Collective Optical Excitations in Nanoparticle Chains for Potential Applications in Optical Sensing and Imaging

Vadim Markel
University of Pennsylvania
Departments of Radiology and Bioengineering
Philadelphia
vmarkel@mail.med.upenn.edu
http://whale.seas.upenn.edu/vmarkel/

Potential Uses of Metal Nanoparticles

- SERS
- Biosensors
- Imaging beyond diffraction limit
- Therapy

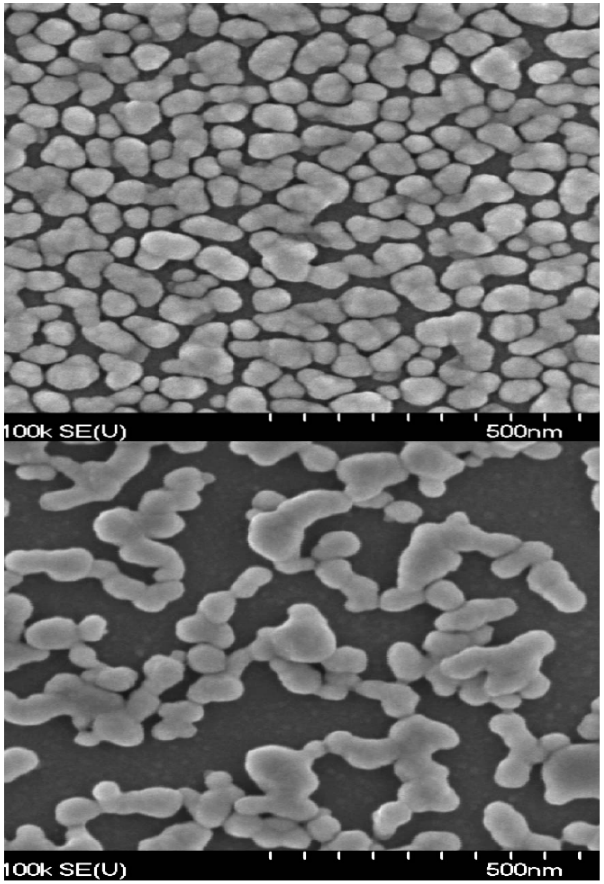


Figure 5: FE-SEM images ($1.2\mu m \times 1.2\mu m$) of AMF of 11-nm mass thickness before (top) and after protein deposition and washing inside spot (bottom).

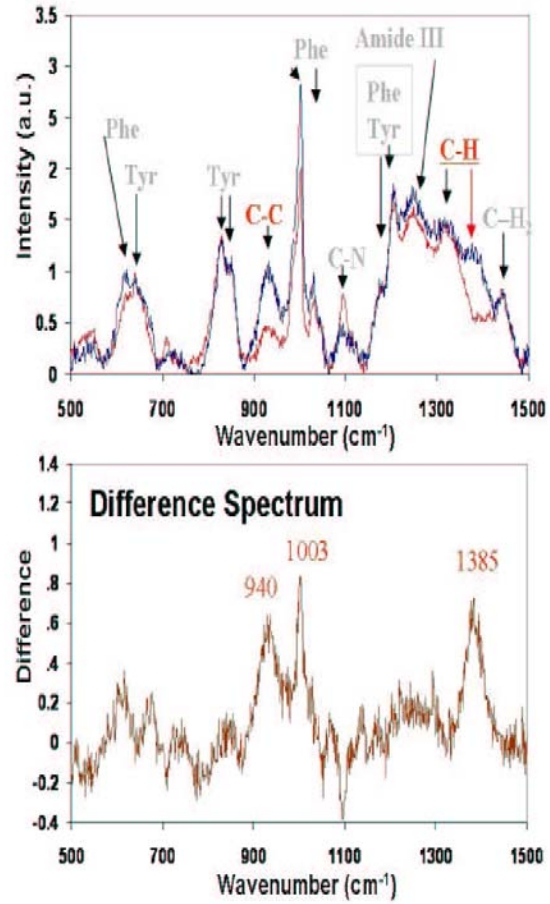


Figure 6: SERS spectra at 568nm incident laser wavelength for human insulin (blue) and insulin lispro (red) on AMF substrates. The SERS difference spectrum (insulin lispro) in the lower panel clearly shows the observed spectral differences between the two isomers.

THE ABOVE IMAGES IMAGES HAVE BEEN PUBLISHED IN:

V.P.Drachev, M.D.Thoreson, V.Nashine, E.N.Khaliullin, D.Ben-Amotz, V.J.Davisson and V.M.Shalaev, *J. Raman Spectr*., **36**, 648-656 (2005)

V.P.Drachev, M.D.Thoreson, E.N.Khaliullin, V.J.Davisson and V.M.Shalaev, *J. Phys. Chem*. **108**, 18046-18052 (2004)

(Experiments were performed in Shalaev's group, ECE, Purdue)

Why Metal Nanoparticles are Useful?

- Field Enhancement
- Field Localization

$$\alpha = \frac{V}{4\pi}\frac{1}{\frac{1}{\varepsilon - 1} + \nu} \; ; \quad 0 < \nu < 1 \quad [\nu = \frac{1}{3} \text{ for a sphere}]$$

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \;\Rightarrow\; \alpha = -\frac{V}{4\pi}\frac{\omega_p^2}{\omega^2 - \omega_F^2 + i\gamma\omega}$$

$$\omega_F = \sqrt{\nu}\,\omega_p$$

Resonance polarizability

$$\alpha_{\text{res}} = \alpha(\omega = \omega_F) = i\frac{V}{4\pi}\frac{\omega_p}{\gamma\sqrt{\nu}}$$

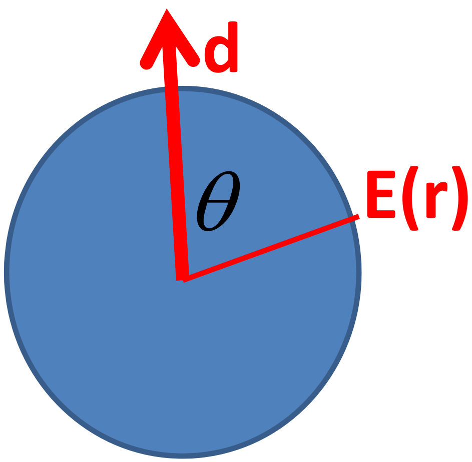
$$\omega_p/\gamma \approx 500 \quad \text{(silver)}$$

First radiative correction to the polarizability:

$$\frac{1}{\alpha} = \frac{1}{\alpha_{\text{quasistatic}}} - i\frac{2k^3}{3} \quad ; \quad [k = \frac{\omega}{c}]$$

$$\alpha = \frac{\alpha_{\text{quasistatic}}}{1 - i2k^3\alpha_{\text{quasistatic}}/3}$$

Resonance Field Enhancement Near a Sphere Surface



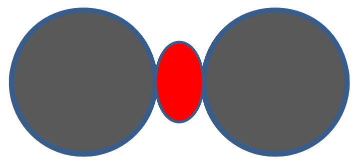
$$|\mathbf{E}_{\text{surface}}| = \frac{|\alpha|}{a^3}E_0\sqrt{1+3\cos^2\theta}$$

$$\frac{|\alpha_{\text{res}}|}{a^3} = \frac{\omega_p}{\gamma\sqrt{3}} \sim 300 \; ; \; G_{\text{SERS}} \sim \left|\frac{E_{\text{surface}}}{E_0}\right|^4$$

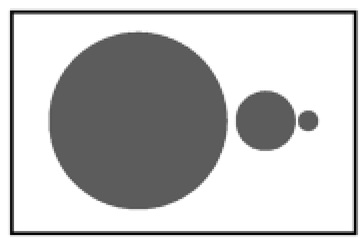
From Single to Aggregated Nanoparticles

Even stronger local field enhancements

-- Single molecule SERS in a nanojunction



-- Nanoscale focusing in a "nanolens"

