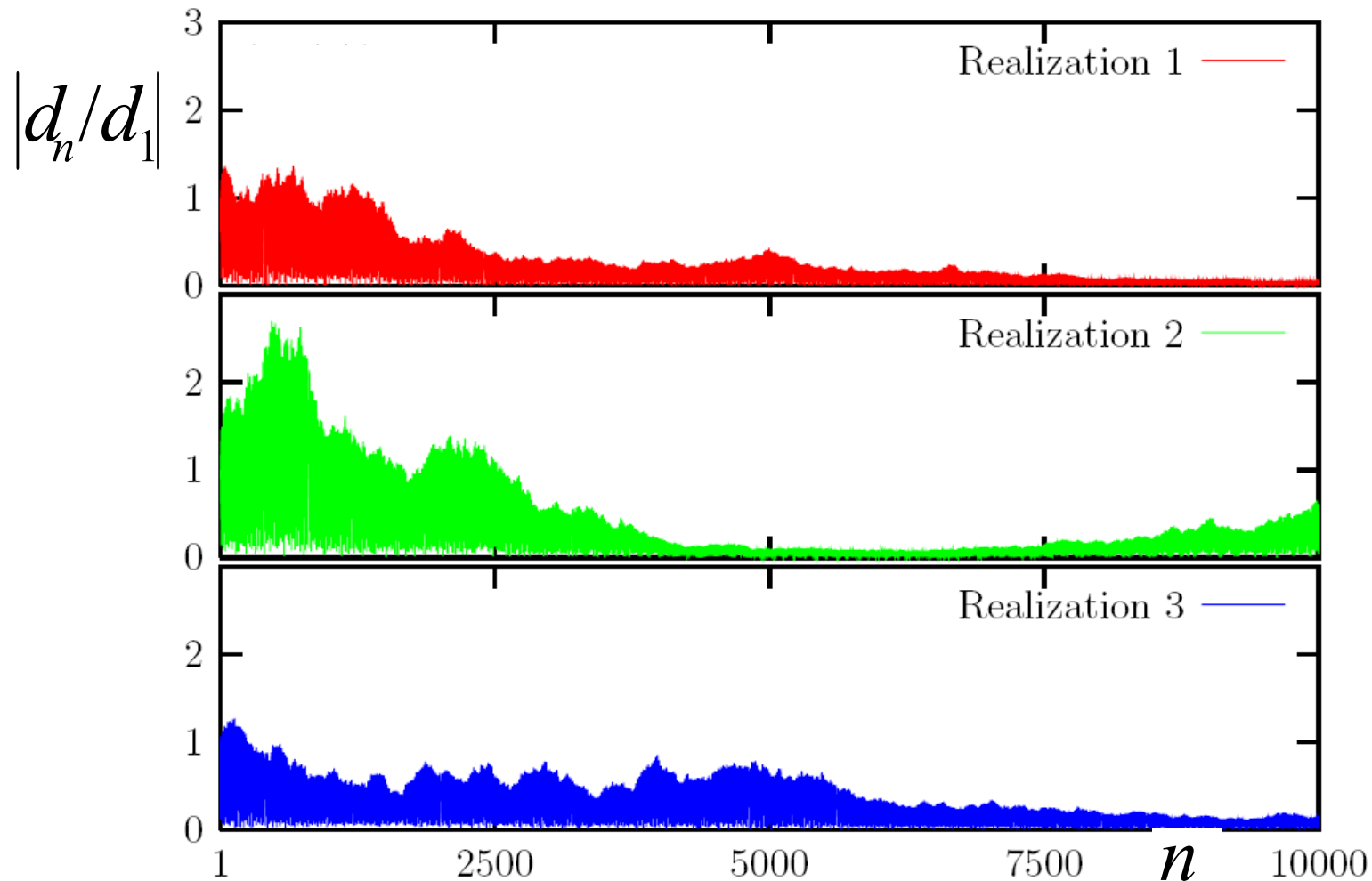
$$\omega = \omega_F$$

$$\frac{\gamma}{\omega_F} = 0$$

$$\lambda = \frac{2\pi c}{\omega} = 10h$$

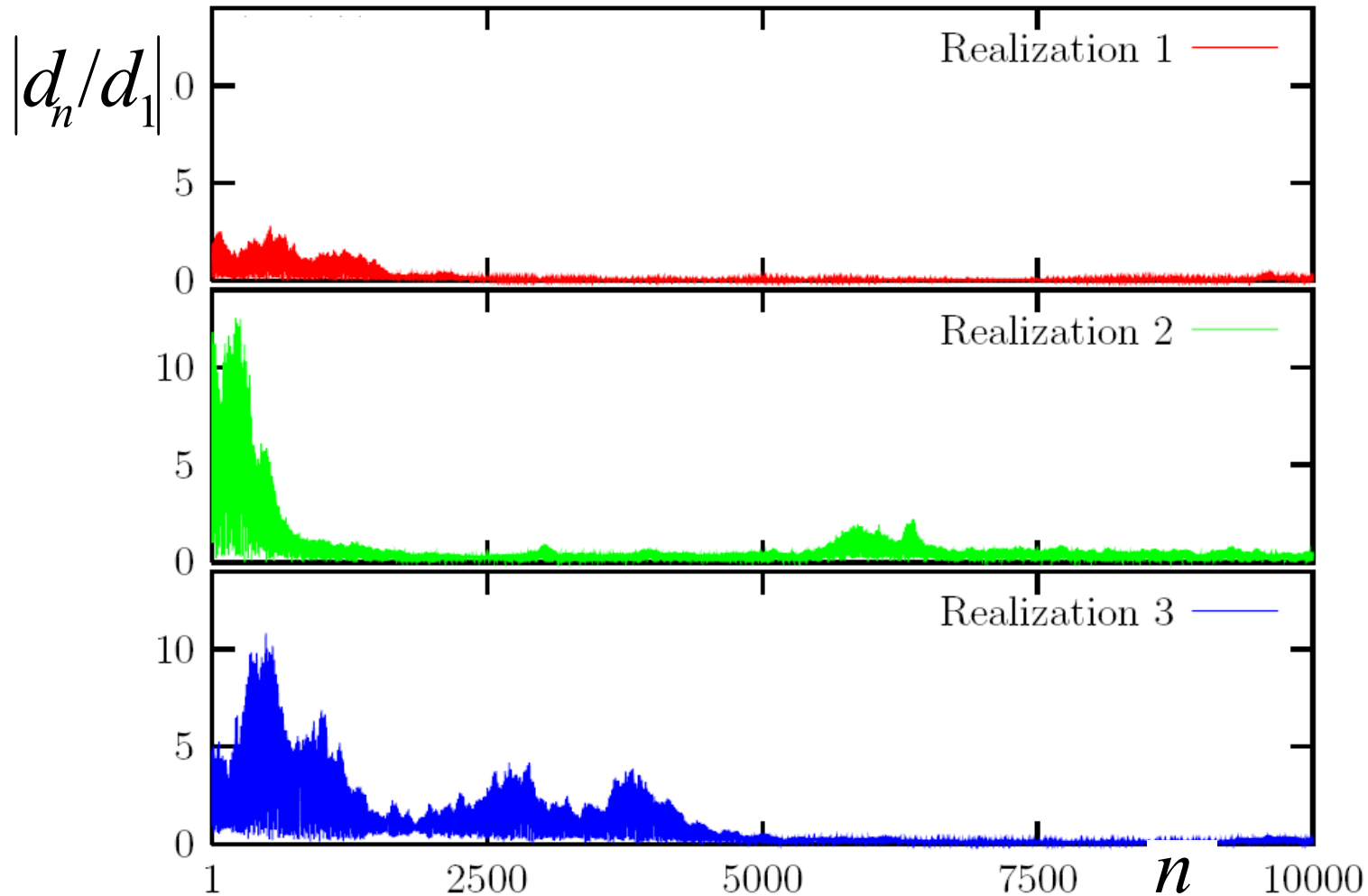
$$h = 4a$$

# Different Realization of Disorder at the Level $A=0.01$



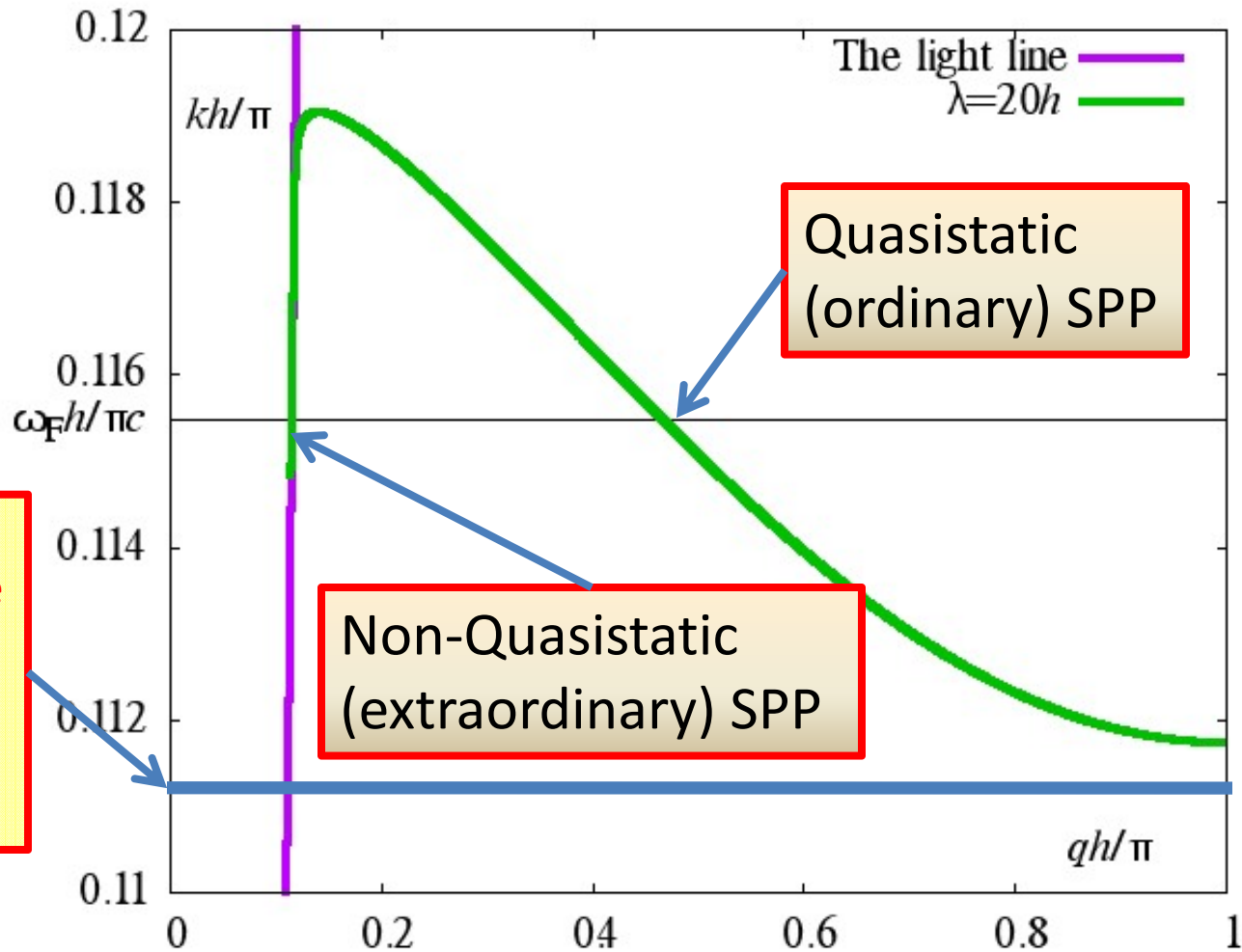


