The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR: 1643/5

WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS IN NANOSCIENCE AND NANOTECHNOLOGY

(7 - 18 February 2005)

"Optical Properties of Plasmonic Nanosystems"- II

presented by:

M. Stockman
Georgia State University
Atlanta
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Support:

Theory of Nanoplasmonics 2: Optical Properties of Plasmonic Nanosystems

Mark I. Stockman

Department of Physics and Astronomy,
Georgia State University, Atlanta, GA
30303, USA

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

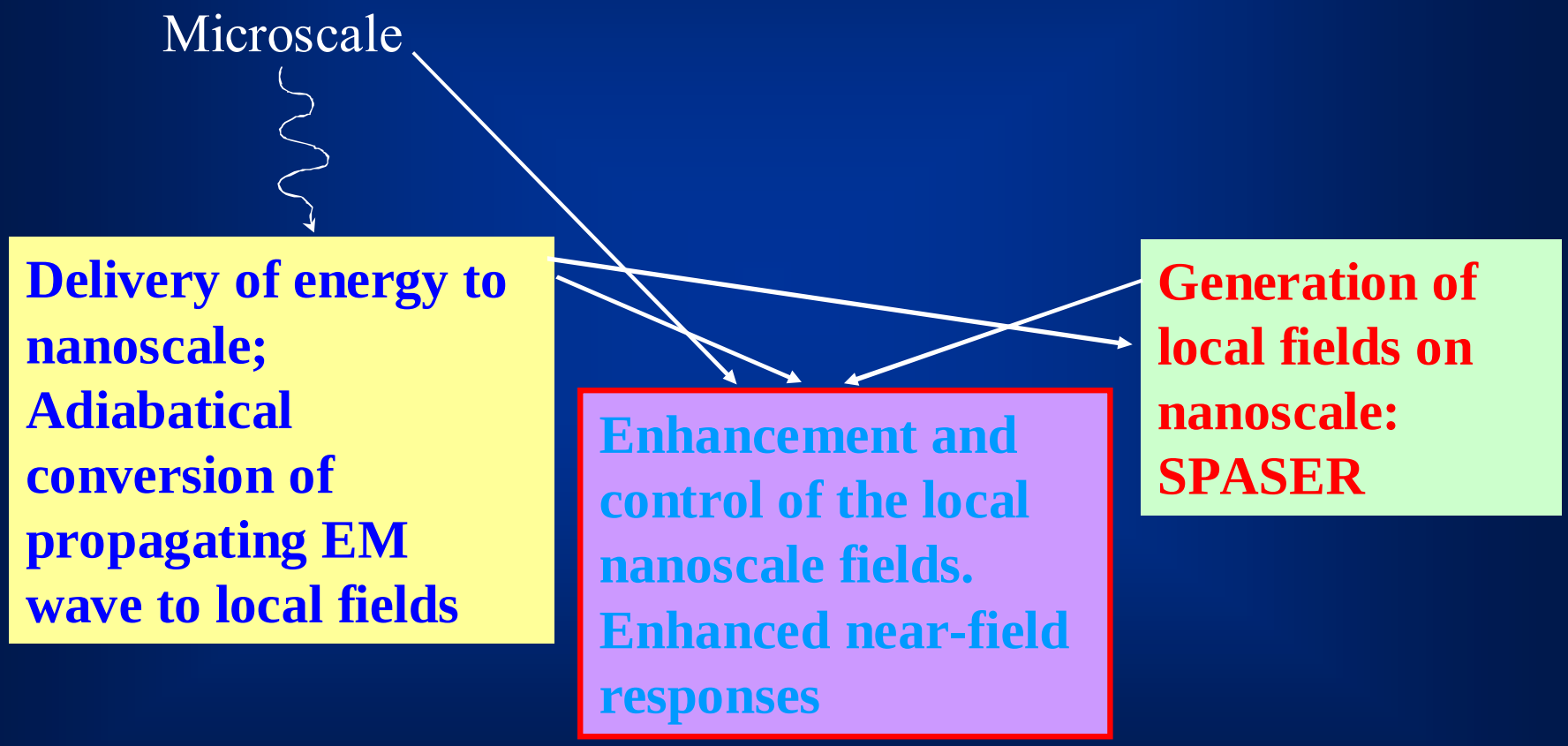
LECTURE 2

Nanoplasmonics of Nanosystems

1. Introduction; Local fields of a sphere
2. Quasistatic eigenmodes; Theorem on Anderson localization
3. Giant SERS in fractals
4. Nanospheres and their aggregates; Efficient nanolens made of nanospheres
5. Enhancement, depolarization and dephasing of SHG

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

PROBLEMS IN NANOOPTICS



Quasistatic Approximation and Eigenmodes

For a nanosystem, size is much less than the radiation wavelength. In this case, one can neglect retardation, and describe the system by quasistatic equations for electrostatic potential.

Quasistatic approximation does not imply that the excitation processes are slow. Just to the opposite, the neglectable retardation allows one to use and study ultrafast processes in nanostructures.

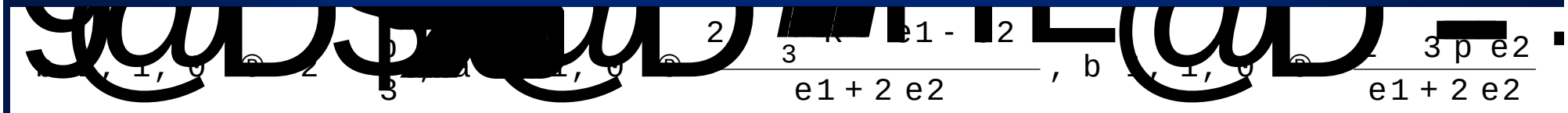
Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Example: Quasistatic fields as expansion over eigenmodes for spherical particles

Multipolar (*l*,*m*) polarizability:

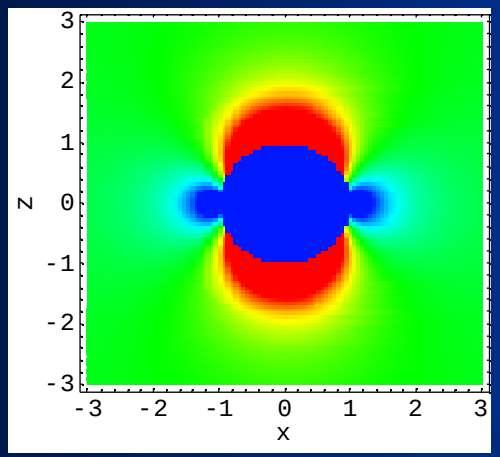
$$\frac{l\,R^{1+2l}}{e2+l}\,\frac{e1-e2}{e1+e2}$$

Coefficients of eigenmodes expansion:

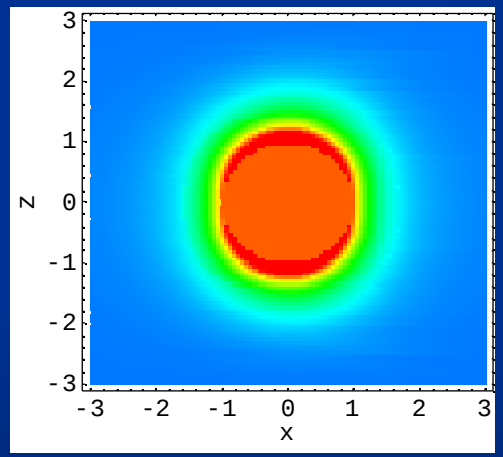


Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

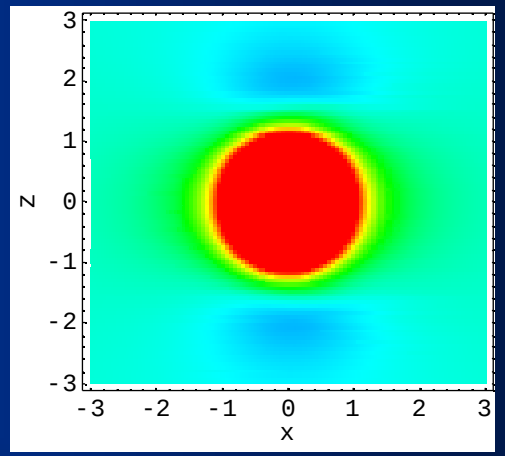
Quasistatic local field intensity for silver sphere



$\omega < \omega_{SP}$



$\omega = \omega_{SP}$



$\omega > \omega_{SP}$

We will follow the spectral theory that allows one to *separate the material and geometric properties of the system.*

1. M. I. Stockman, S. V. Faleev, and D. J. Bergman, *Anderson Localization vs. Delocalization of Surface Plasmons in Nanosystems: Can One State Have Both Characteristics Simultaneously?*, Phys. Rev. Lett. **87**, 167401-1-4 (2001).
2. M. I. Stockman, D. J. Bergman, and T. Kobayashi, *Coherent Control of Nanoscale Localization of Ultrafast Optical Excitation in Nanosystems*, Phys. Rev. B. **69**, 054202-1-10 (2004).

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Quasistatic field equations and boundary conditions

$$\frac{\partial}{\partial \mathbf{r}} \varepsilon(\mathbf{r},\omega) \frac{\partial}{\partial \mathbf{r}} \varphi(\mathbf{r}) = 0\,, \quad \varphi(x,y,0) = 0\,, \quad \varphi(x,y,L_z) = 1\,,$$

$$\left.\frac{\partial}{\partial x}\varphi(x,y,z)\right|_{x=0,L_x} = \left.\frac{\partial}{\partial y}\varphi(x,y,z)\right|_{y=0,L_y} = 0\,.$$

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Eigenmode problem (depending only on geometry, material independent!)

$$\frac{\partial}{\partial \mathbf{r}}\theta(\mathbf{r})\frac{\partial}{\partial \mathbf{r}}\varphi_n(\mathbf{r}) = s_n \frac{\partial^2}{\partial \mathbf{r}^2}\varphi_n(\mathbf{r}),$$

where $\theta(\mathbf{r} \in \text{inclusion}) = 1$ and $\theta(\mathbf{r} \in \text{host}) = 0$;

$$\varphi_n(x, y, 0) = \varphi_n(x, y, L_z) = 0,$$

and

$$\left.\frac{\partial}{\partial x}\varphi_n(x, y, z)\right|_{x=0,L_x} = \left.\frac{\partial}{\partial y}\varphi_n(x, y, z)\right|_{y=0,L_y} = 0.$$

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Physical surface plasmons are elementary excitation whose complex frequency can be found from an equation $s(\omega_n + i\gamma_n) = s_n$,

where the spectral parameter $s(\omega) = \left(1 - \frac{\varepsilon_{\text{metal}}(\omega)}{\varepsilon_{\text{host}}(\omega)}\right)^{-1}$