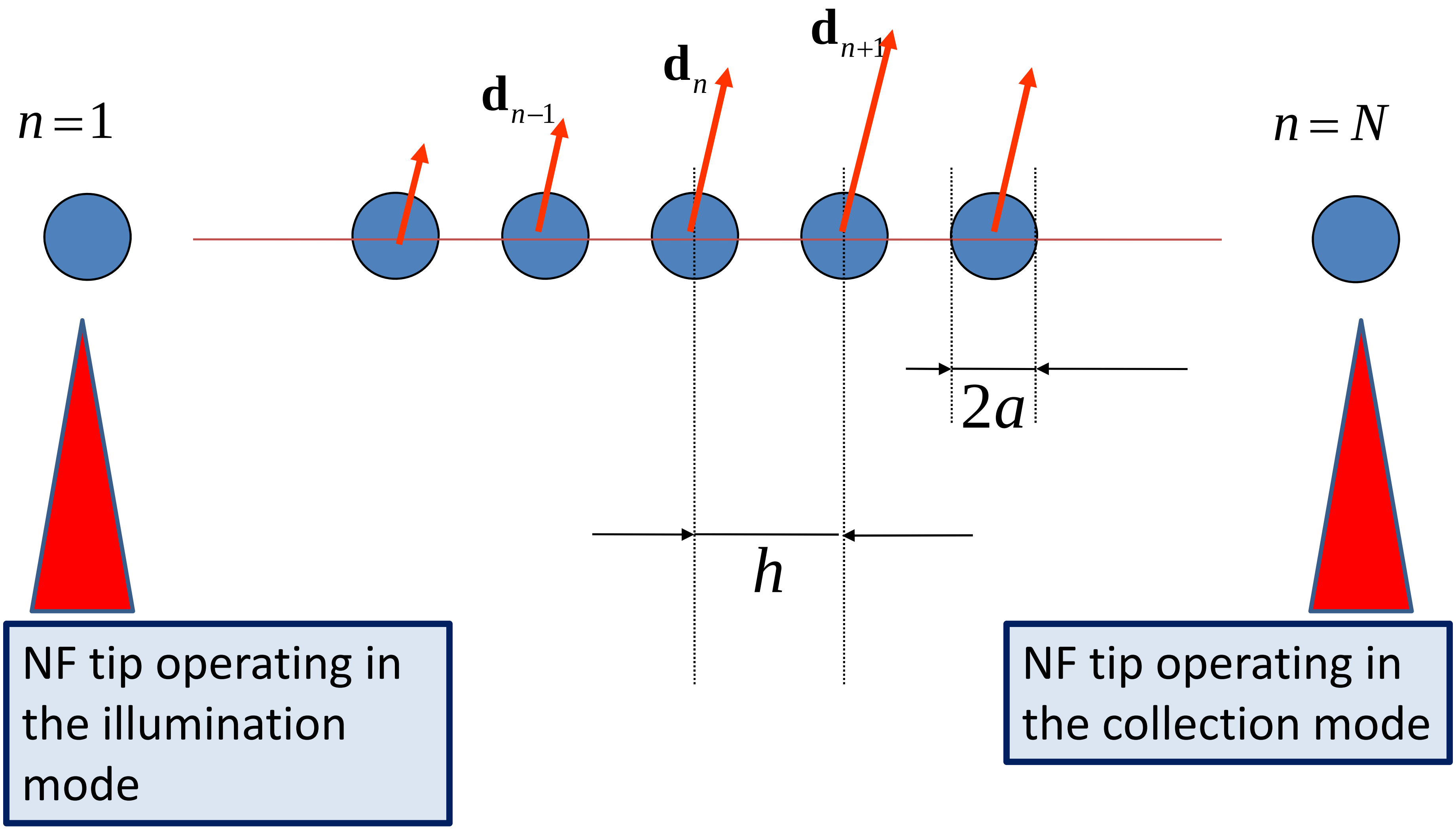


[K. Li, M.I. Stockman, D.J. Bergman, PRL **91**, 227402-1-4 (2003)]

Collective optical excitations allow even more controllability

From surface plasmons to surface polaritons
Linear chains have been lately of particular interest…

Physical Model



The Dipole Approximation

$$\mathbf{d}_n = \alpha_n \left[\mathbf{E}_n + \sum_{m \neq n} \hat{G}_k(x_n, x_m)\mathbf{d}_\mathbf{m} \right]$$

The coupled-dipole equation in the frequency domain

$k = \dfrac{\omega}{c} = \text{const}$

α_n - Polarizability of the *n*-th particle

$\hat{G}_k(x_n, x_m)$ - Green's function for the electric field in vacuum

$\mathbf{E}_n \propto \delta_{n1}$ - Electric field produced by the firsrt tip (the incidentb field)

Model for the Polarizability, α

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$ [Drude model for the dielectric function]

$$\mathrm{Re}\left(\frac{1}{\alpha}\right) = \frac{1}{a^3}\left[1 - \left(\frac{\omega}{\omega_F}\right)^2\right] \; ; \quad \mathrm{Im}\left(\frac{1}{\alpha}\right) = -i\left(\frac{2k^3}{3} + \frac{1}{a^3}\frac{\omega\gamma}{\omega_F^2}\right)$$

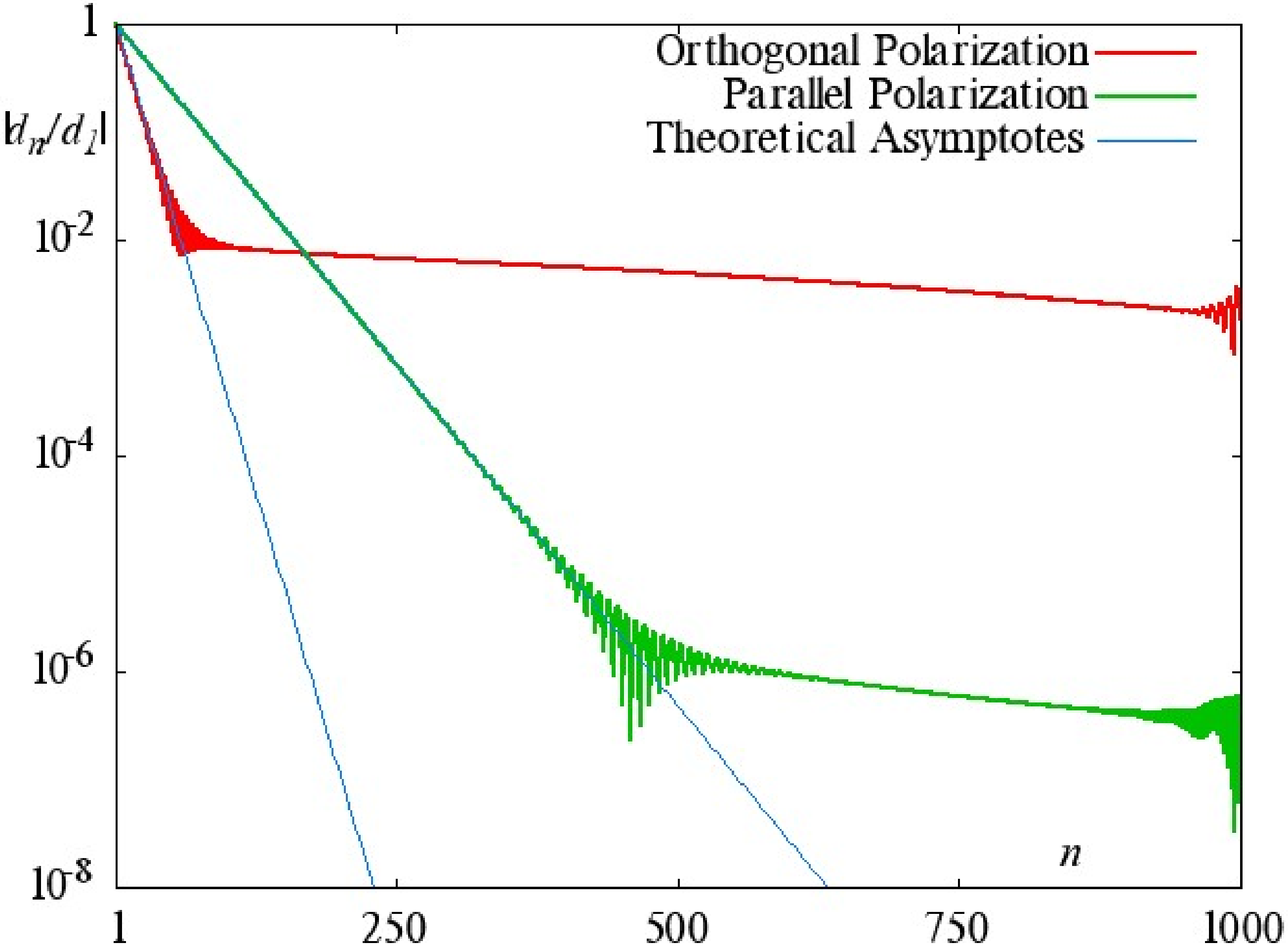
[Quasistatic approximation + first radiative correcton]

a - Nanosphere radius

$\omega_F = \omega_p/\sqrt{3}$ - Frohlich frequency

$k = \omega / c$

Simulation in a Finite Chain of *N*=1000 Identical Nanospheres



Parameters:

$\omega = \omega_F$

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

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

$h = 4a$

Analytical Solution in an Infinite Periodic Chain

$$d_n^{(\|,\perp)} = \int_{-\pi/h}^{\pi/h} \frac{E_n^{(\|,\perp)} e^{iqx_n}}{1/\alpha - S^{(\|,\perp)}(k,q)} \frac{dq}{2\pi}$$

$$S^{(\|,\perp)}(k,q) = 2\sum_{n>0} G_k^{(\|,\perp)}(0,x_n)\cos(qx_n) \quad \text{[The dipole sum]}$$

$$\text{If } q > k,\ \text{Im}[S^{(\|,\perp)}(k,q)] = -\frac{2k^3}{3}$$

The dispersion equation:

$$Z(k,q) = 1/\alpha - S^{(\|,\perp)}(k,q) = 0 \quad \Rightarrow \quad \omega = f(q)$$