# Different realization of disorder at the level $A=0.02$



$$\omega = \omega_F$$

# Non-quasistatic SPP at different levels of disorder

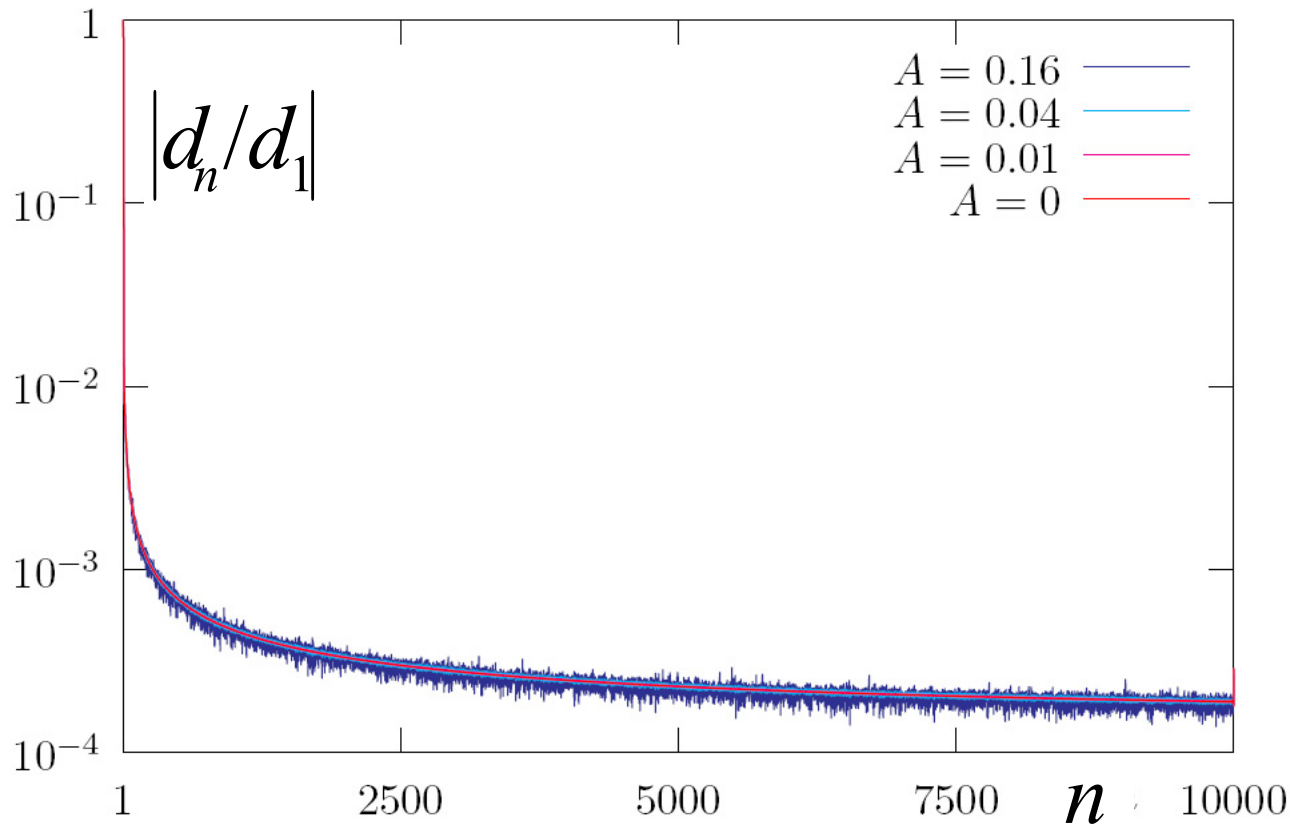


Let the frequency be small enough so that the ordinary SPP is not excited

Quasistatic (ordinary) SPP

Non-Quasistatic (extraordinary) SPP