Green's function as an eigenmode expansion:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{s_n}{s(\omega) - s_n} \varphi_n(\mathbf{r}) \varphi_n^*(\mathbf{r}')$$

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Local fields on nanoscale for harmonic excitation with external field $\varphi_0(\mathbf{r})$ at frequency ω:

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) - \int \varphi_0(\mathbf{r}')\nabla^2_{\mathbf{r}'} G(\mathbf{r},\mathbf{r}';\omega)\, d^3r',$$

Local fields on nanoscale for short-pulse excitation with pulse field $\varphi_0(\mathbf{r},t)$

$$\varphi(\mathbf{r},t) = \varphi_0(\mathbf{r},t) -$$
$$\int \varphi_0(\mathbf{r}',t')\nabla^2_{\mathbf{r}'} G(\mathbf{r},\mathbf{r}';t-t')\, d^3r'\, dt',$$

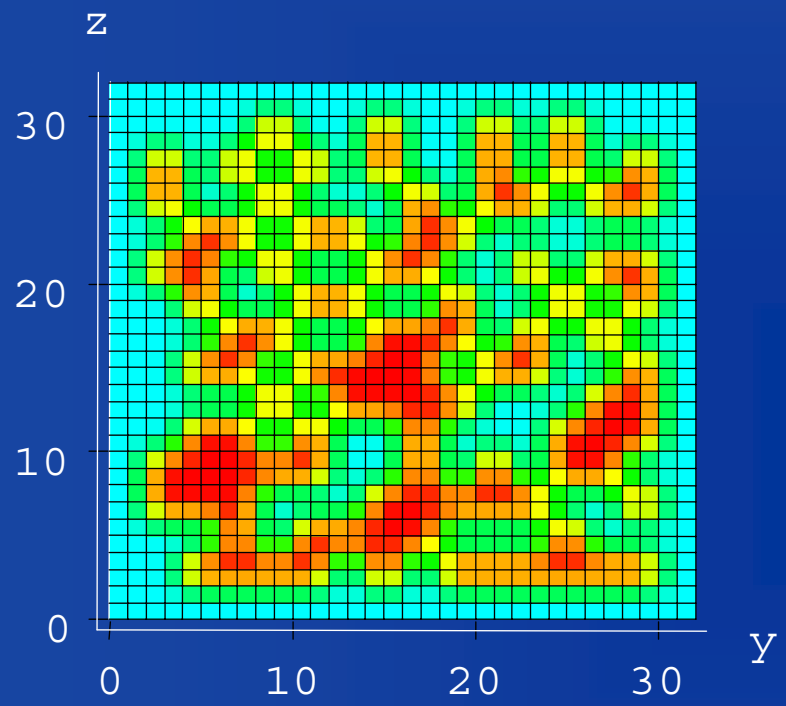
Theorem on Localization of Surface Plasmons:

Any Anderson-localized (or, strongly localized) mode is dark.

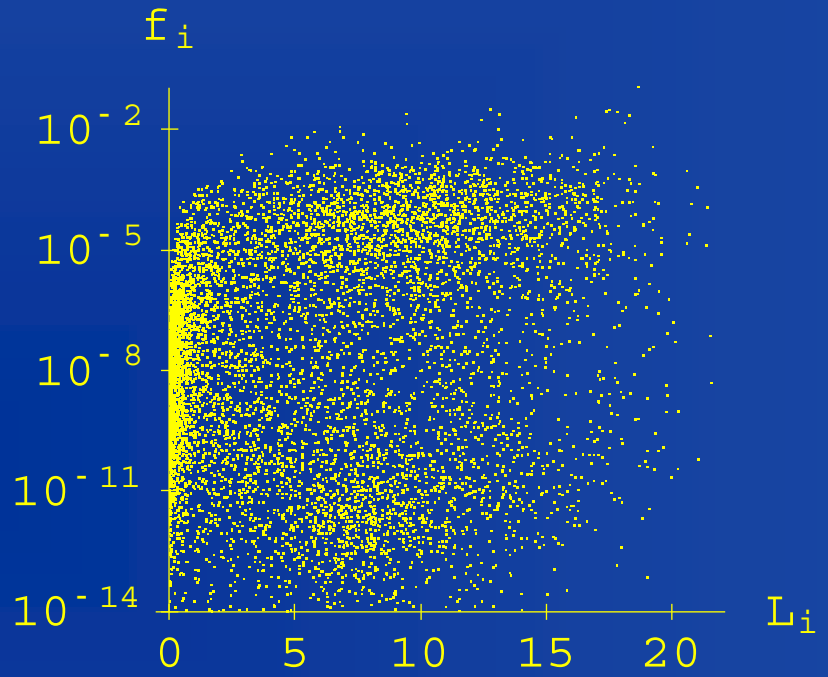
Corollary:

It is impossible that all surface-plasmon modes of any system are Anderson-localized (or, strongly localized).