The Quasi-Particle Pole Approximation

Let, for a given value of k, $Z(k,q_0) \approx 0$ and $q_0 > k$

$$Z(k,q_0) = 1/\alpha - S(k,q_0) \approx 0$$

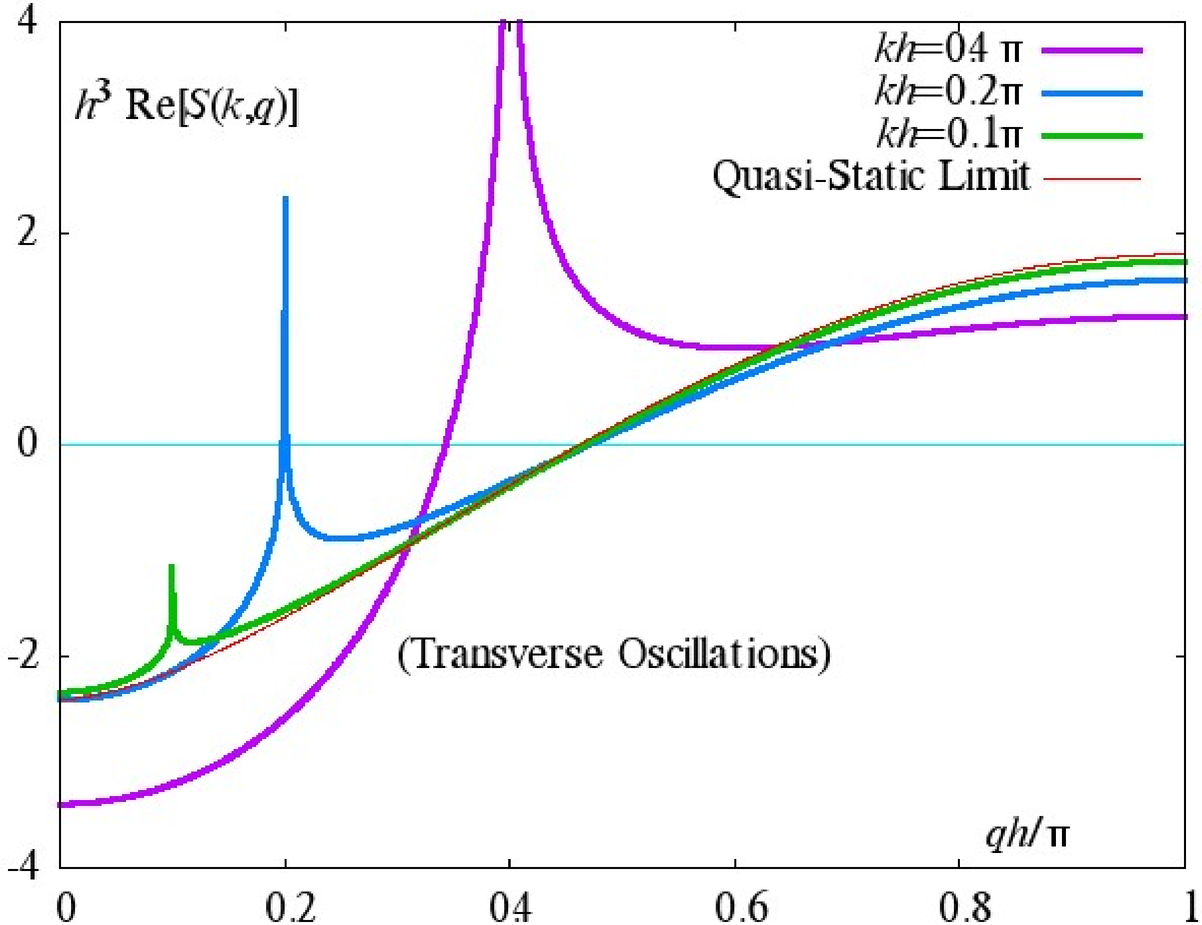
Then we write approximately:

$$S(k,q) \approx \mathrm{Re}\, S(k,q_0) + (q - q_0) \left.\frac{\partial\, \mathrm{Re}\, S(k,q)}{\partial q}\right|_{q=q_0} - i\,\frac{2k^3}{3}$$

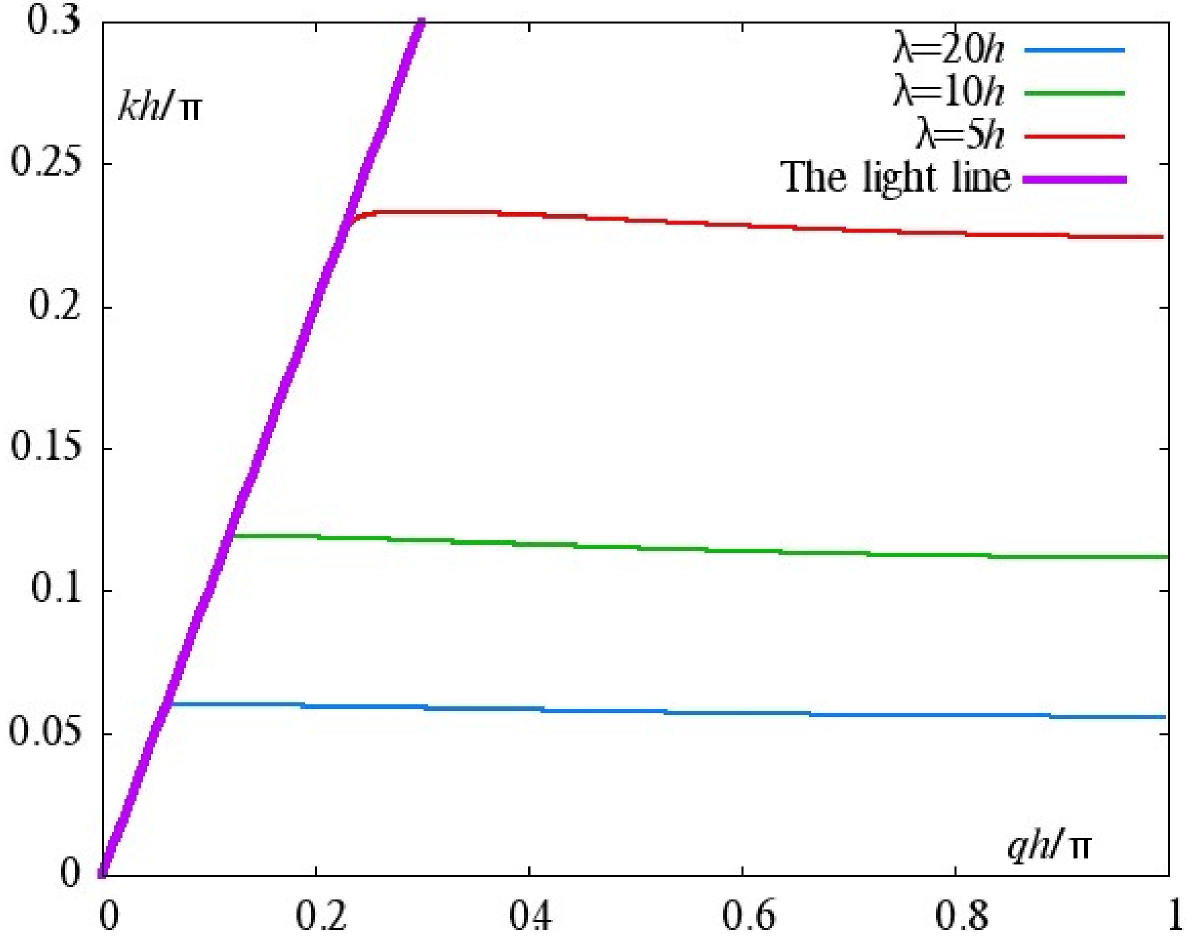
$$\ell = \frac{1}{\delta} \left|\frac{\partial\, \mathrm{Re}\, S(k,q)}{\partial q}\right|_{q=q_0}$$ [Decay length]

$$\delta = -\mathrm{Im}(1/\alpha) - 2k^3/3$$ [Absorption strength]

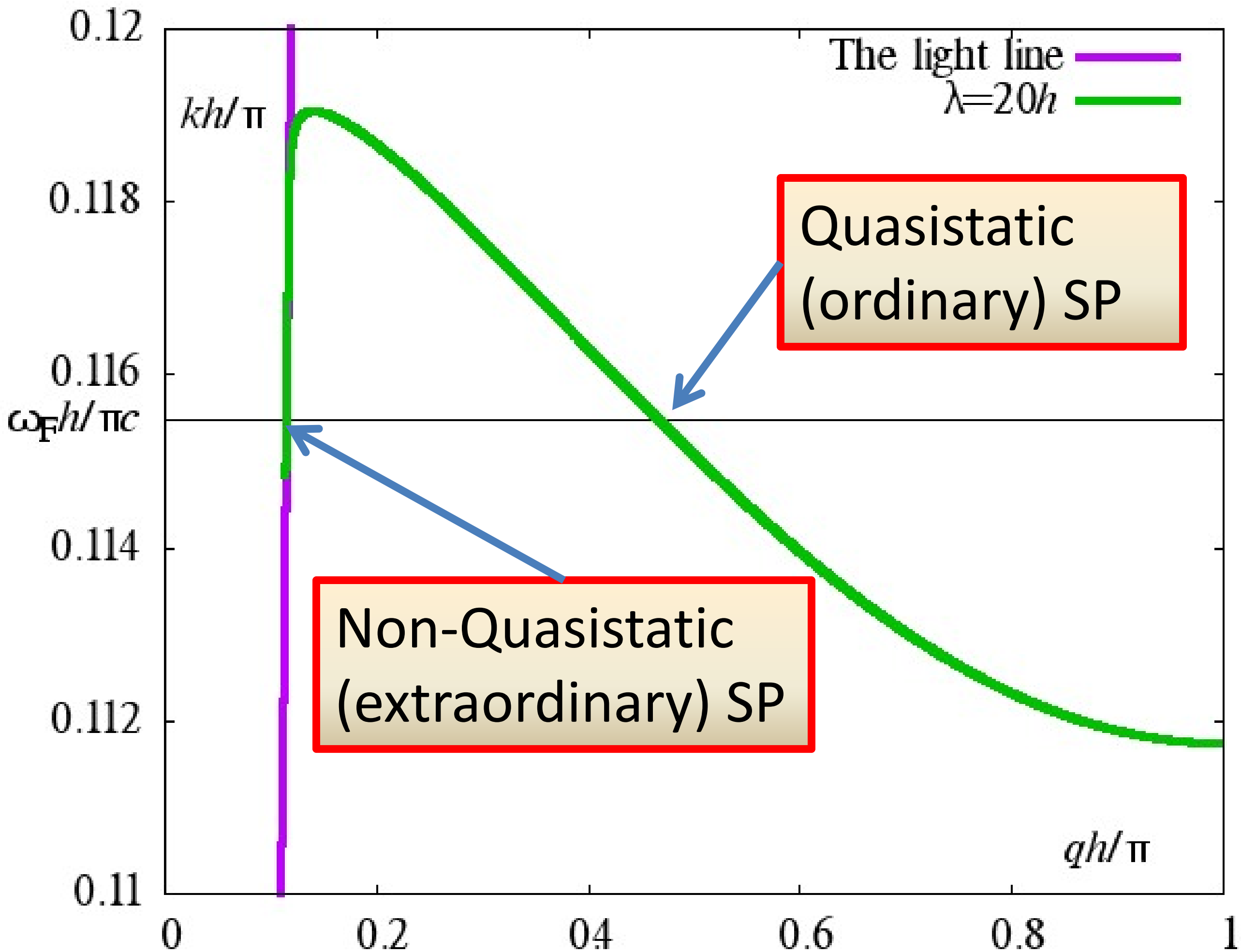
The Dipole Sum (Transverse Oscillations in an Infinite Periodic Chain