# Non-quasistatic SPP at different levels of disorder (continued)

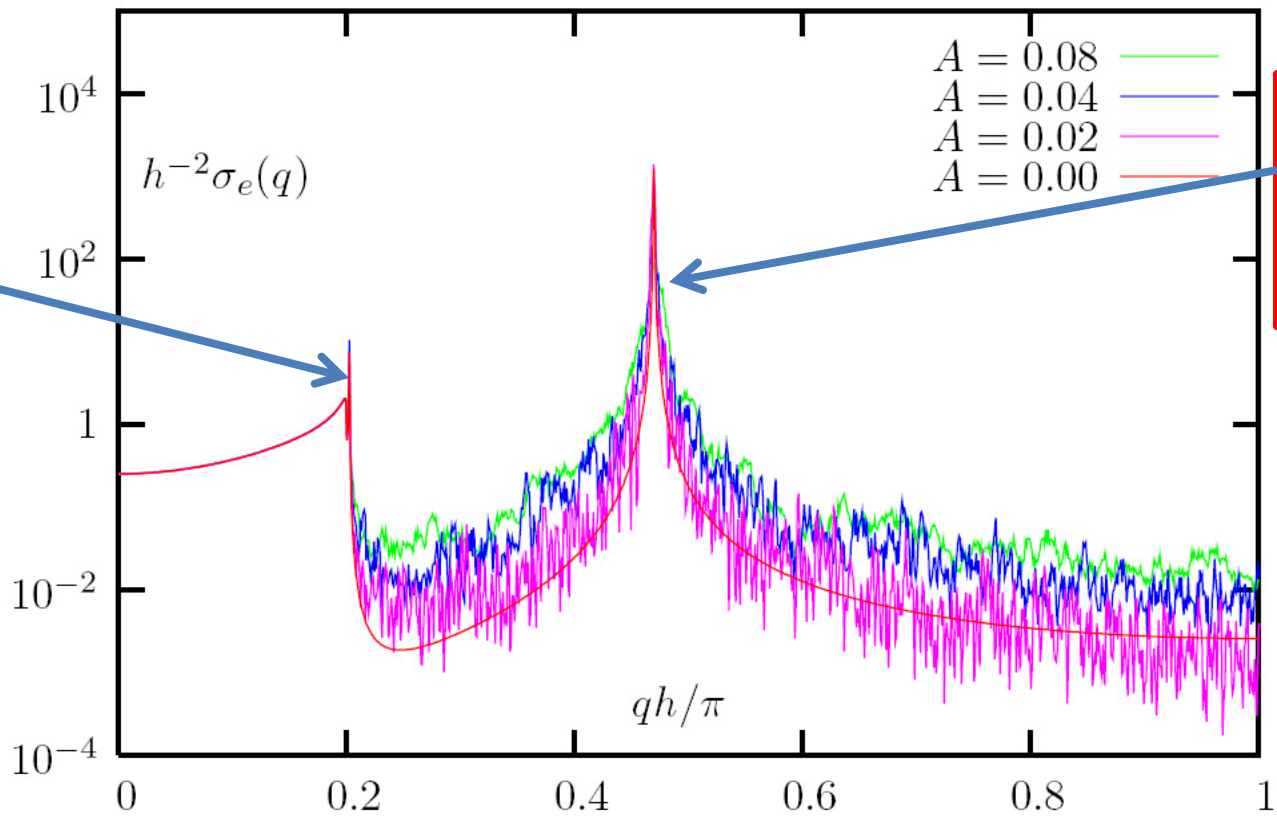


$$\frac{\omega}{\omega_F} = 0.984$$

(small enough  
so that the  
ordinary SP  
is not excited)

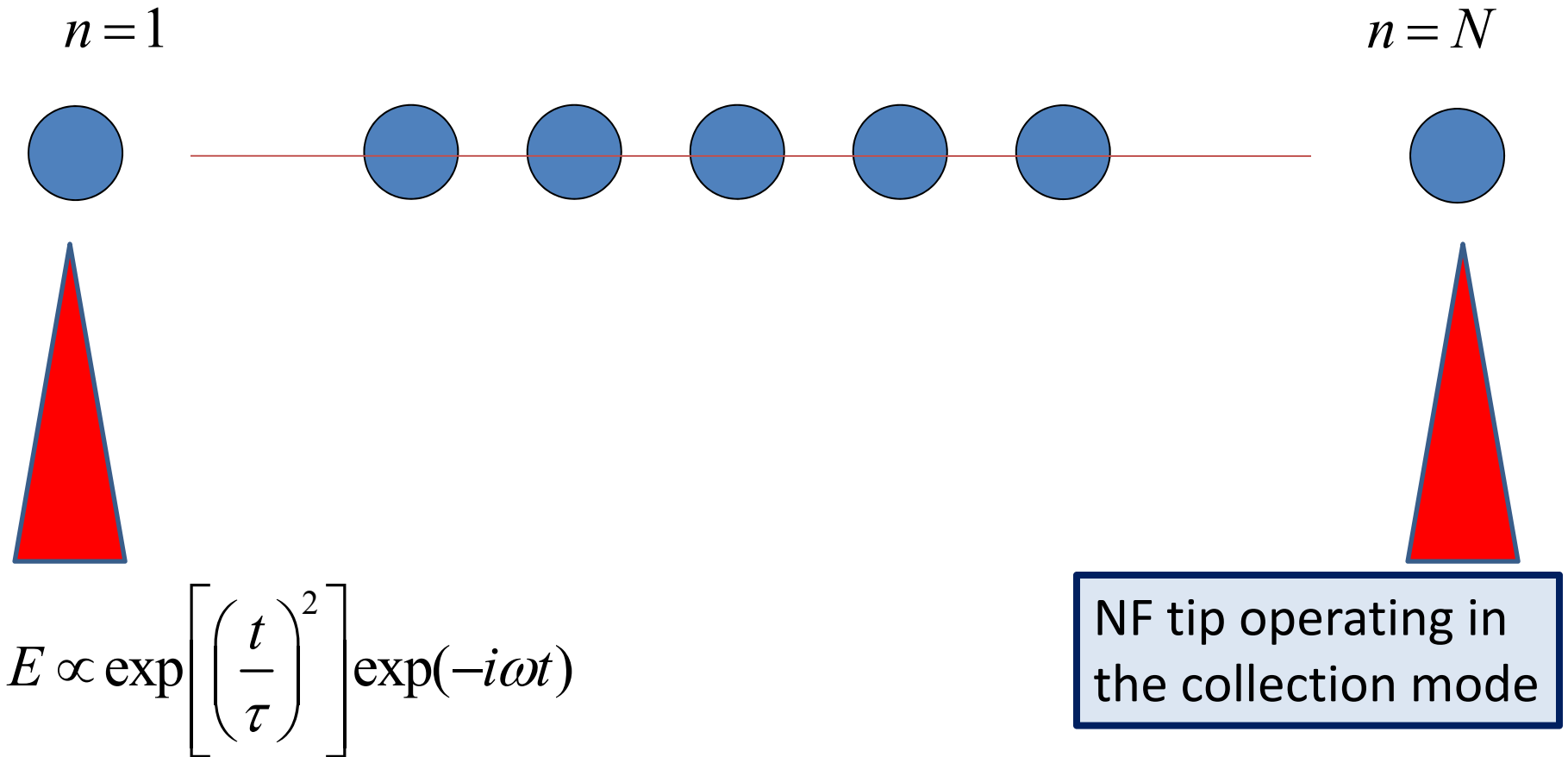
Specific extinction for excitation by a plane wave  
 $\exp(iqx)$   
(e.g., created by the TIR,  $q$  can be larger than  $k$ )