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083



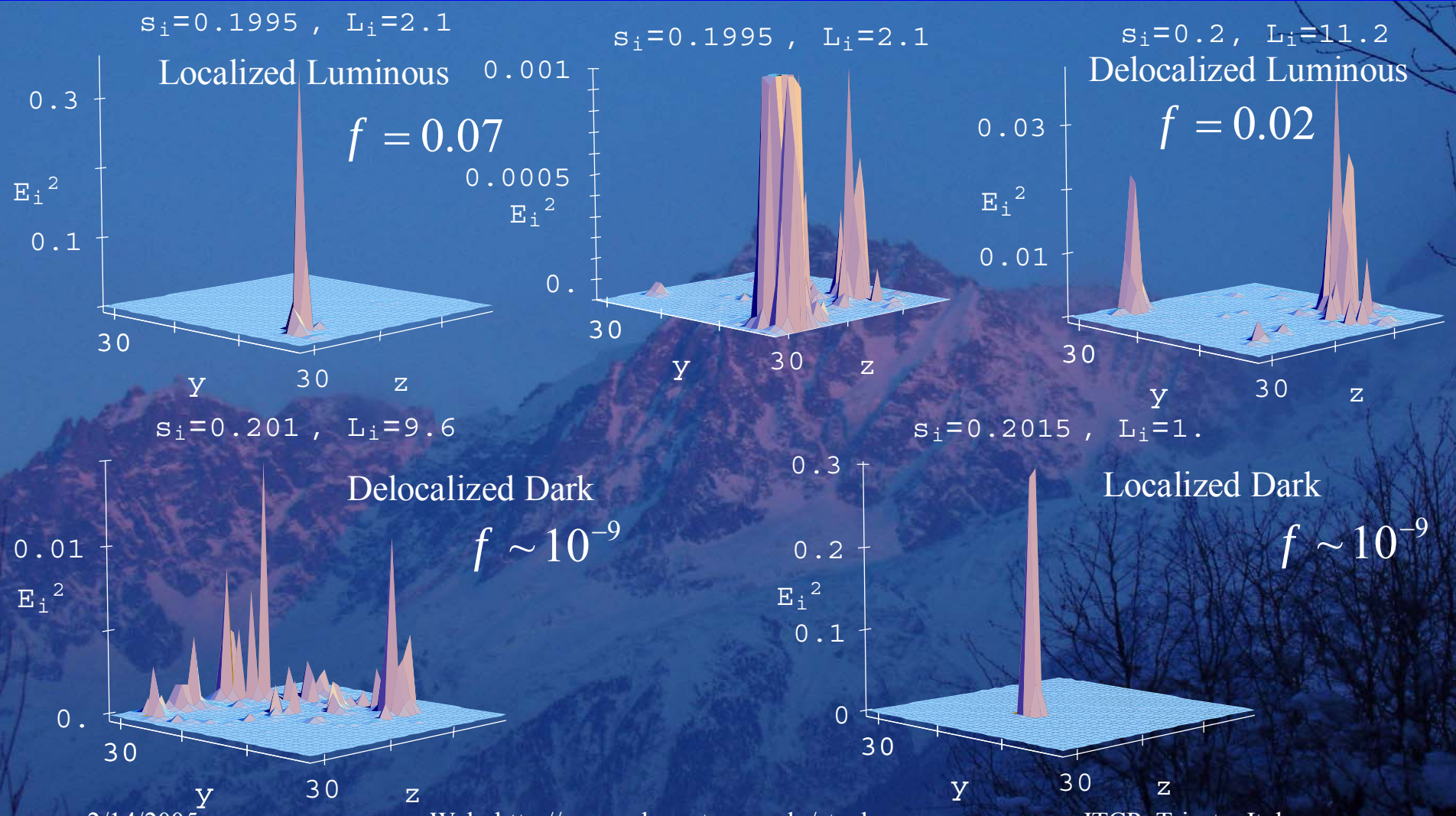
Geometry of Random Planar Composite



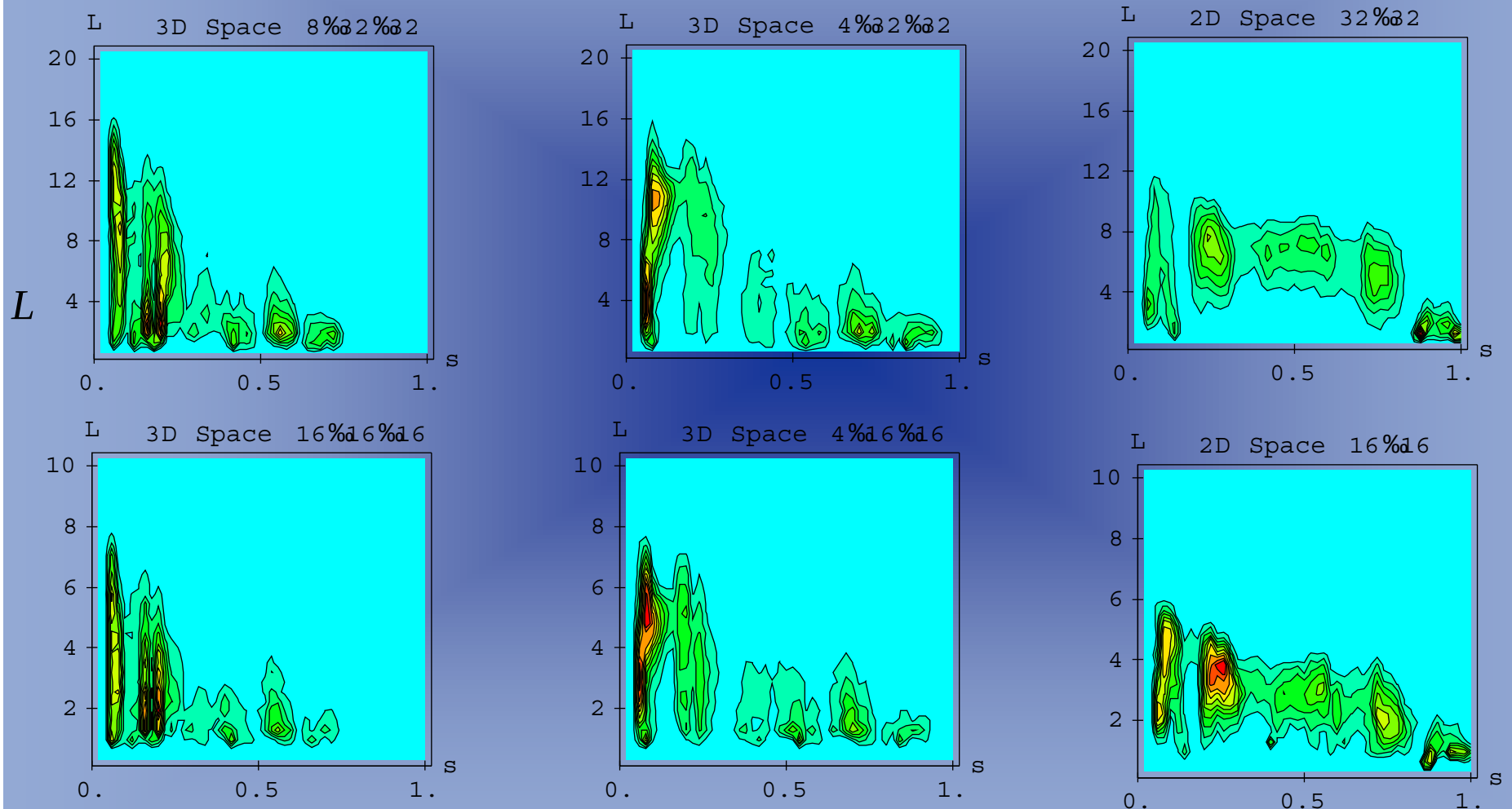
Distribution of Eigenmodes over their Oscillator Strength f_i and Localization Radius L_i

Phys. Rev. Lett. **87**, 167401 (2001).

Local Field Intensities for Four Eigenmodes Representative of Each Class of Eigenmodes



Distribution of Eigenmodes over their Localization Length and Spectral Parameter



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Giant Surface Enhanced Raman Scattering

M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, *Enhanced Raman Scattering by Fractal Clusters: Scale Invariant Theory*, Phys. Rev. B **46**(5), 2821-2830 (1992).

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

SERS Enhanced by factor of $\sim 10^{13}$

Single-molecule Surface-Enhanced Raman Scattering:

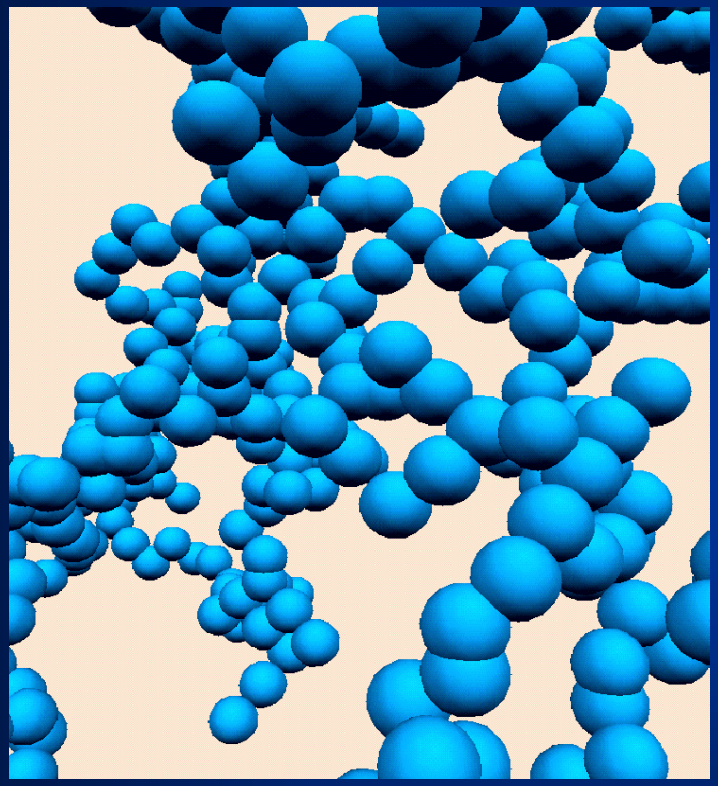
•K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, and M. S. Feld, *Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)*, Phys. Rev. Lett. **78**, 1667-1670 (1997).

•S. M. Nie and S. R. Emery, *Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering*, Science **275**, 1102-1106 (1997).

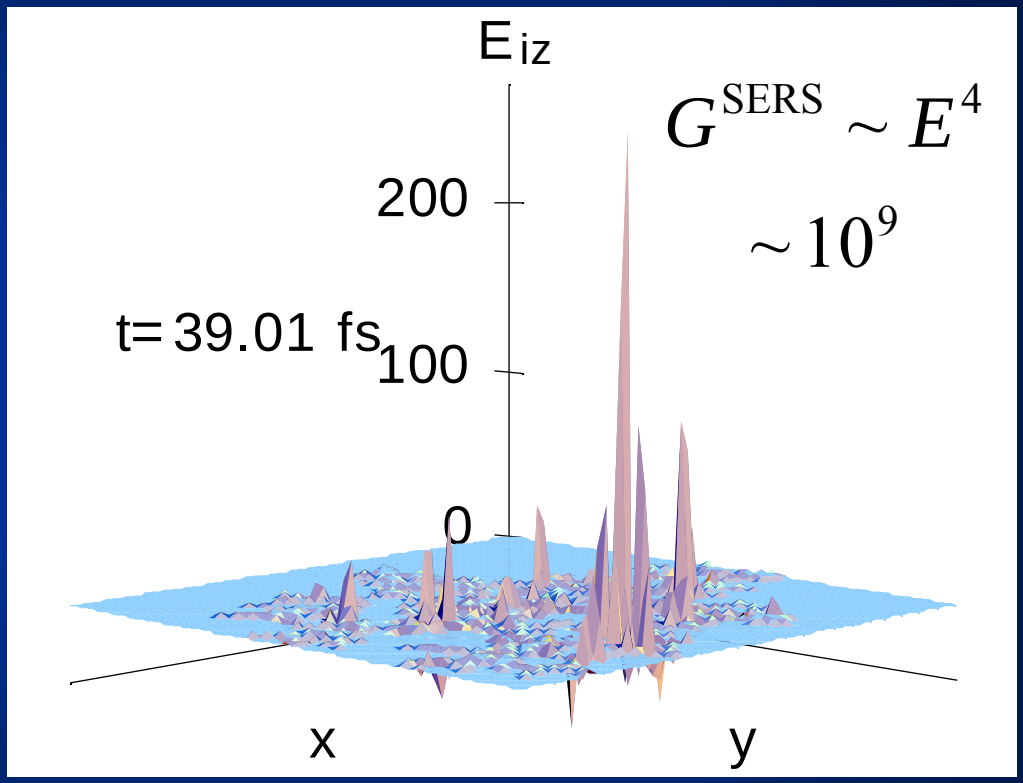
•Z. J. Wang, S. L. Pan, T. D. Krauss, H. Du, and L. J. Rothberg, *The Structural Basis for Giant Enhancement Enabling Single-Molecule Raman Scattering*, Proc. Natl. Acad. Sci. USA **100**, 8638-8643 (2003).

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Enhancement of Optical Responses in Fractals



Self-similar fractal geometry



Local optical fields in fractal cluster [MIS, Phys. Rev. Lett. **84**, 1011 (2000)].

SERS enhanced by a factor 10^{12} - 10^{14}

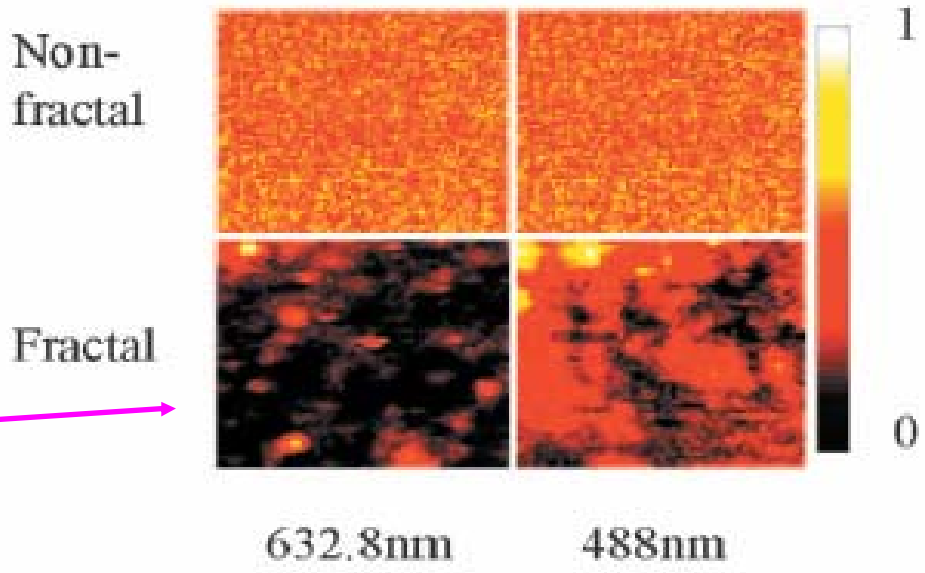
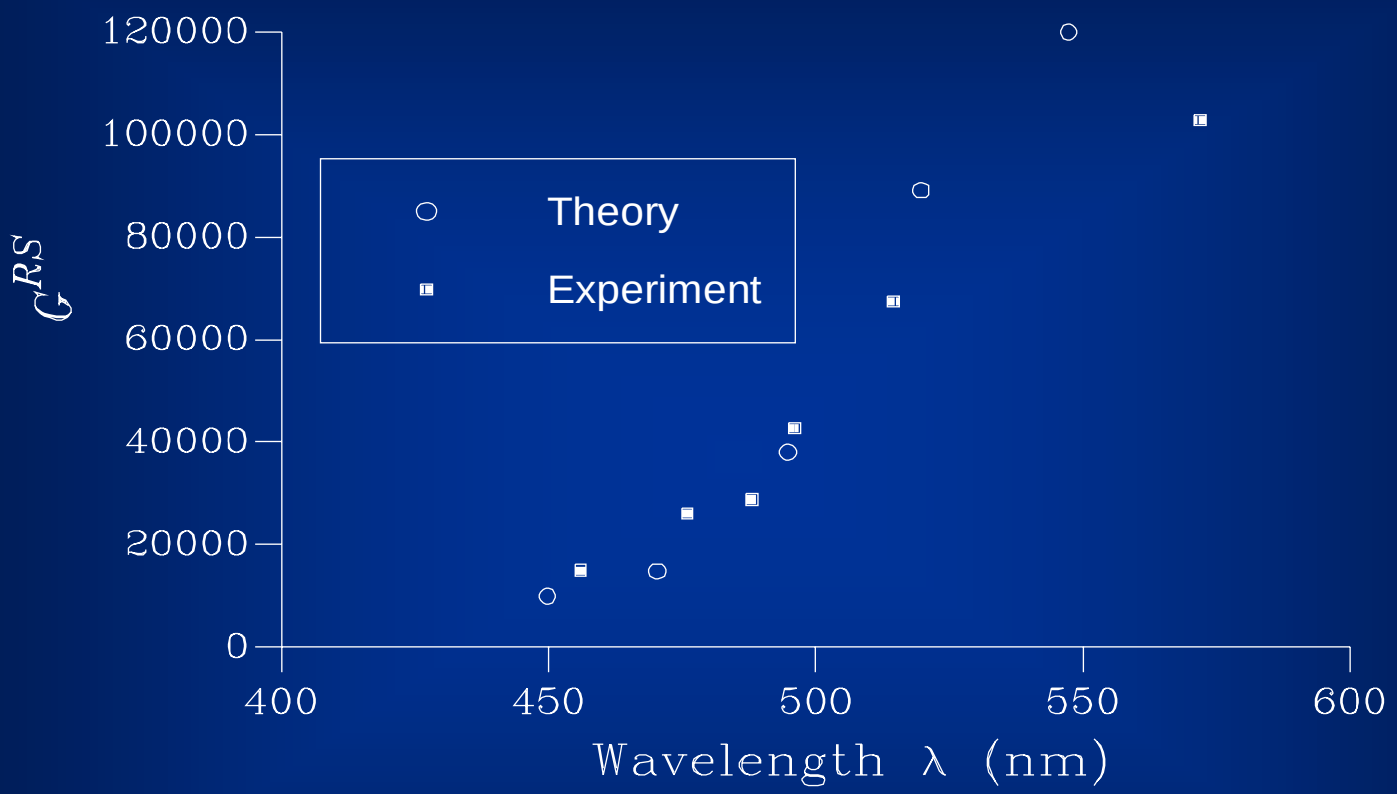