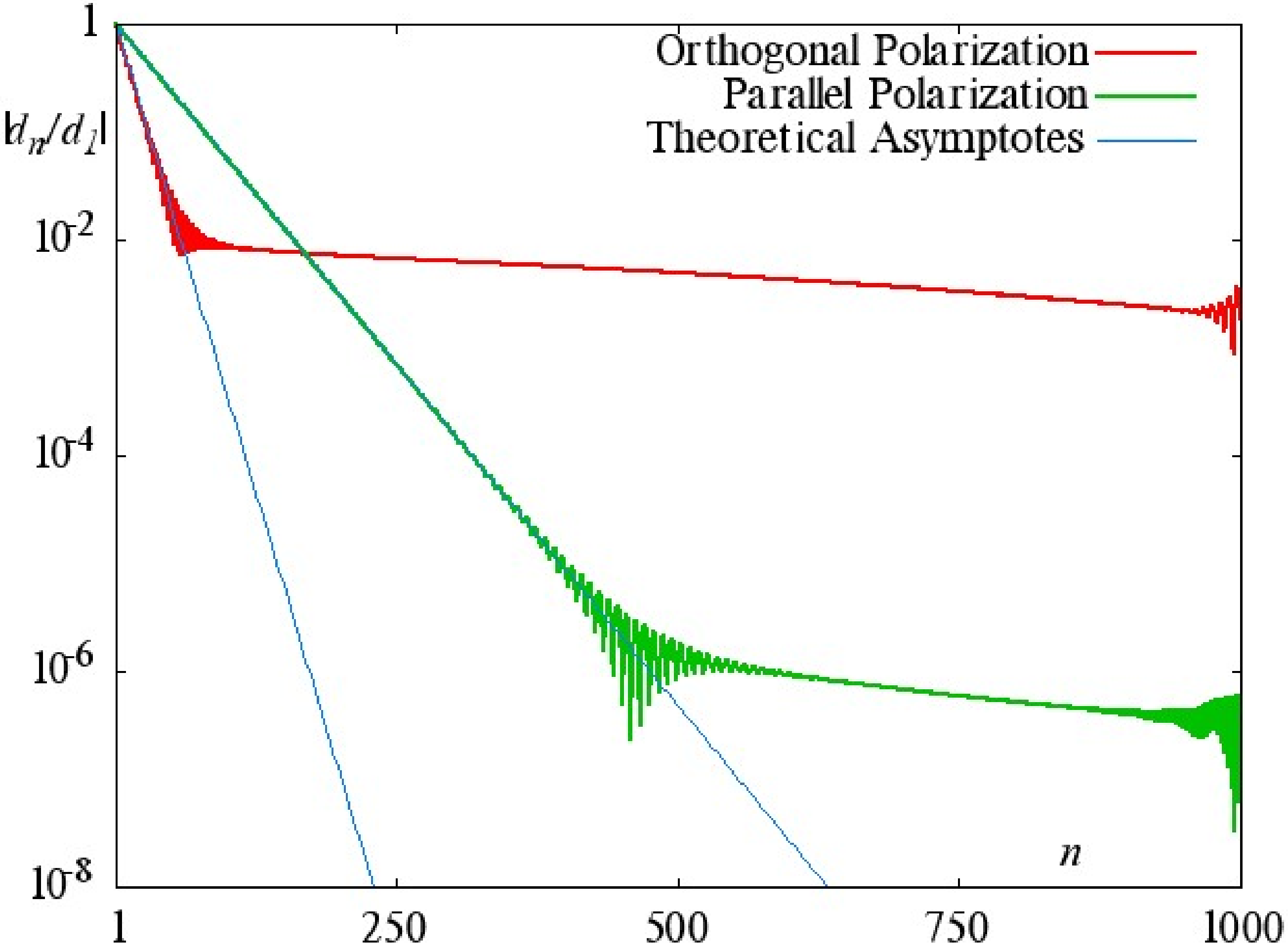
The Dispersion Curve (Transverse Oscillations in an Infinite Ordered Chain)



Dispersion Curves (continued)



Simulation in a Finite Chain of *N*=1000 Identical Nanospheres



Parameters:

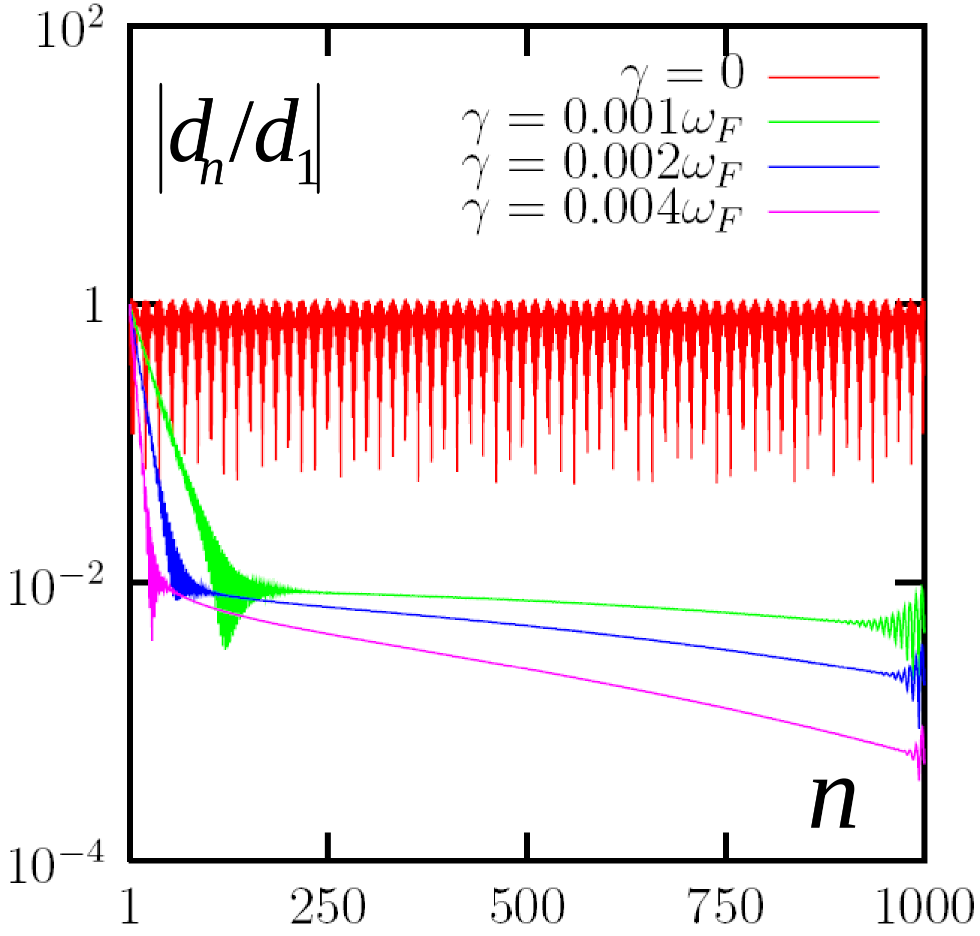
$\omega = \omega_F$

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

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

$h = 4a$

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

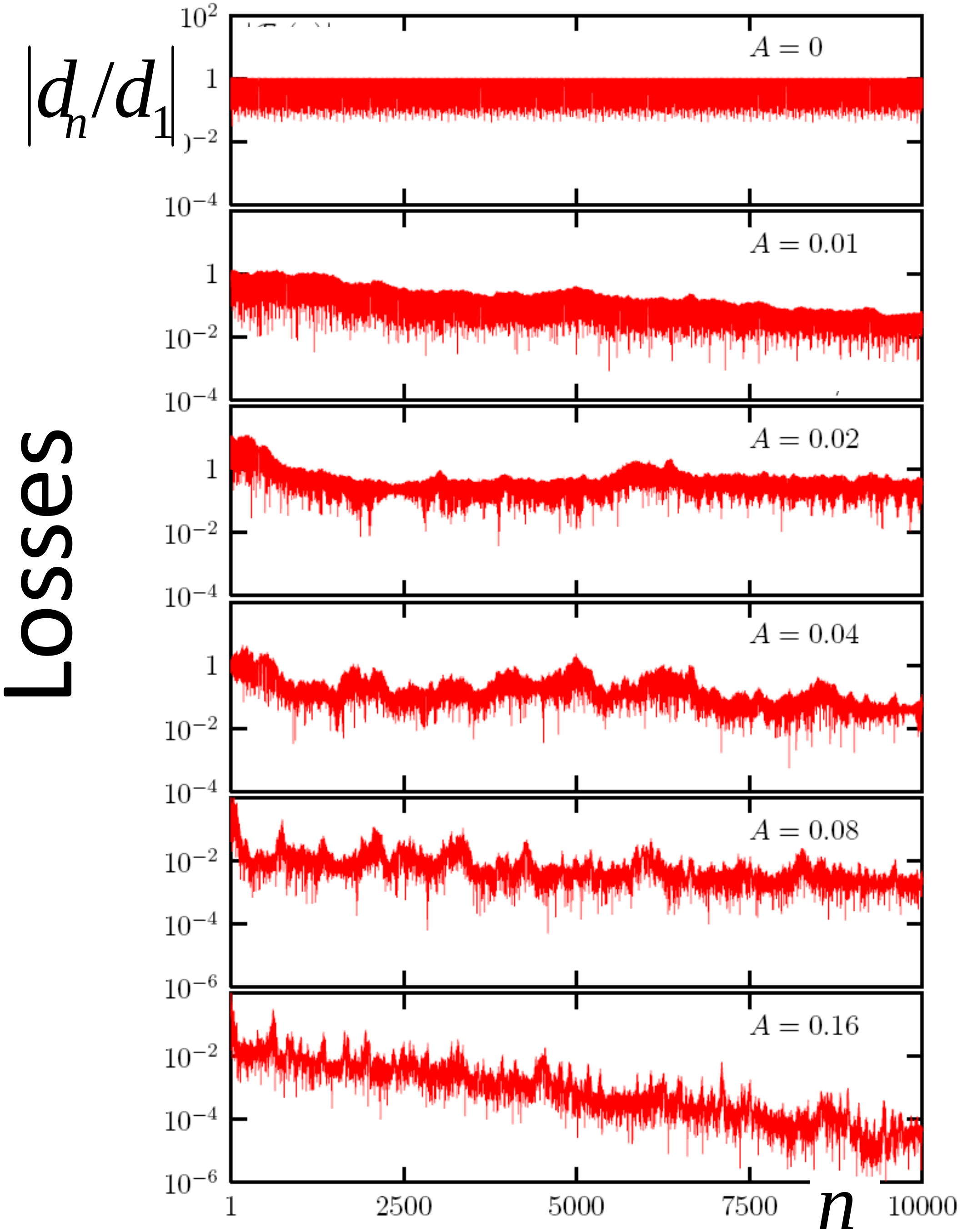
- Off-diagonal disorder (disorder in the nanoparticle positions)