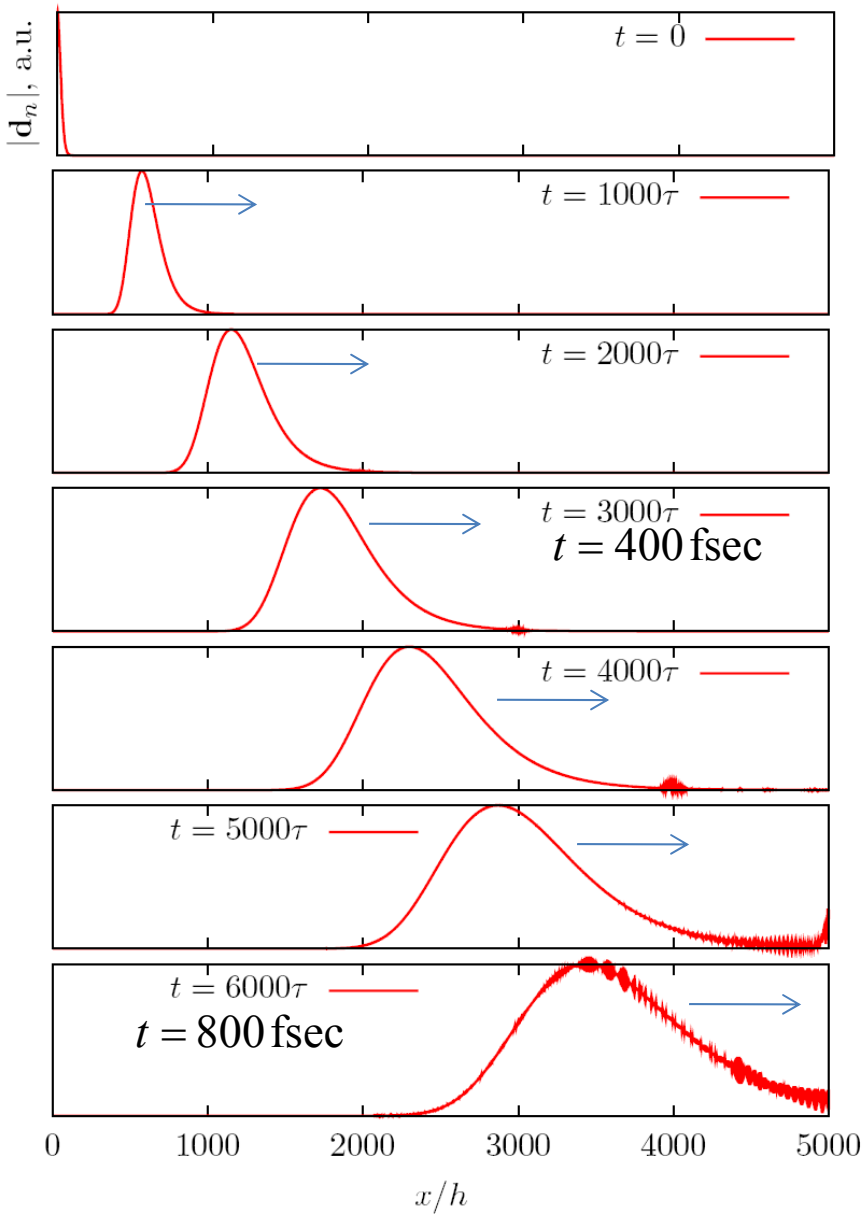
Extraor-  
dinary  
(non-  
quasi-  
static)  
SPP



Ordinary  
(quasista-  
tic) SPP

# 5. PROPAGATION. TRANSIENT PHENOMENA





$$v_g \approx 0.58c$$

$$L = 200\mu\text{m}$$

### Chain Parameters:

$$h = 40\text{ nm}$$

$$b = 10\text{ nm}$$

$$\xi = \frac{b}{a} = 0.15$$

$$N = 5000$$

$$\tau = \frac{h}{c} = 0.133\text{ fsec}$$

### Host Medium:

$$\varepsilon_h = 2.5$$

### Metal Parameters

(Ag)