Fig. 6. Raman images of a single area on selected fractal and nonfractal surfaces for different excitation wavelengths. (*Upper*) The Raman images of immersion oil on the 100-nm-thick silver film. (*Lower*) The Raman images of 4-mercaptopyridine adsorbed on cluster–cluster aggregated films. The size of each image is 5 μm × 5 μm. Note that each image is internally normalized to its maximum so that relative intensities between images cannot be compared. In particular, the hot spots on fractal surfaces have orders of magnitude more Raman scattering than counterparts of similar color on nonfractal surfaces.

PNAS | July 22, 2003 | vol. 100 | no. 15 | 8641

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

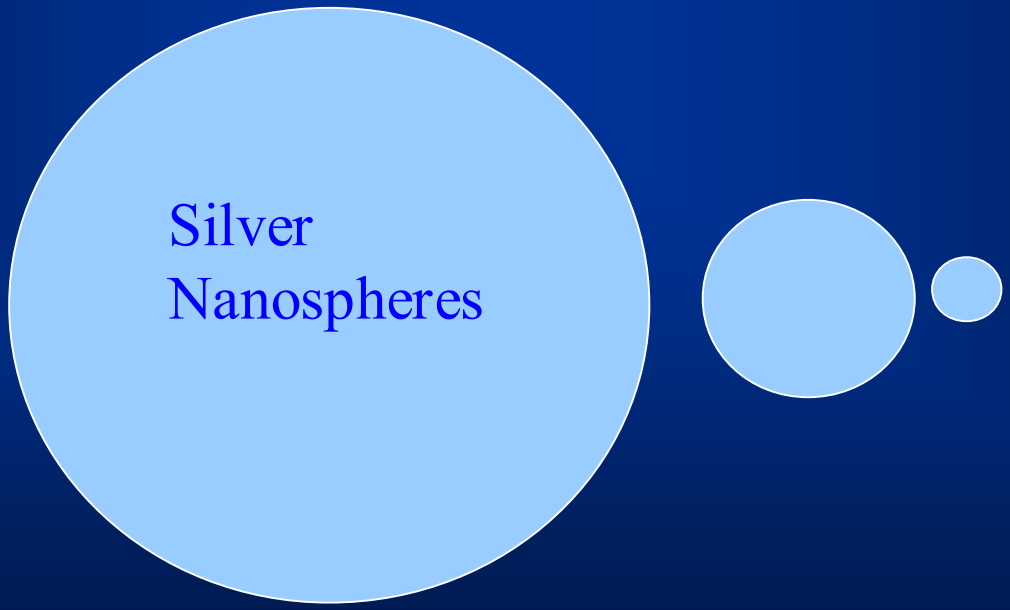


Comparison of theoretical predictions and experimental data for the SERS enhancement coefficient from silver colloid clusters.

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

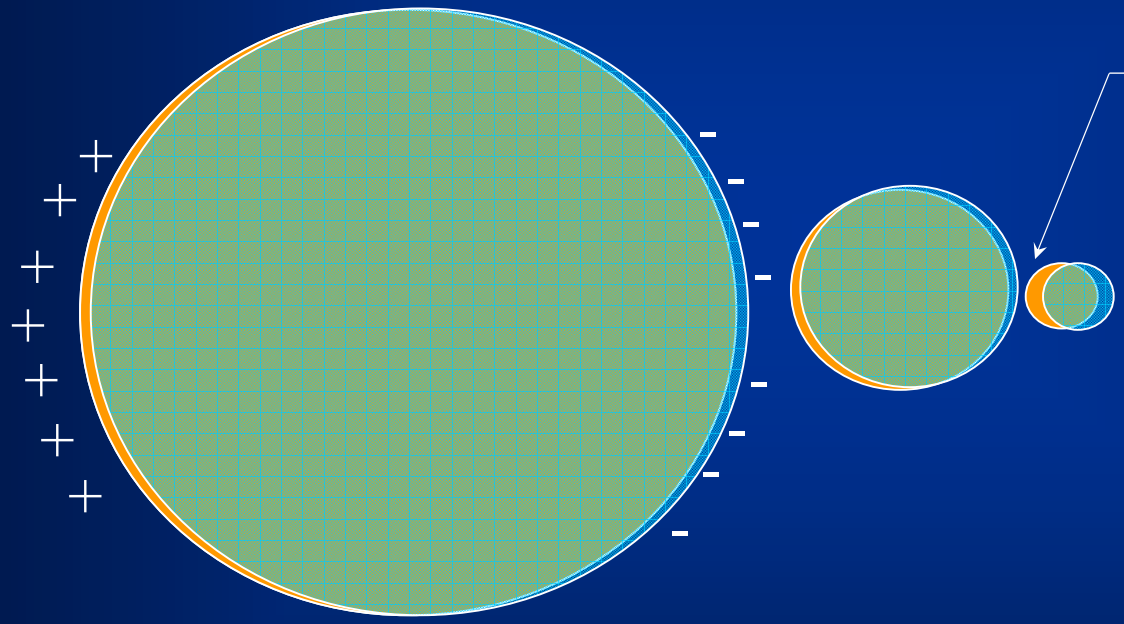
Efficient Self-Similar Nanolens of Nanospheres

K. Li, M. I. Stockman, and D. J. Bergman, *Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens*, Phys. Rev. Lett. **91**, 227402 (2003).



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Underlying physics of local field enhancement in efficient nanolens: Cascade enhancement



Giant local fields in the minimum gap: Nanoscale localization of optical energy

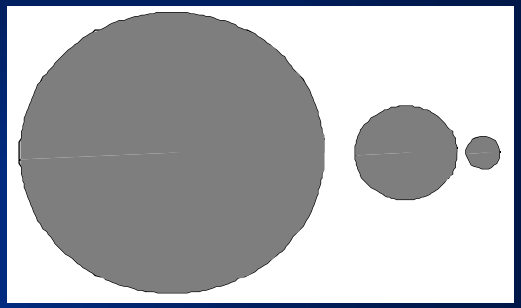
Optical Electric Field

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

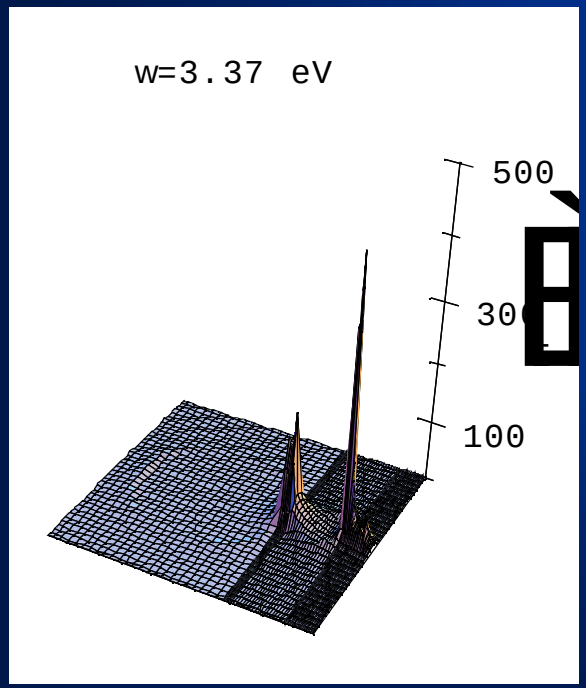
Giant Local Field Enhancement in Nanolens