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

- 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



Parameters:

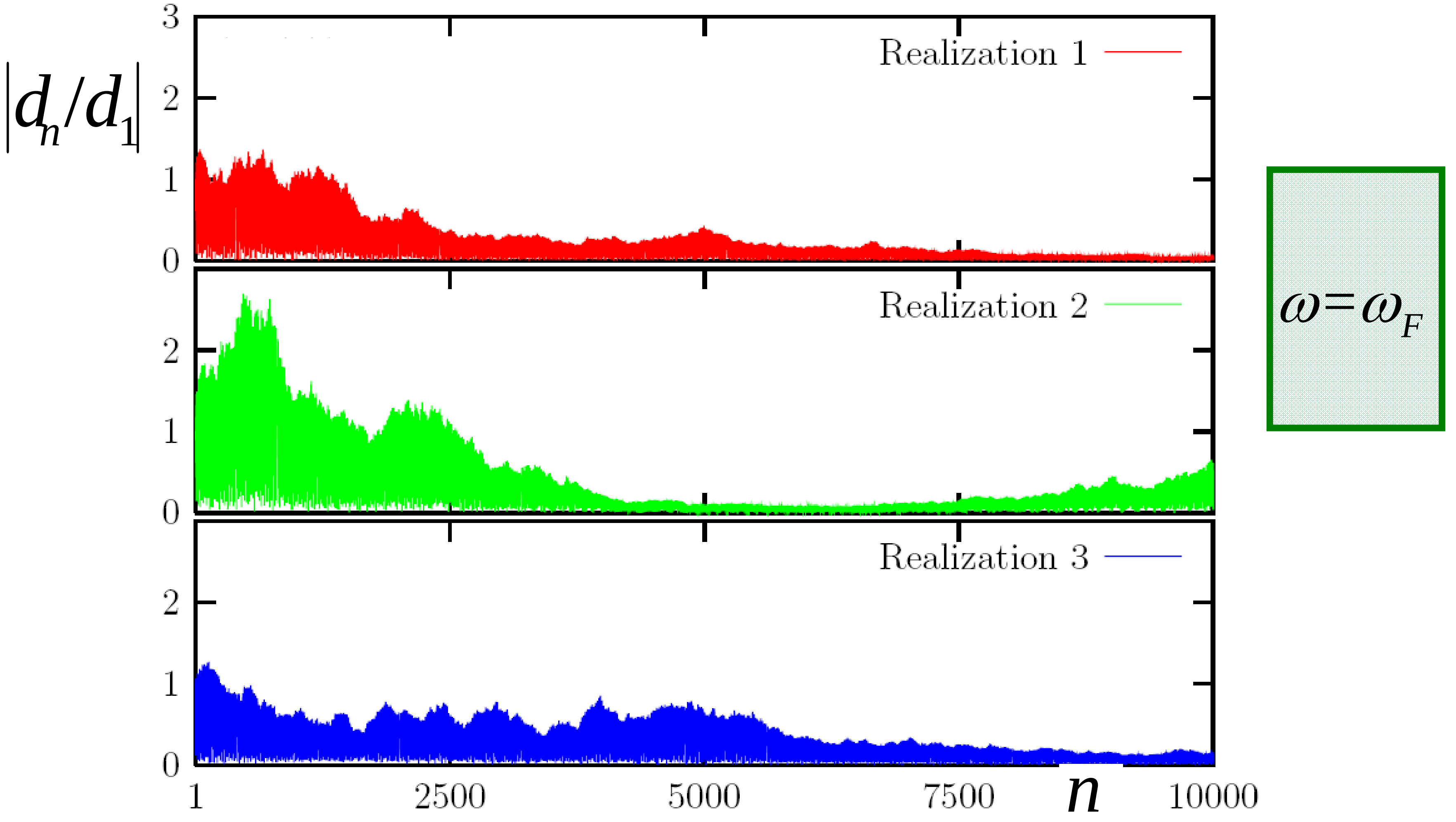
$\omega = \omega_F$

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

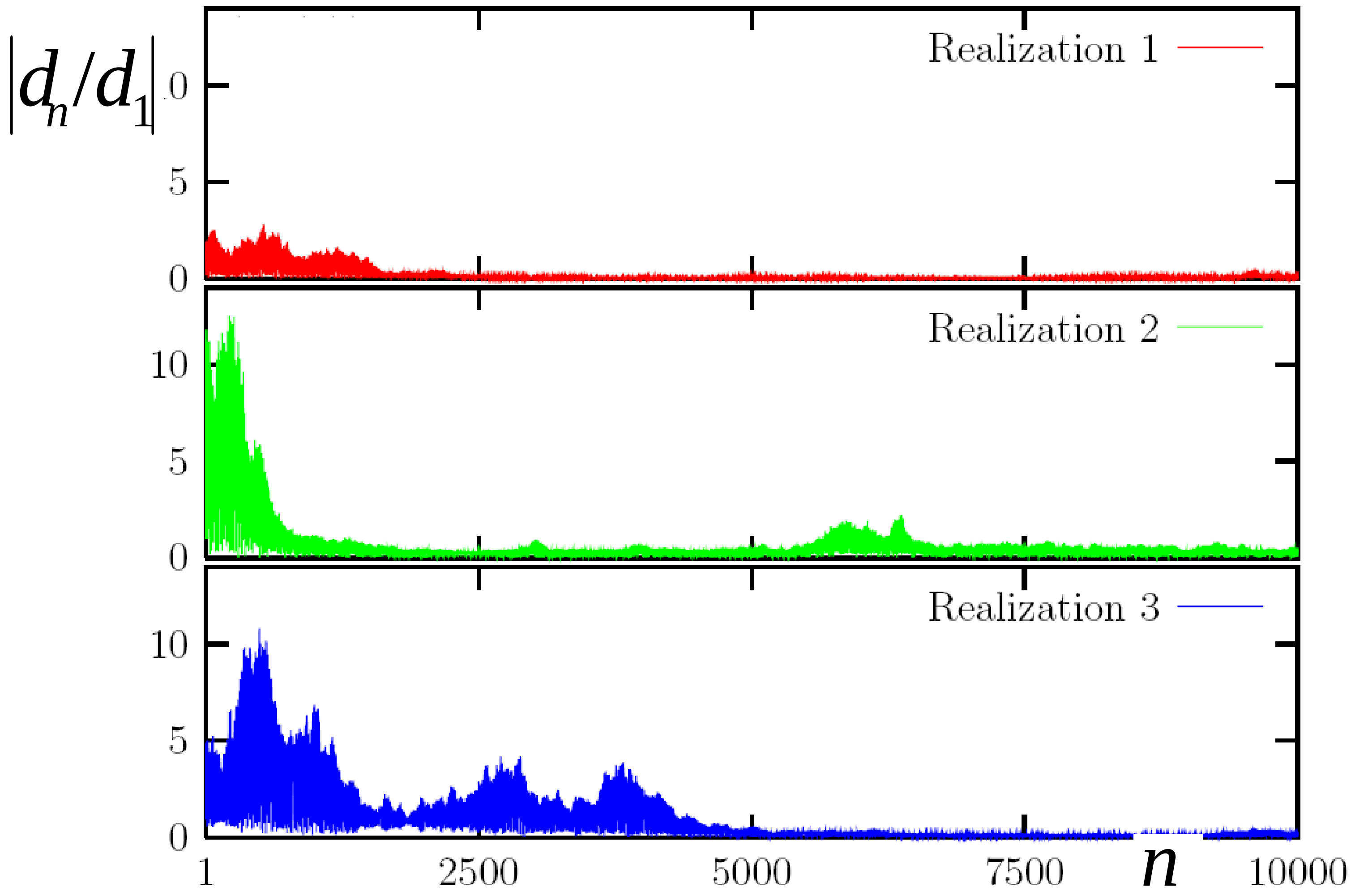
$\lambda = \frac{2\pi c}{\omega} = 10h$

$h = 4a$

Different Realization of Disorder at the Level A=0.01