$$\varepsilon = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

$$\lambda_p = \frac{2\pi c}{\omega_p} = 136\text{ nm}$$

$$\gamma/\omega_p = 0.002$$

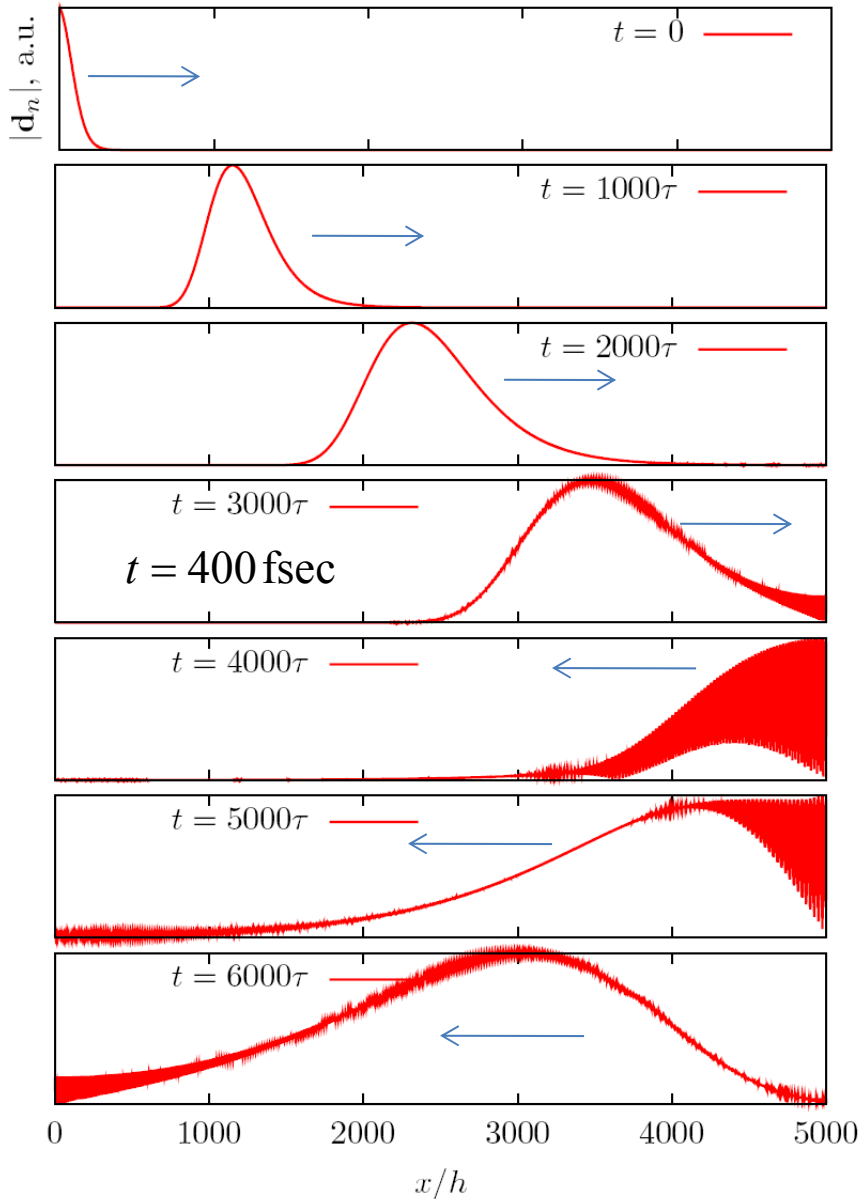
$$\varepsilon_0 = 5$$

### Pulse Parameters:

$$\omega_0 = 0.1\omega_p \quad [\lambda_0 = 1.36\mu\text{m}]$$

$$\Delta t = 7.2\text{ fsec}$$

$$\Delta\omega/\omega_0 = 0.2$$



$$v_g \approx 1.17c$$

Pulse Parameters Different from the Previous Graph:

$$\omega_0 = 0.05\omega_p \quad [\lambda_0 = 2.72 \mu\text{m}]$$

$$\Delta t = 14.2 \text{ fsec}$$

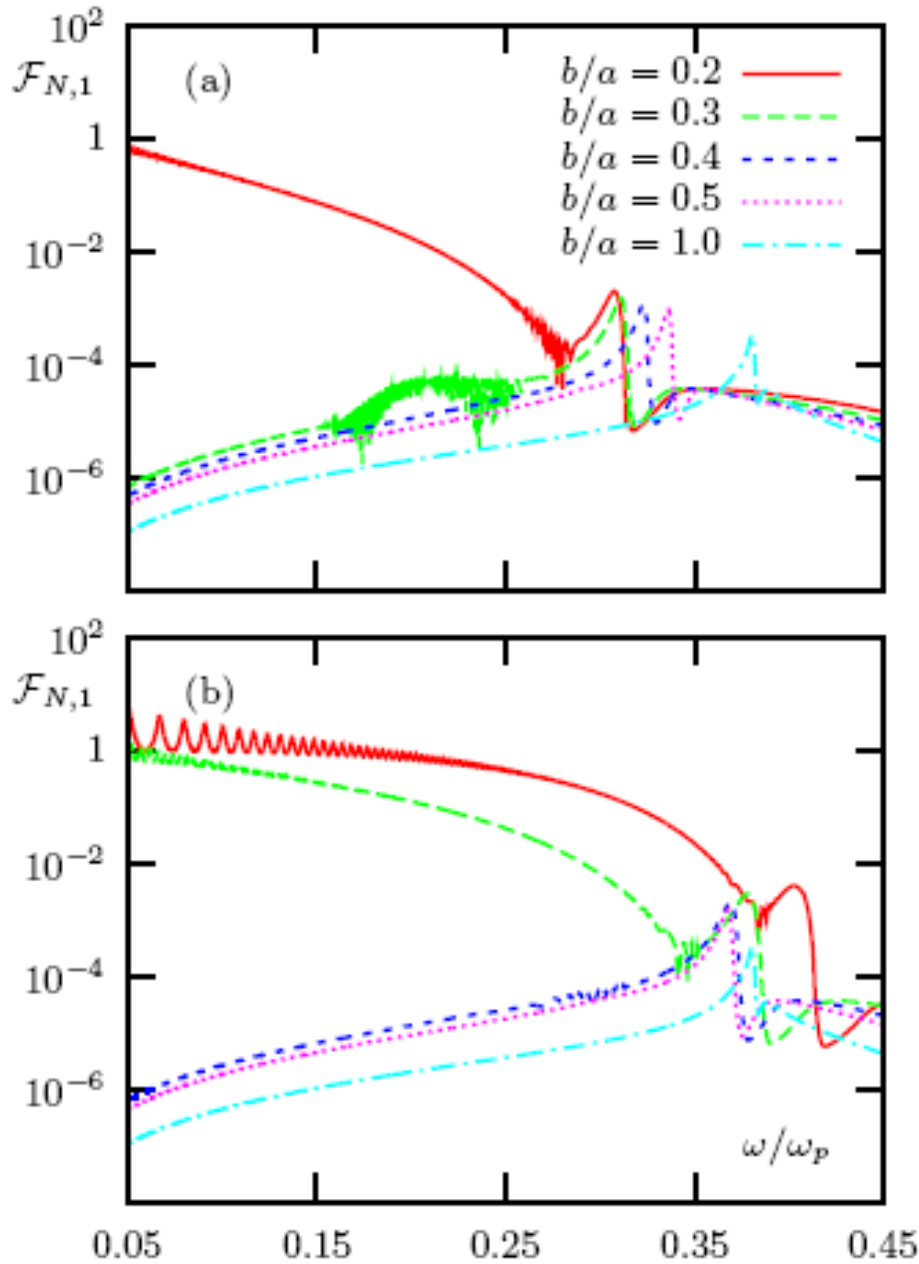
$$\Delta\omega / \omega_0 = 0.2 \text{ [same as before]}$$

(But note that special relativity is not violated. You can ask me why.)