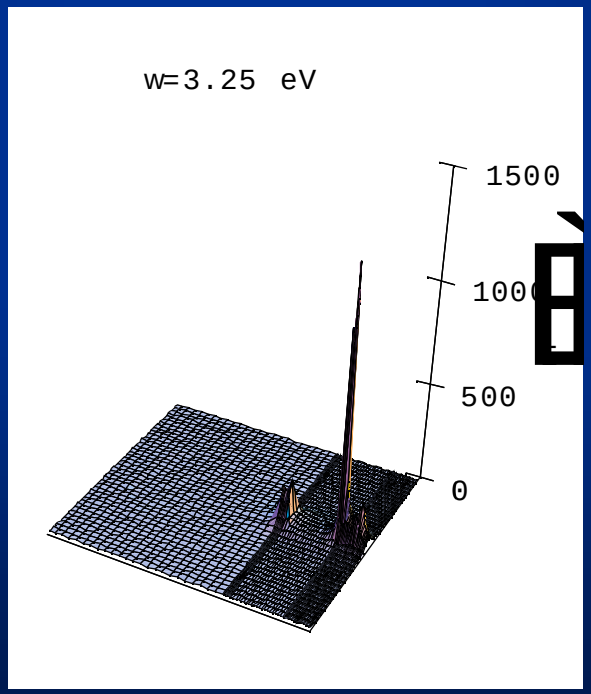
Local Fields for Silver 3-Sphere Nanolens

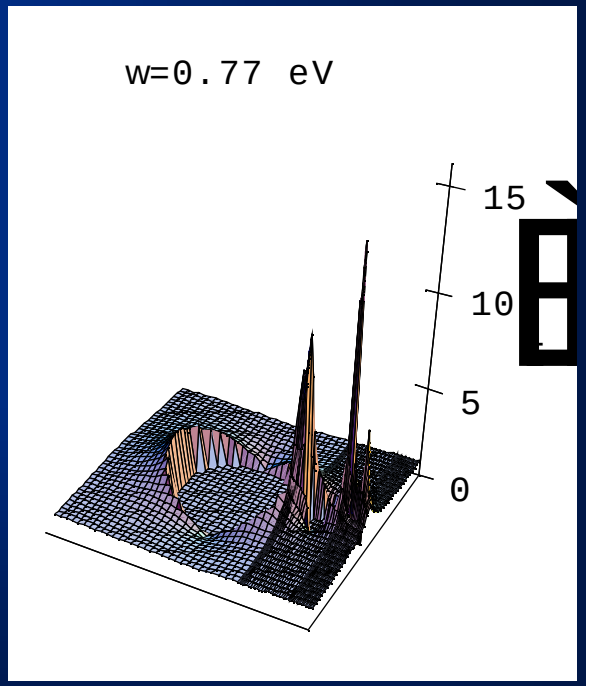
d=0.3R



K. Li, M. I. Stockman, and D. J. Bergman, *Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens*, Phys. Rev. Lett. **91**, 227402 (2003).

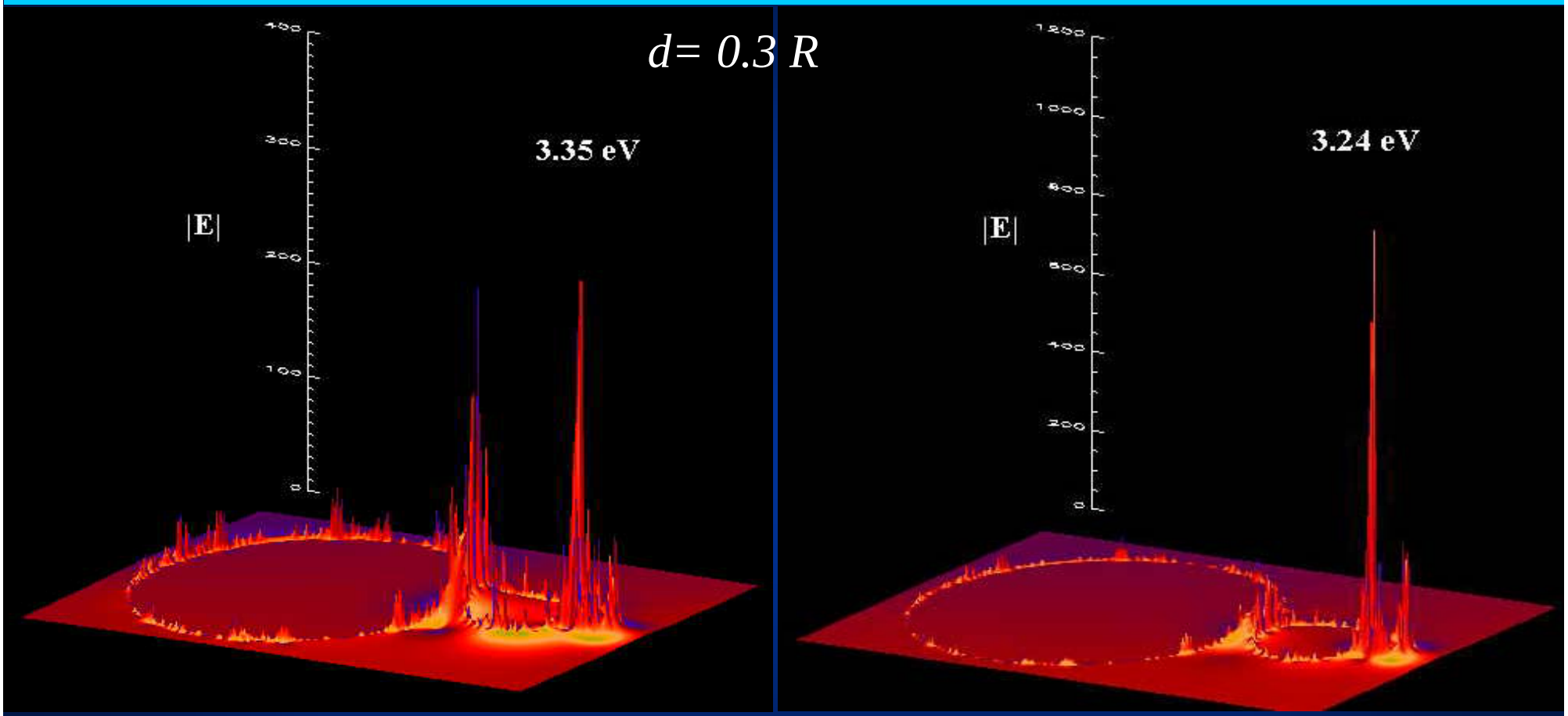




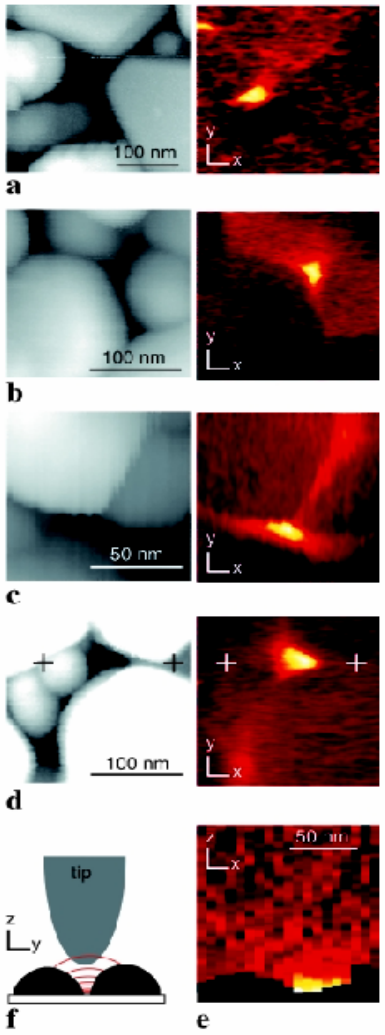


Web: http://www.phy-astr.gsu.edu/stockman
E-mail: mstockman@gsu.edu

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083



FDTD computations. C. Oubre and P. Nordlander (Private Communication).



5 Evidence of gap modes

Very highly confined near-fields are expected to exist in gaps between resonant metal particles. Such hot spots were conjectured to explain the extremely high Raman cross-section of a single molecule bridging two plasmon-resonant grains [11]. Calculations indicated that the resonant fields would be several hundred-fold enhanced for the narrowest assumed gap width of 1 nm [34]. To search for gap mode plasmons in very narrow spaces, we chose to use uncoated Si tips because they are sharper than the PtIr coated tips. This experiment yielded evidence of localized, very sharp light spots between Au clusters, clearly confirming the existence of gap modes (Fig. 5). The sample used contains particles of different sizes and shapes in close proximity. Some, as for example the two in the upper right part of Fig. 5b, have an optical near-field amplitude signal at least twofold enhanced and phase gradients (not shown), indicative of plasmon resonance. Compared to these, optical amplitude signals tenfold higher are observed in gaps between particles, with spot sizes between 10 and 50 nm in diameter. Where these bright spots occur is not determined by the local shape of a gap alone but also by the constellation of neighboring particles, otherwise there would be more than one hot spot at similar gap locations, e.g. in Fig. 5b. Figure 5e shows a cross-sectional image taken between the two marks in Fig. 5d. Clearly, the near-field maximum is at the lowest point that the probe tip can reach into the gap. As sketched in Fig. 5f, we suggest that even higher fields exist further down. These could be explored by a *s*-SNOM equipped with a narrower tip, possibly a carbon nanotube.

6 Conclusions

Our microscope has opened a window to nanoscale light fields bound to material objects and structured by details of their surface. We have for the first time spatially resolved the near-field patterns of optically resonant plasmon particles, and in particular viewed their optical phase structures and field singularities. The highest field confinement observed in gap modes (10 nm) could be improved by optimizing optical antennae and by spectral tuning, and should be useful for the microscopy of single nano-objects and the spectroscopy of single molecules [12]; the achievable brightness is a key to exploiting non-linear optical interactions for nanoscience. The

R. Hillenbrand and F. Keilmann, *Optical oscillation modes of plasmon particles observed in direct space by phase-contrast near-field microscopy,* Appl. Phys. B 73, 239–243 (2001)

CONCLUSIONS

- A self-similar chain of metal nanospheres makes an efficient nanolens focusing energy of optical field, concentrating it a nanoscale gap between the smallest nanosphere
- The optical field in the nanofocus is enhanced by more then three orders of magnitude
- A molecule adsorbed in this nanofocus will exhibit Raman scattering enhanced by a factor on order or greater than 10^{13}.