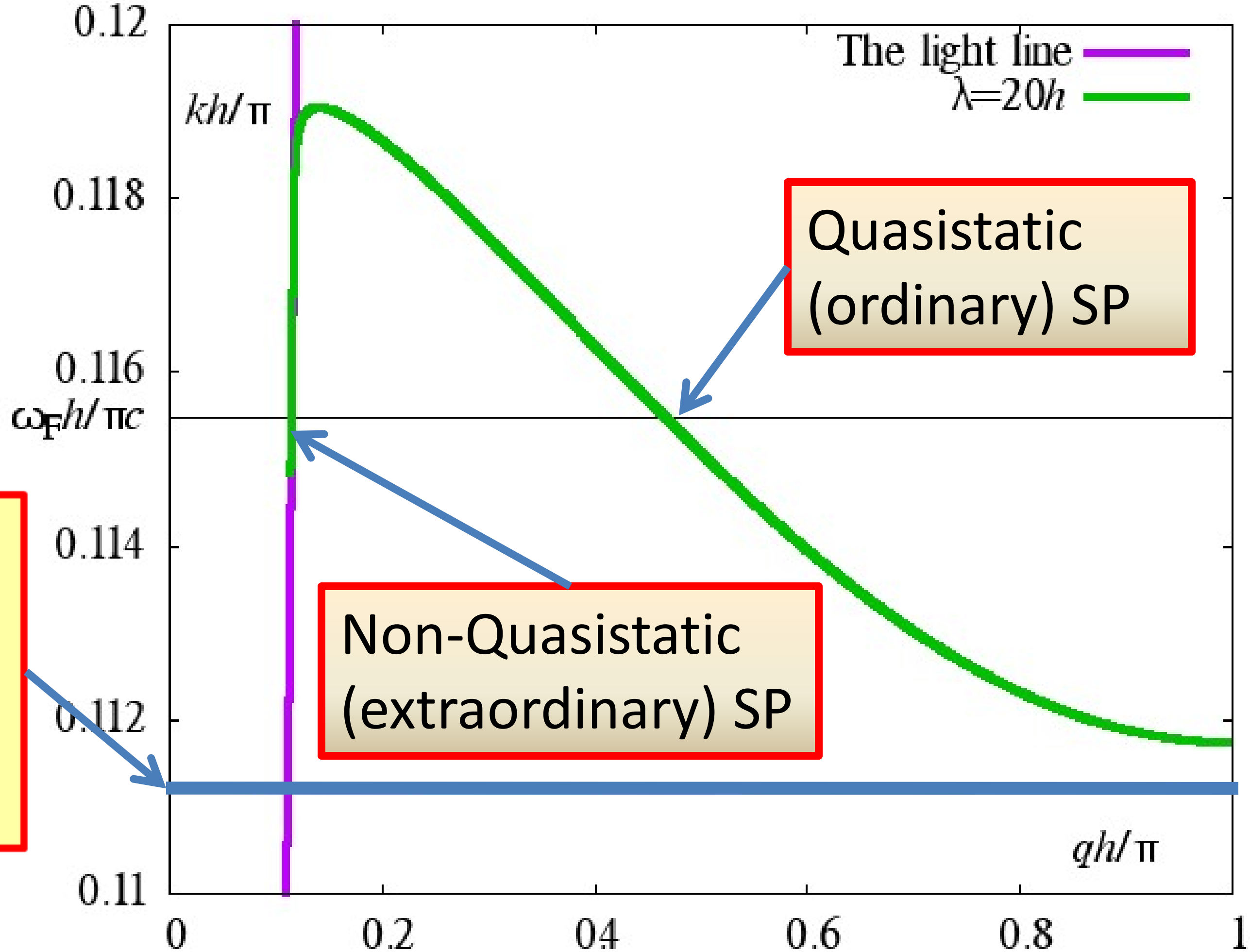


Different Realization of Disorder at the Level A=0.02



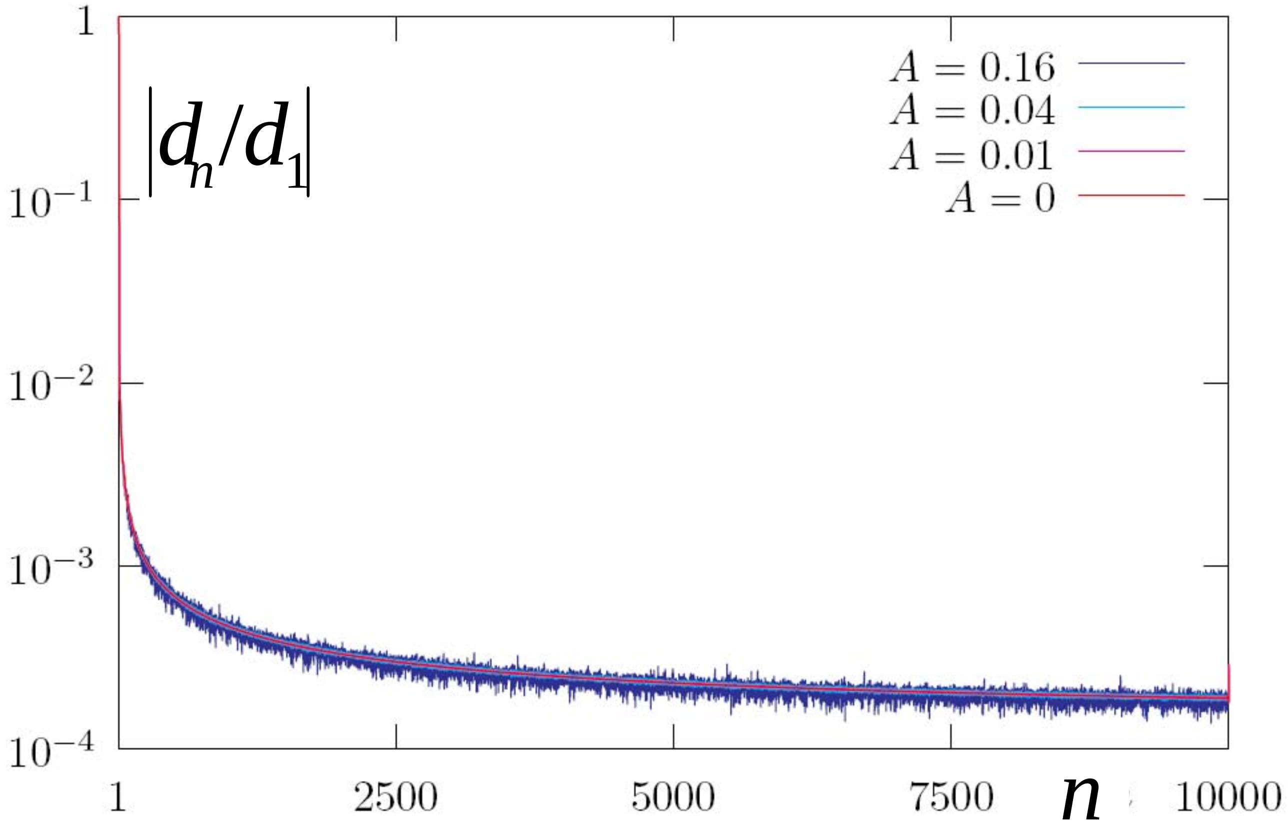
$\omega=\omega_F$

Non-Quasistatic SP at Different Levels of Disorder



Let the frequesncy be small enough so that the ordinary SP is not excited

Non-Quasistatic SP at Different Levels of Disorder (continued)