$t = 800 \text{ fsec}$

PROLATE  
Axis of symmetry parallel  
to chain

OBLATE  
Axis of symmetry perpendicular  
to chain



$$F_{N1} = \frac{|\mathbf{d}_N|}{|\mathbf{d}_1|}$$

$$N = 1001$$

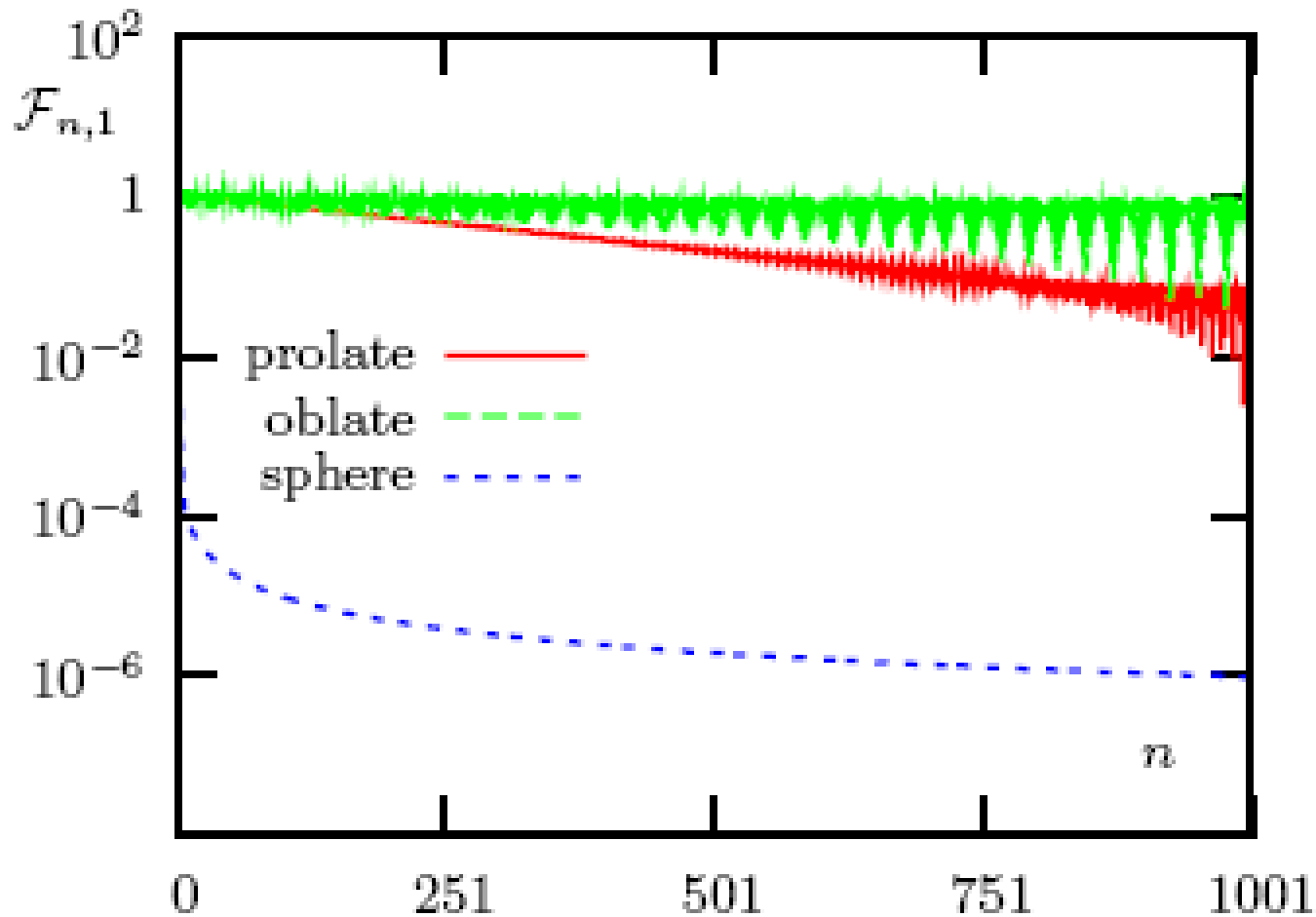
$$h = 24\text{nm}$$

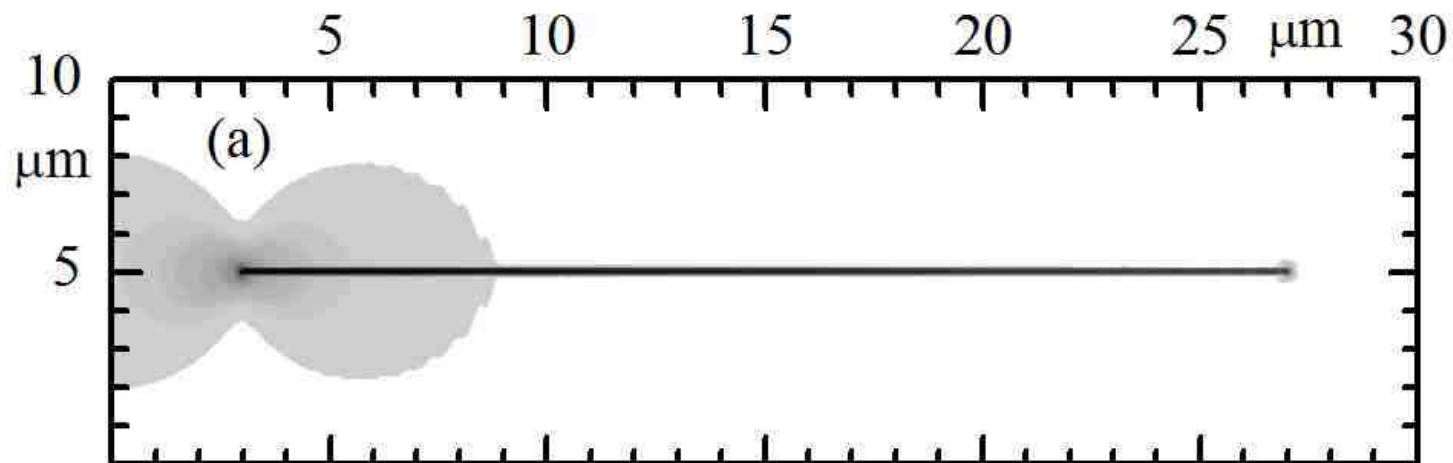
$$b = 8\text{nm}$$

$$L = 24\mu\text{m}$$

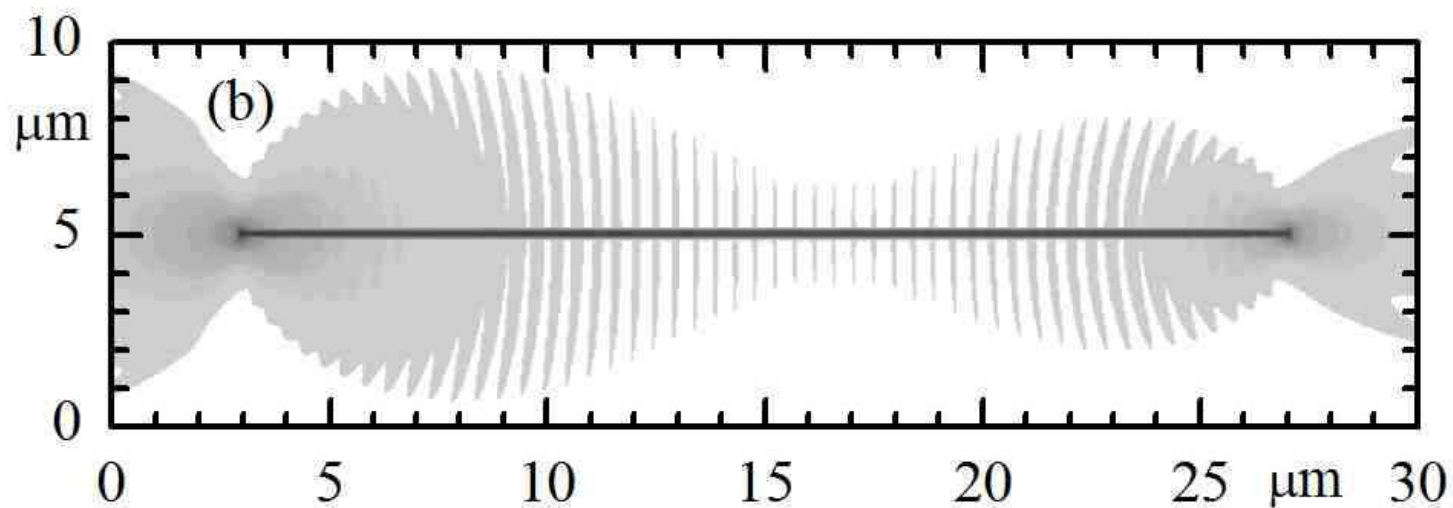


# Spheres vs Prolate and Oblate Spheroids





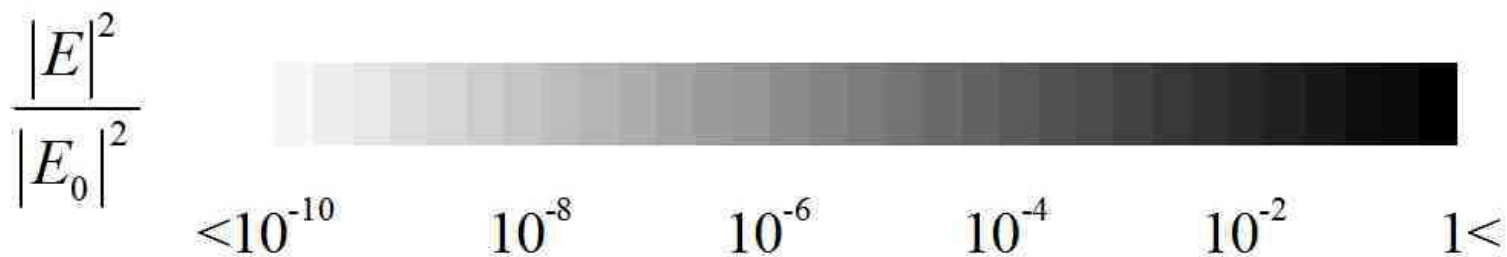
PROLATE



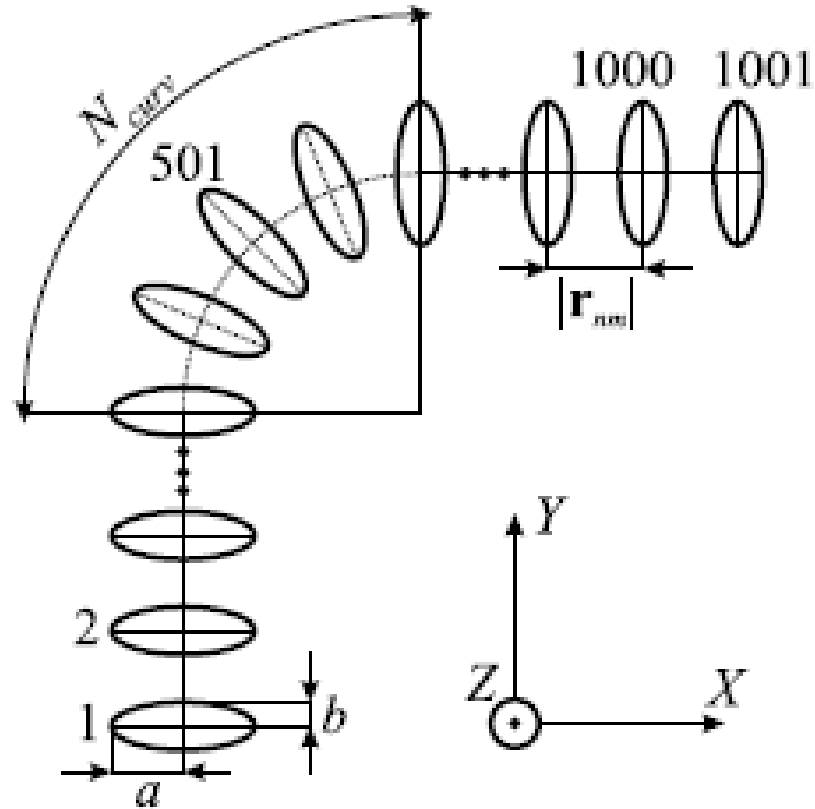
OBLATE