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

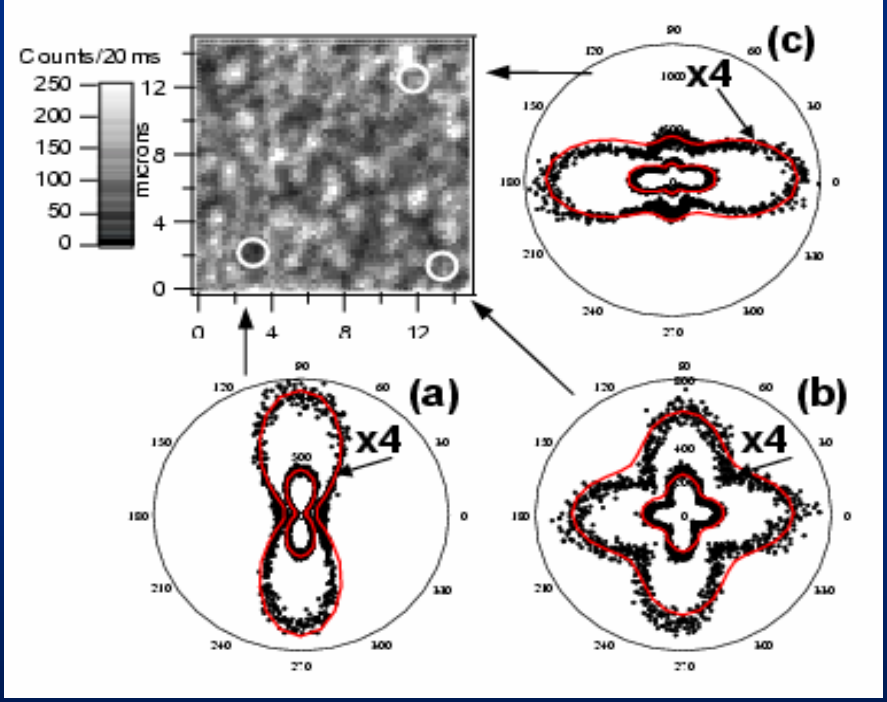
DEPOLARIZATION AND DEPHASING IN SECOND HARMONIC GENERATION IN RANDOM METAL NANOSTRUCTURED SYSTEMS

Mark I. Stockman, David J. Bergman, Cristelle Anceau, Sophie Brasselet, and Joseph Zyss, *Enhanced Second Harmonic Generation By Metal Surfaces with Nanoscale Roughness: Nanoscale Dephasing, Depolarization, and Correlations*, Phys. Rev. Lett. 92, 057402-1-4 (2004).

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Experimental evidence of strong depolarization, dephasing, and giant fluctuations of SHG:

C. Anceau, S. Brasselet, J. Zyss, and P. Gadenne, *Local second harmonic generation enhancement on gold nanostructures probed by 2-photon microscopy*, Opt. Lett. **28**, 713 (2003).



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

S. I. Bozhevolnyi, J. Beermann, and V. Coello, Phys. Rev. Lett. **19**, 197403 (2003)

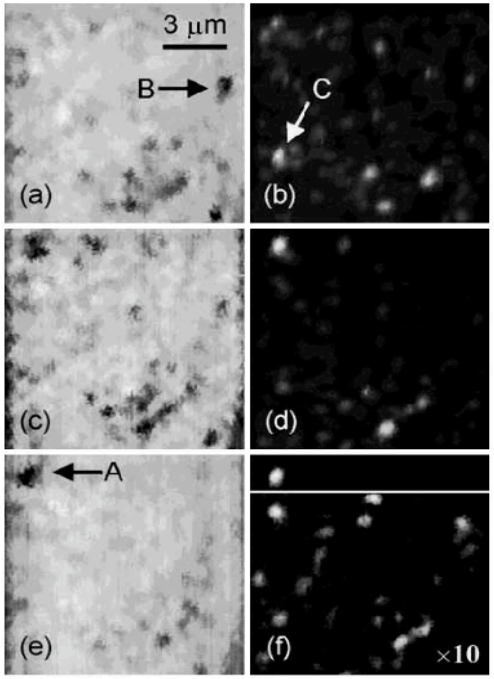


FIG. 2. Gray-scale (a),(c),(e) FH and (b),(d),(f) SH images ($11.5 \times 11.5\ \mu m^2$) of the random structure taken at the FH wavelength $\lambda \equiv$ (a),(b) 750, (c),(d) 790, and (e),(f) 830 nm. The polarization of the incident FH and detected SH radiation was vertical with respect to the presented images. The maximum of the SH signal corresponds to (b) 325, (d) 120, and (f) 145 kcps.

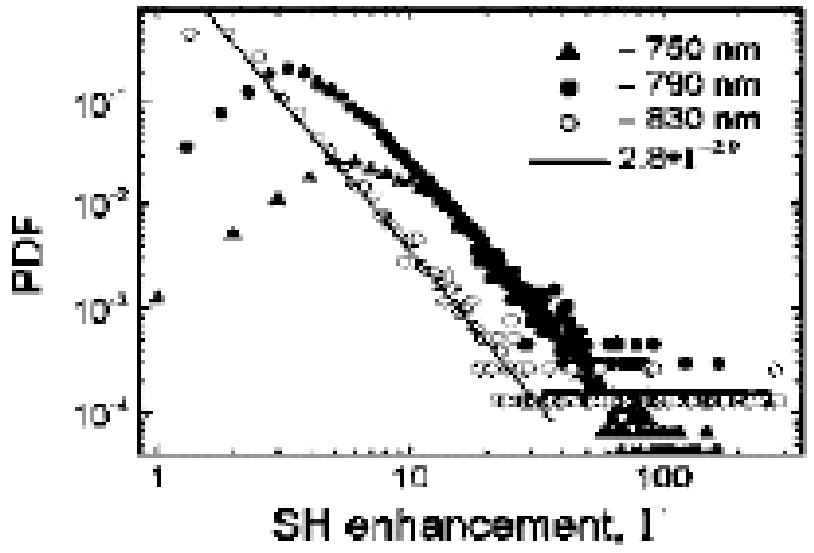


FIG. 4. The PDF calculated from the SH signal data (normalized by the signal from flat regions) shown in the images of Fig. 2 along with the power-law fit (solid line) for the data obtained with the FH wavelength of 830 nm. Each PDF was calculated from the 13225 image data points dividing the interval between the maximum and minimum signals by 500 sampling intervals.

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

$$P_{NL}^{(2)}(\mathbf{r}) = \chi^{(2)} E^2(\mathbf{r}) \frac{\partial \theta(\mathbf{r})}{\partial \mathbf{r}}$$

The SH potential is calculated as:

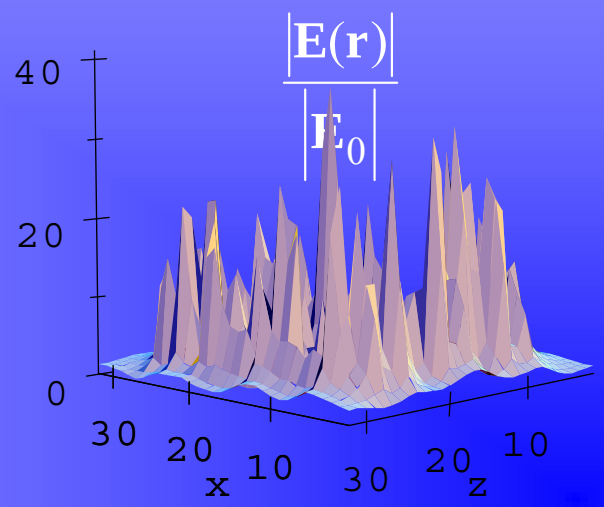
$$\varphi^{(2)}(\mathbf{r}) = \frac{4\pi}{\varepsilon_{host}} \int \left[\frac{\partial}{\partial \mathbf{r}'} \mathbf{P}_{NL}^{(2)}(\mathbf{r}') \right] \cdot G^r(\mathbf{r}, \mathbf{r}'; 2\omega)\, d^3 r'$$

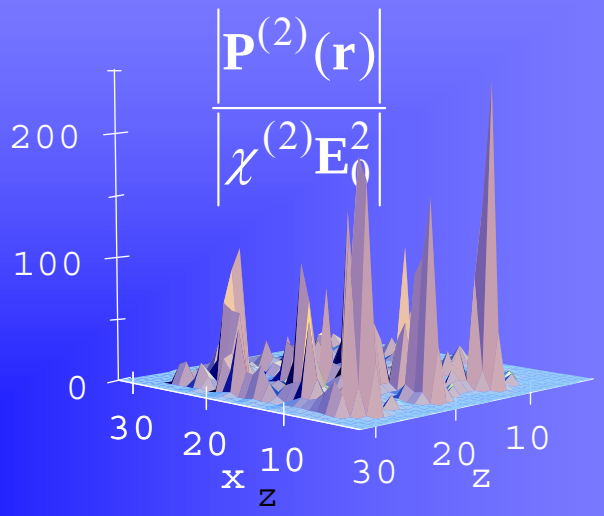
The total SH Polarization is found as:

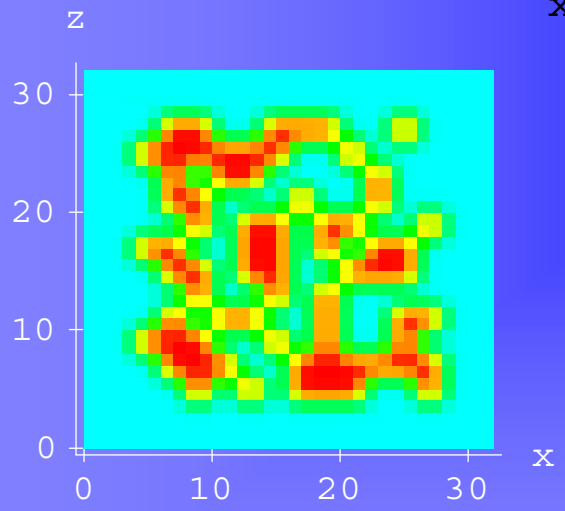
$$P_{\text{total}}^{(2)}(\mathbf{r}) = P_{\text{NL}}^{(2)}(\mathbf{r}) - \frac{\varepsilon(\mathbf{r}, 2\omega) - 1}{4\pi} \nabla \varphi^{(2)}(\mathbf{r}),$$

where $\varepsilon(\mathbf{r}, 2\omega) = \varepsilon_{\text{host}} \left[1 - \frac{\theta(\mathbf{r})}{s(2\omega)} \right]$

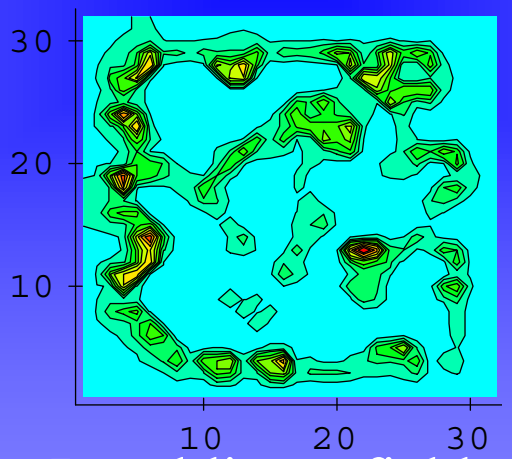
Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083