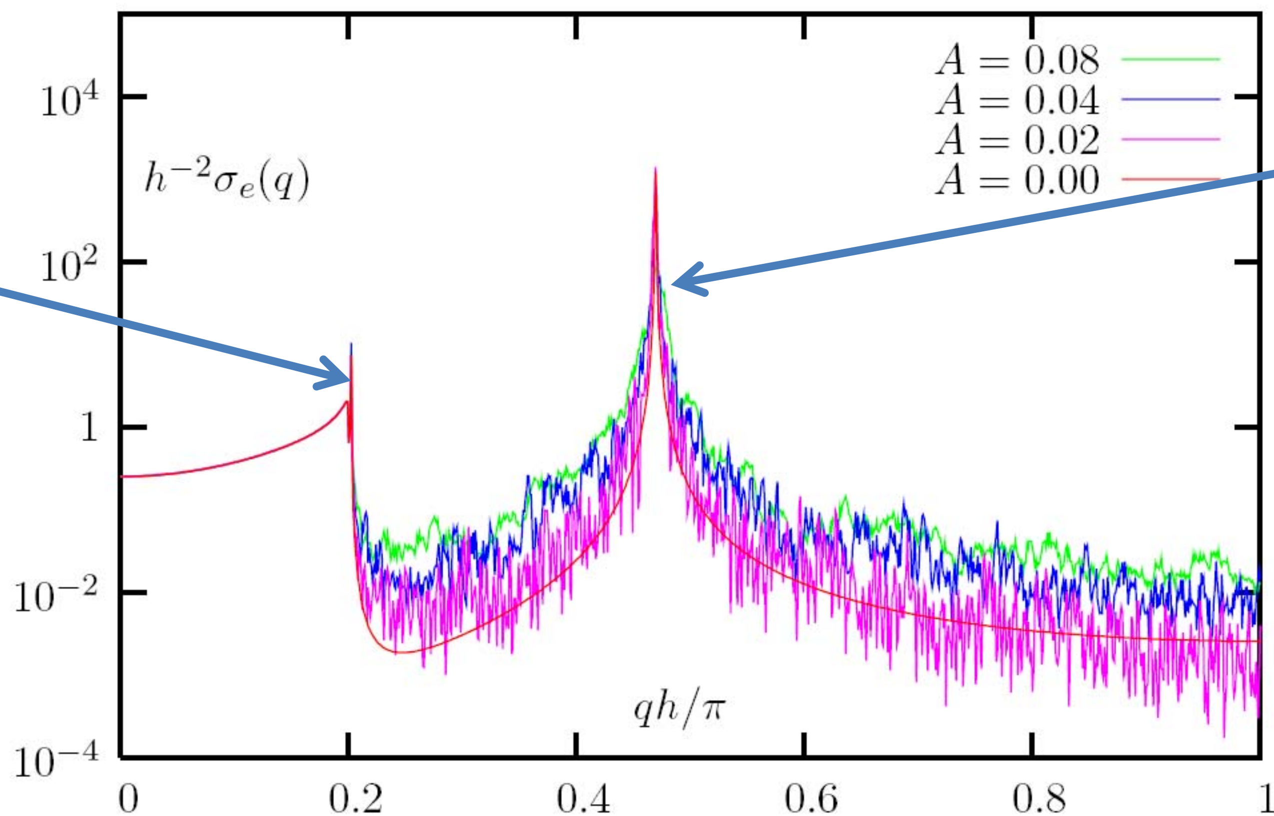


$\frac{\omega}{\omega_F}$=0.984

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

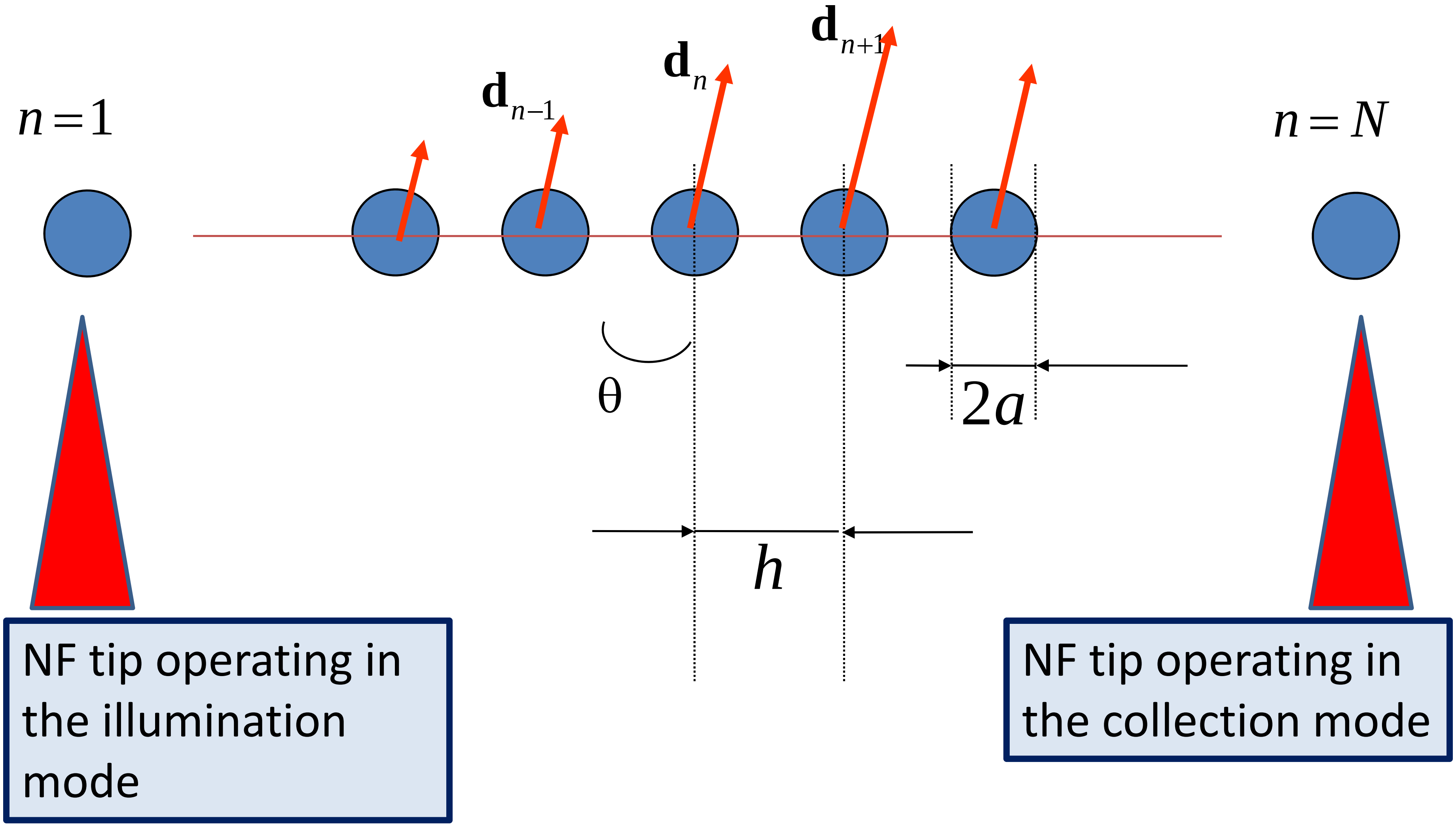
Specific Extinction for Excitation by a Plane Wave exp(*iqx*)
(e.g., created by the TIR, *q* can be larger than *k*)

Extraor-dinary (non-quasi-static) SP

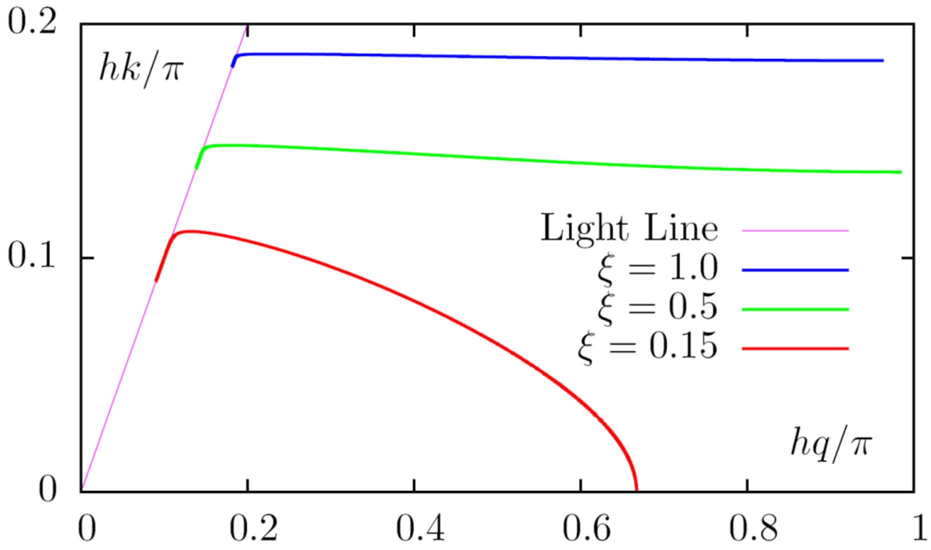


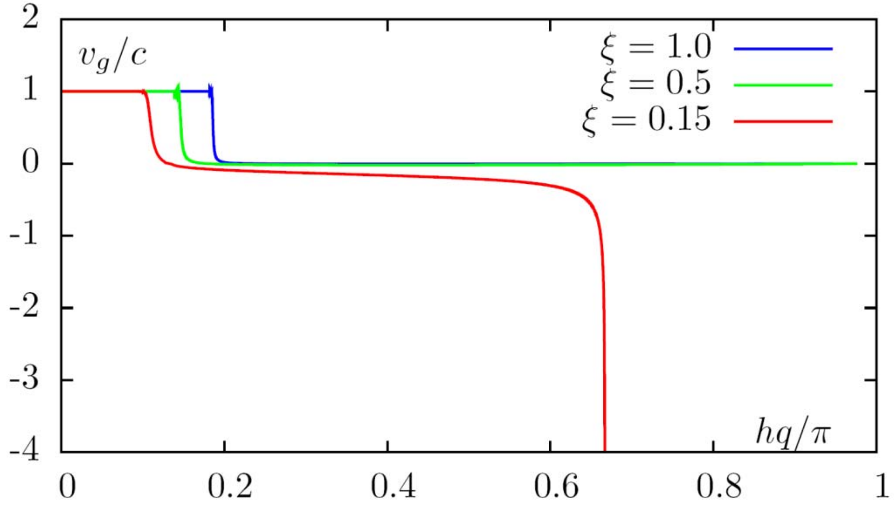
Ordinary (quasistatic) SP

II. SURFACE PLASMON POLARITONS IN CHAINS OF NANOPARICLES



Dispersion Relations and Group Velocity for Different Aspect Ratios of Nanoparticles