MAP drawn  
10nm  
above the top  
edge of particles

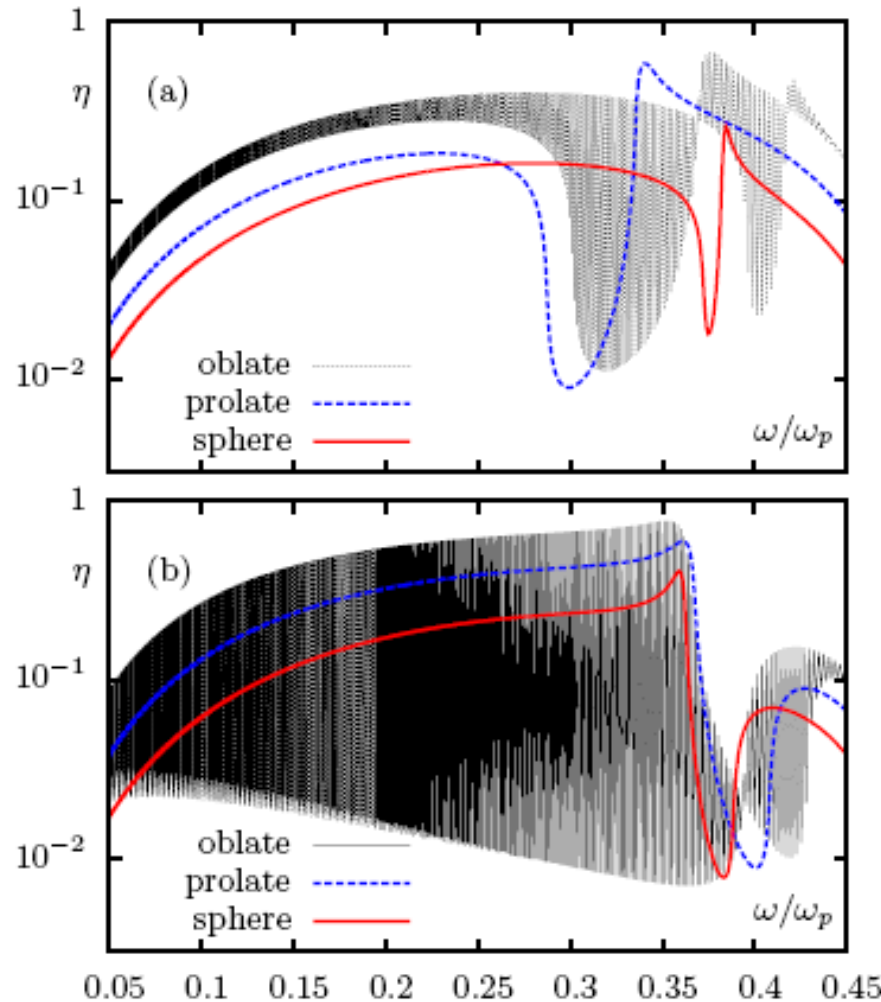
$b/a=0.2$



# 7. CURVED CHAINS



# Rective/active Impedance



$$\eta = \frac{Q_s}{Q_e}$$

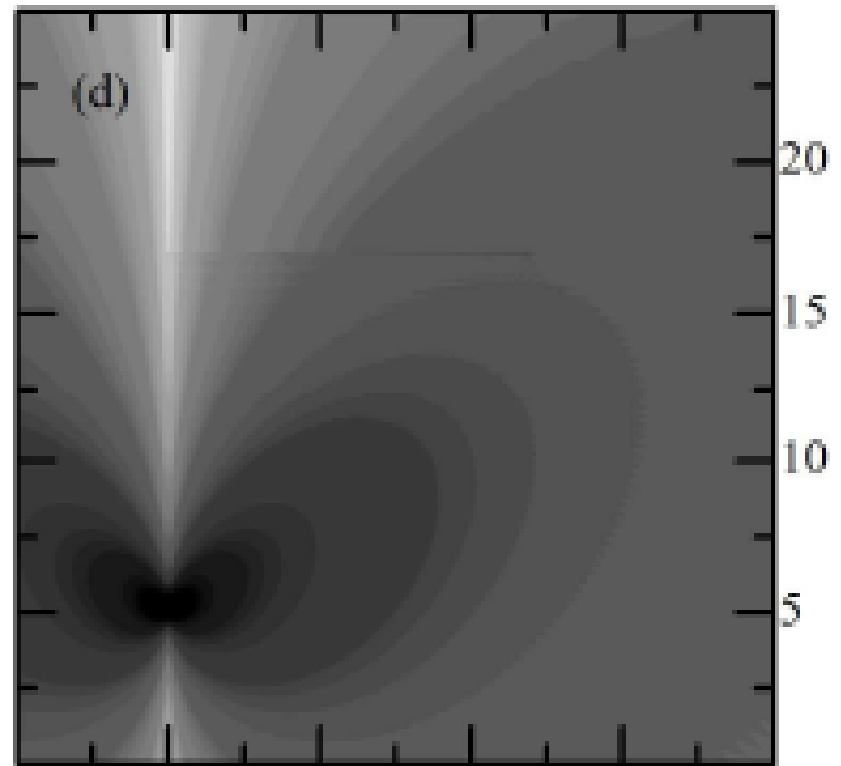
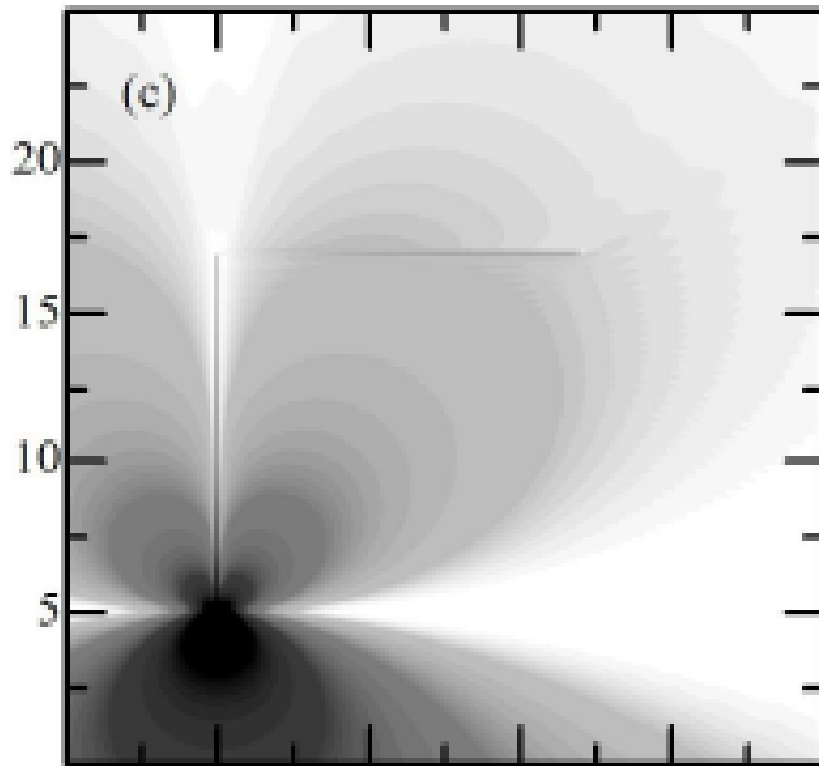
Corner

$$b/a = 0.5$$

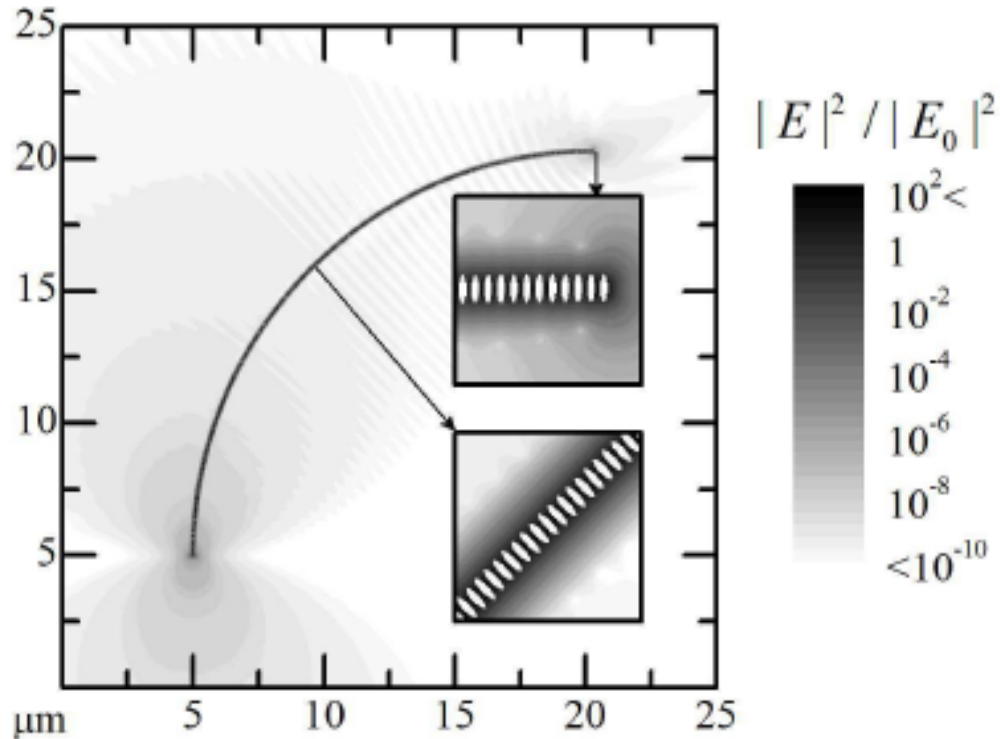
a) X-polarization

b) Y-polarization

# Prolate Spheroids Left:X, Right:Y at



# OBLATE SPHEROIDS -- LOCALIZATION



$$\eta = 10^{-3}$$

FIG. 10: Electric field distribution for quarter-circle chain of oblate nanospheroids ( $b/a = 0.3$ ) at frequency  $\omega = 0.15\omega_p$  for X polarization. Centers of nanospheroids located on plane of observation.

# CONCLUSIONS

- Plasmonic chains have promising applications in spectroscopy, sensing and waveguiding
- Theory and simulations are needed to guide the experiments and optimize design
- There is a complex interplay between the active impedance of the chain and field localization pattern.
- You can have high field localization if you are willing to heat the chain up!