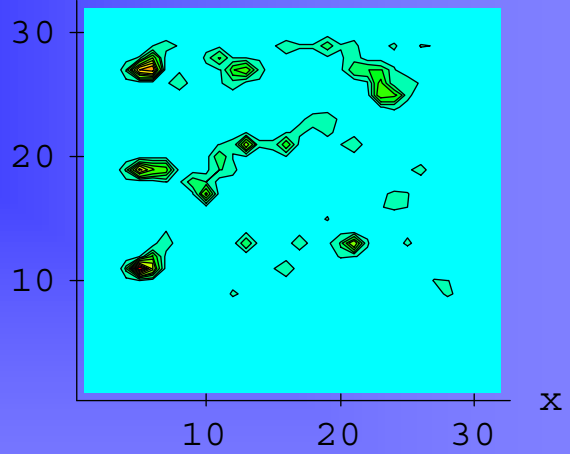




Geometry of the system



Local linear field

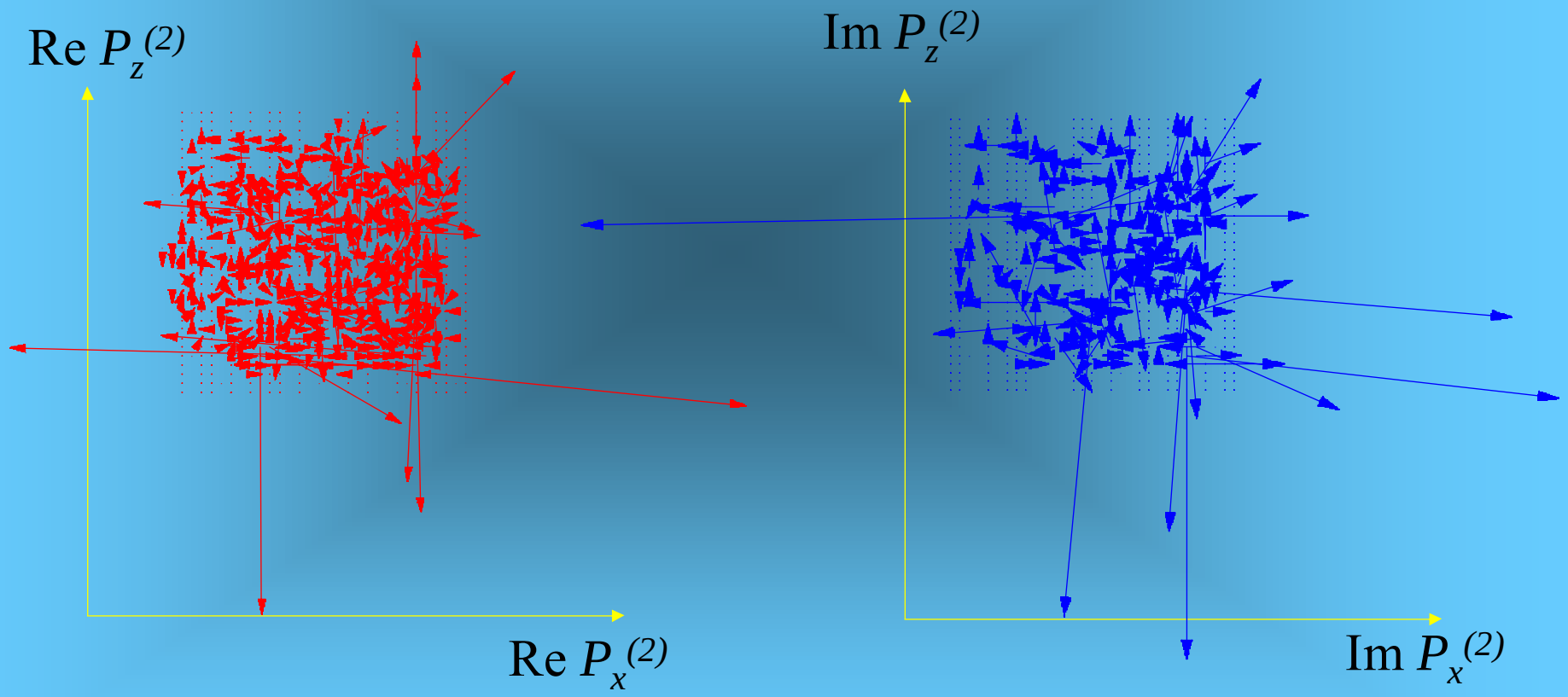


SH Polarization

Web: http://www.phy-astr.gsu.edu/stockman
E-mail: mstockman@gsu.edu

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

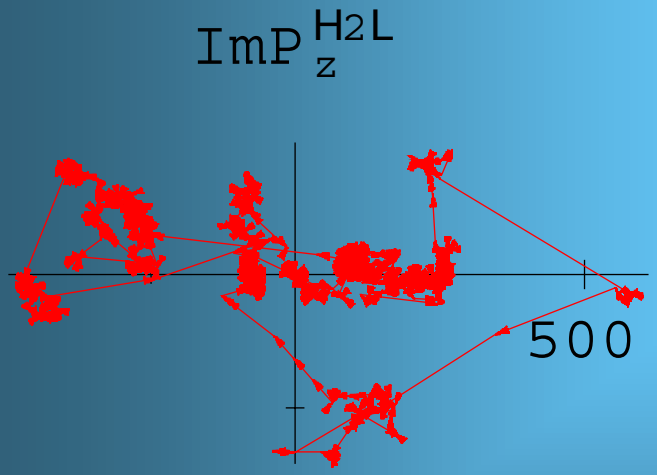
Depolarization of SH



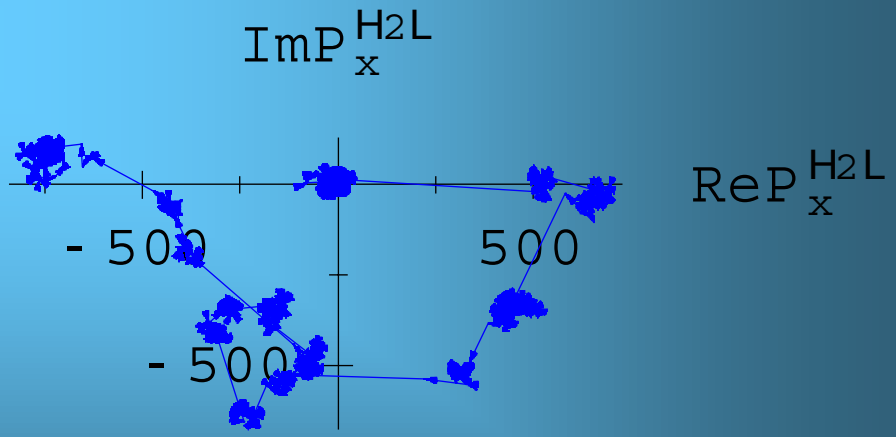
Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Dephasing of SH

Polarized component



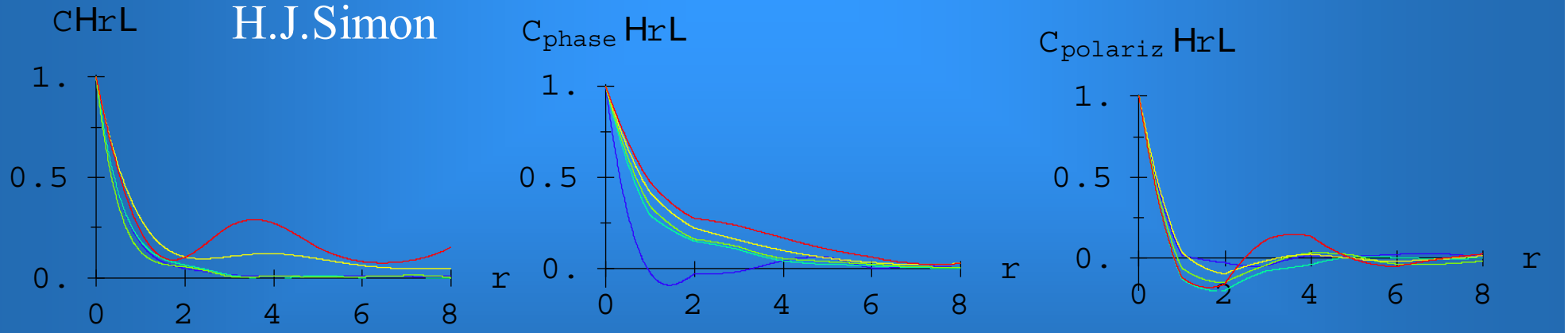
Depolarized component



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

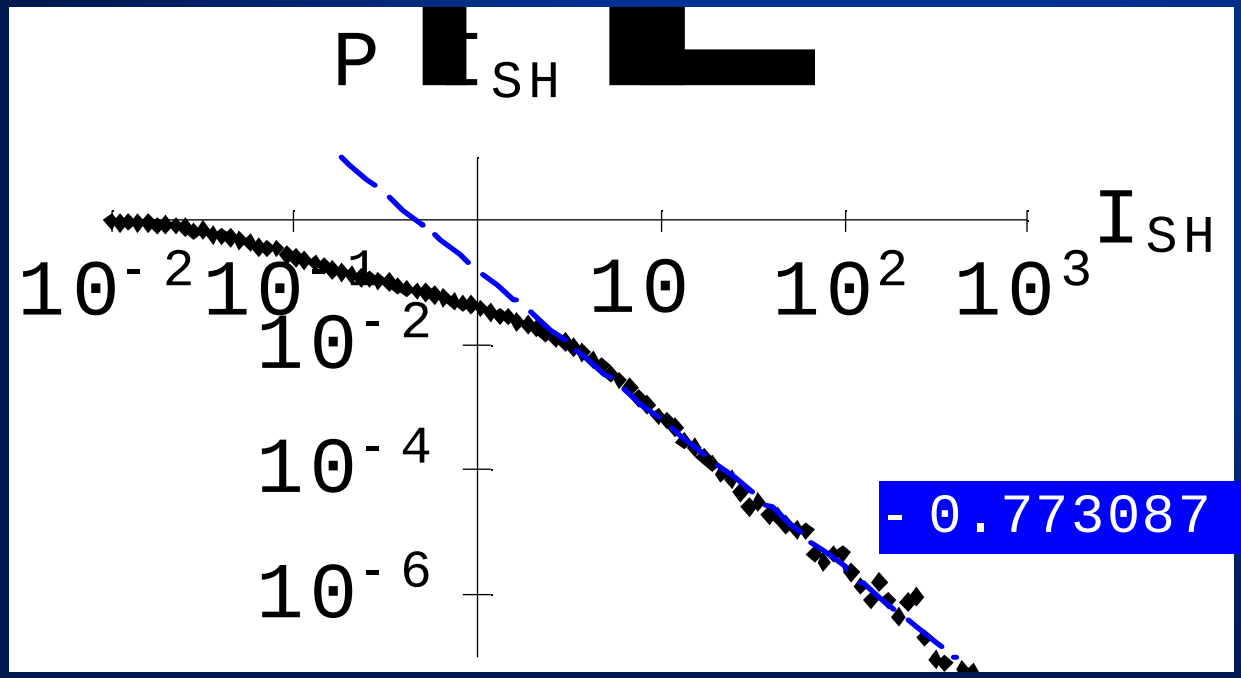
Correlation Functions for Different Fill Fractions *p* (Color Coded):