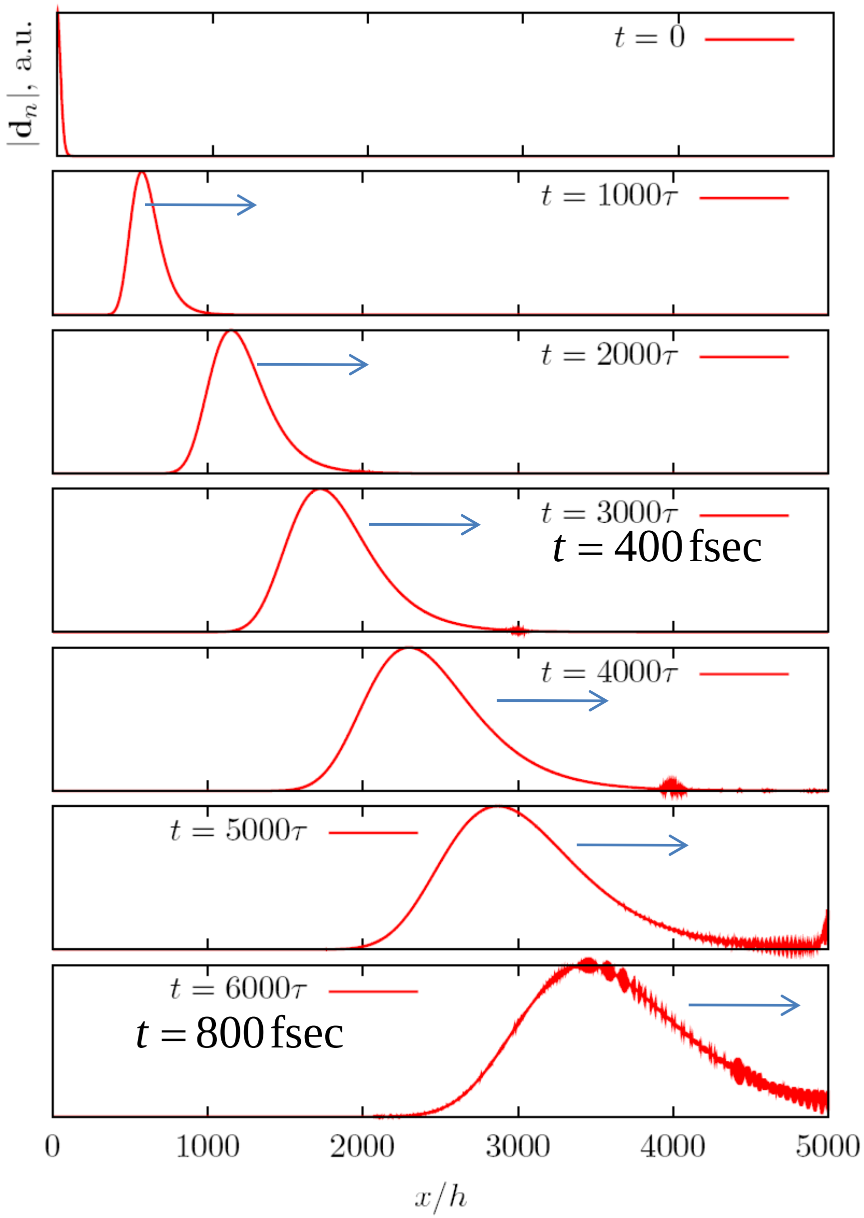


Propagation of SPP Wave Packets in Chains

$$\mathbf{E}_n(t) = \delta_{n1}\mathbf{A}\exp\left[-i\omega_0 t\right]\exp\left[-\left(\frac{t-t_0}{\Delta t}\right)^2\right]$$

$$\tilde{\mathbf{E}}_n(\omega) = \delta_{n1}\mathbf{A}\sqrt{\pi}\Delta t\exp\left[-\left(\frac{\omega-\omega_0}{\Delta\omega}\right)^2\right]$$

$$\Delta\omega = \frac{2}{\Delta t}$$



$v_g \approx 0.58c$

$x = 200\,\mu\text{m}$

Chain Parameters:

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

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

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

$N = 5000$

$\tau = \dfrac{h}{c} = 0.133\,\text{fsec}$

Metal Parameters (Ag)

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

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

$\gamma / \omega_p = 0.002$

$\varepsilon_0 = 5$

Host Medium:

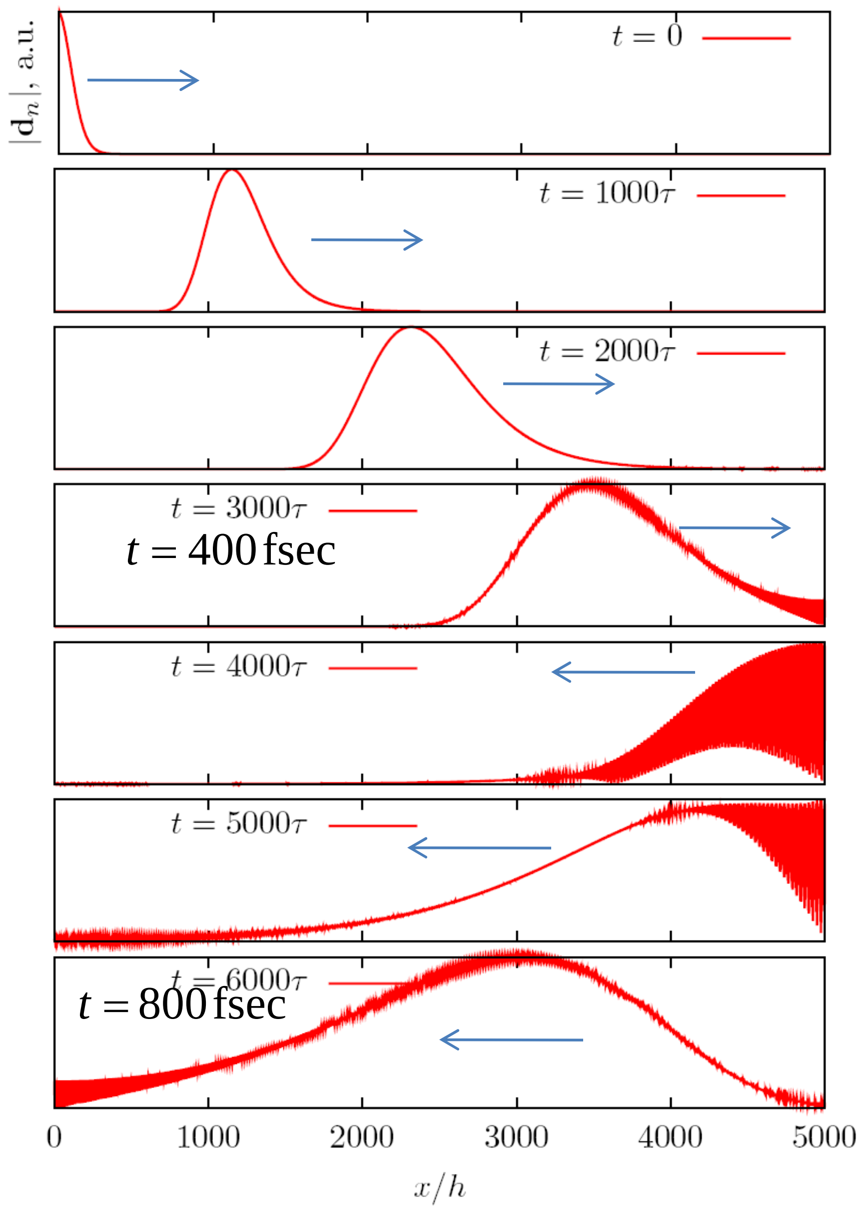
$\varepsilon_h = 2.5$

Pulse Parameters:

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

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

$\Delta\omega / \omega_0 = 0.2$



$v_g \approx 1.17c$

Pulse Parameters Different from the Previous Graph:

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

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

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

THE END

Depolarization factors

Prolate:

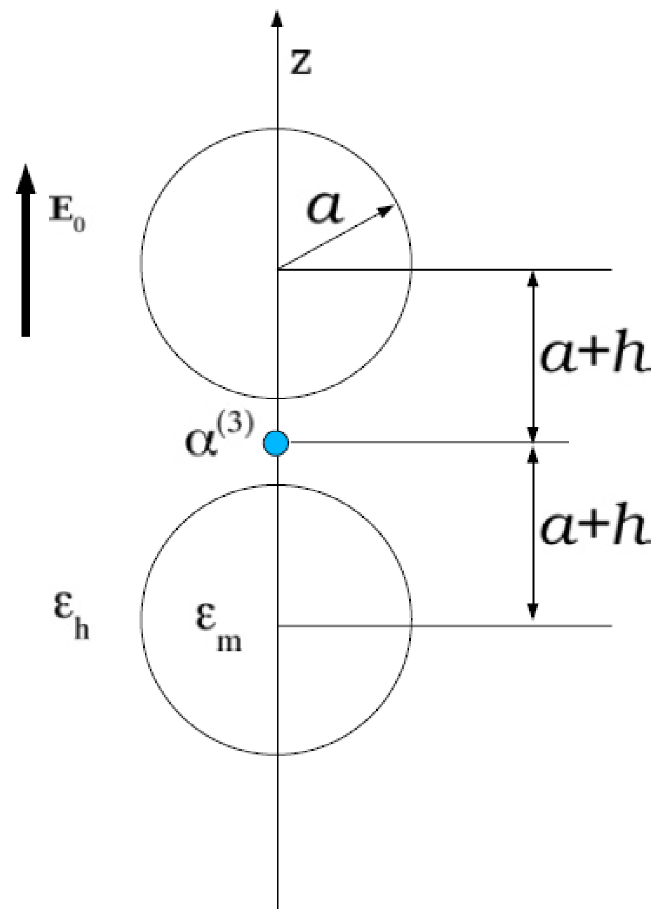
$$\nu = \frac{1-\varsigma^2}{\varsigma^2}\left[-1+\frac{1}{2\varsigma}\ln\left(\frac{1+\varsigma}{1-\varsigma}\right)\right]$$

Oblate:

$$\nu=\frac{\mathrm{g}(\varsigma)}{2\varsigma^2}\left[\frac{\pi}{2}-\mathrm{arctg}\big(\mathrm{g}(\varsigma)\big)\right]; \quad \mathrm{g}(\varsigma)=\sqrt{\frac{1-\varsigma^2}{\varsigma^2}}$$

$$\varsigma = 1-\xi^2; \quad \xi = \frac{a_<}{a_>} < 1$$

I. COHERENTLY TUNABLE THIRD-ORDER NONLINEARITY IN THE NANOJUNCTION OF TWO METAL SPHERES



$$d_z^{(NL)}(t) = \alpha^{(3)} E_z |E_z|^2 = \alpha_{\mathrm{eff}}^{(3)} E_0 |E_0|^2 \exp(-\mathrm{i}\omega t).$$

$$\alpha_{\mathrm{eff}}^{(3)} = G \alpha^{(3)}$$

$$G = \frac{E_z |E_z|^2}{E_0 |E_0|^2}$$