$P = 0.35,\ 0.50,\ 0.60,\ 0.75,\ 0.95$



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Giant fluctuations of local optical fields introduced:
M.I.Stockman, L.N.Pandey, L.S.Muratov, and T.F.George, *Giant Fluctuations of Local Optical Fields in Fractal Clusters*, Phys. Rev. Lett. **72**(15), 2486-2489 (1994).
The universal index –1.5 for fundamental and –2.5 for SH



Giant fluctuations of SHG local fields (new result)

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

CONCLUSIONS

- Second harmonic polarization $\mathbf{P}^{(2)}(\mathbf{r})$ in a nonlinear random planar composite is a highly singular function concentrated in hot spots. $\mathbf{P}^{(2)}(\mathbf{r})$ is significantly different from local fields $\mathbf{E}(\mathbf{r})$.
- SHP $\mathbf{P}^{(2)}(\mathbf{r})$ is both dephased and depolarized at the *nanoscale*. SHG from a random composite on any microscopic scale is incoherent, i.e., hyper-Raleigh scattering
- The local intensity of SHG undergoes giant (non-Gaussian) fluctuations with scaling distribution function whose index is not universal

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Extreme Nanoplasmonics: Fundamental limit on the minimum scale of the energy concentration/spatial resolution

Ivan A. Larkin and Mark I. Stockman, *Imperfect Perfect Lens*, Phys. Nano Lett. **5,** 339 – 343 (2005)

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

At small distances a, interactions transfer large momentum $p \sim \frac{\hbar}{a}$

or wave vector $k \sim \frac{1}{a}$

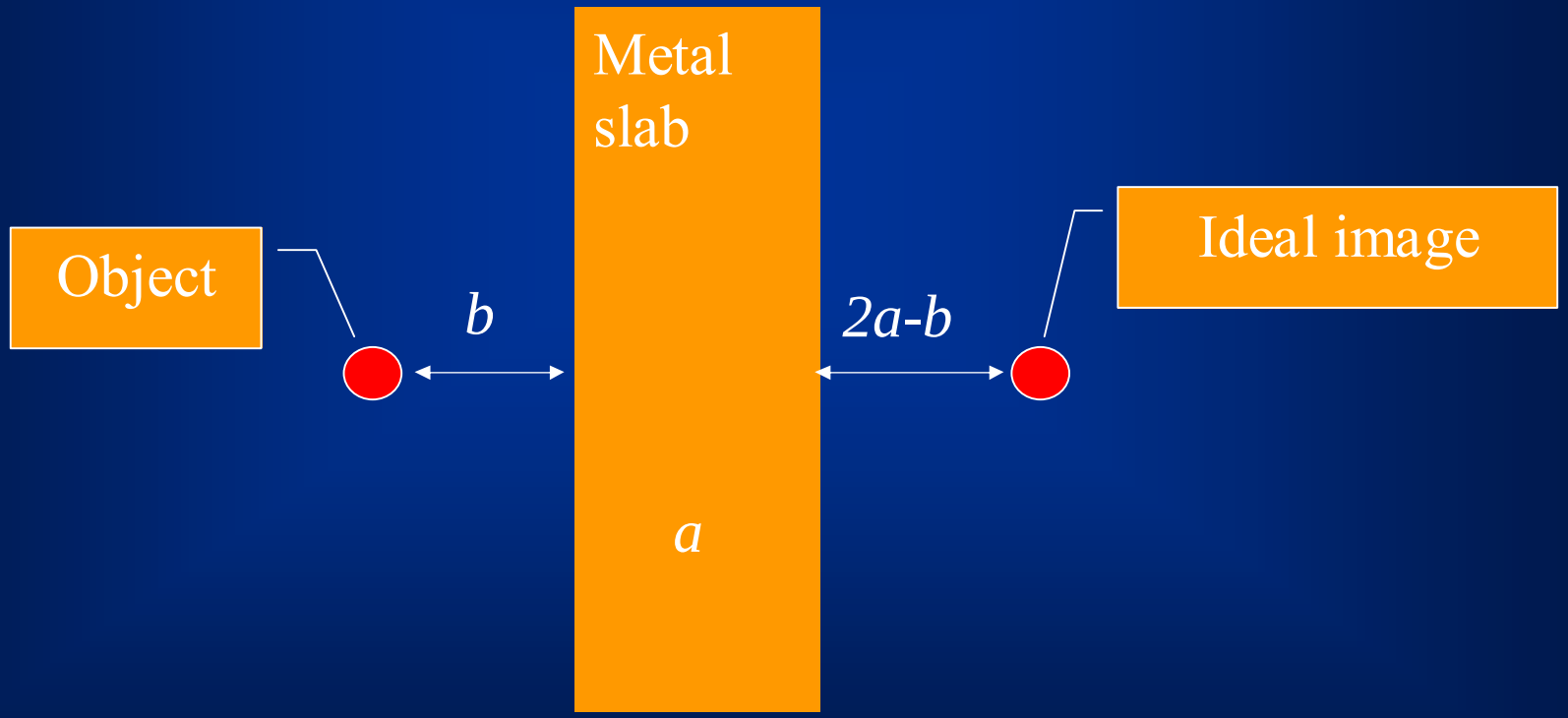
For large enough k, $\frac{\omega}{k} \sim \omega a \le v_F \sim 10^8 \frac{\text{cm}}{\text{s}}$ *interacting* electron system exhibits strong spatial dispersion and Landau damping . These effects are described by Klimontovich-Silin-Lindhart (RPA) formula

$$\varepsilon(\omega, k) = 1 + \frac{3\Omega_e^2}{k^2 v_F^2}\left[1 - \frac{\omega}{2kv_F}\ln\frac{\omega + kv_F}{\omega - kv_F}\right]$$

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Pendry's Perfect Lens in *near field* $a, b << \lambda$

It is required that the relative dielectric permittivity $\varepsilon = -1$



Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Estimate of the ultimate spatial resolution of the "perfect lens"

$$\delta \sim \frac{2b}{|\ln\left[Q^{-2} + |c(\omega,0)/b|^2\right]|}$$

Function $c(\omega,0) \sim v_F/\omega$ dominates δ for $b \lesssim 5$ nm,

where Q~10-100 is the surface plasmon resonance quality factor

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

Imaging

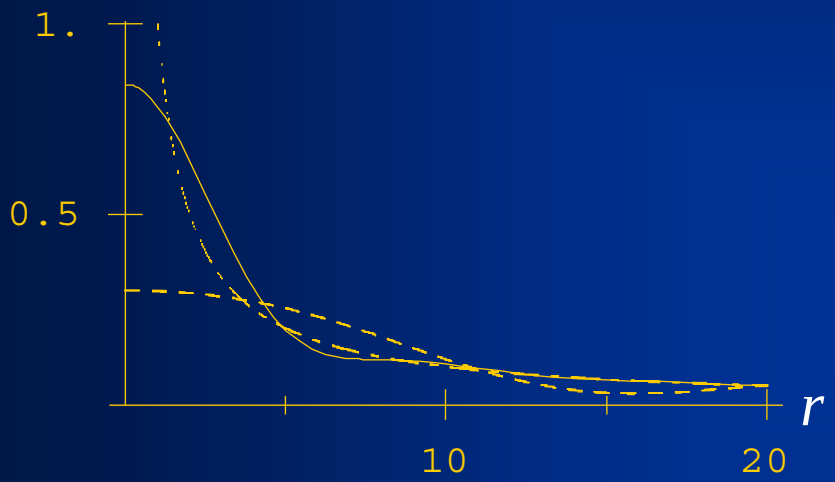


Image of a point charge produced by a 5 nm silver slab in GaAs environment, photon energy: 2.2 eV

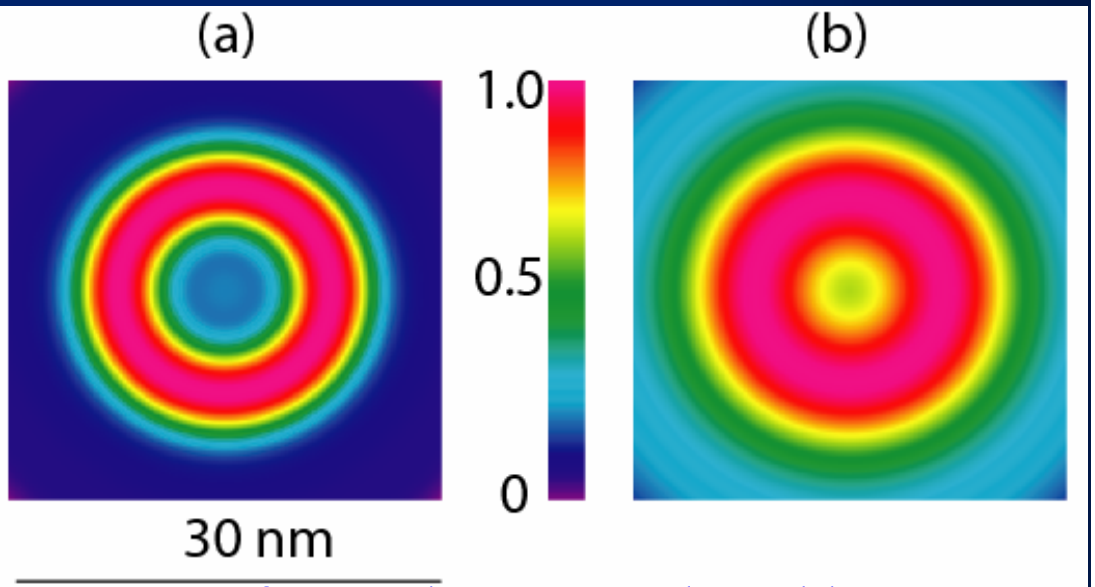


Image of a washer as produced by a silver slab of 5 nm thickness in GaAs host: (a) without spatial dispersion, (b) with spatial dispersion. Photon energy: 2.2 eV.

Department of Physics and Astronomy
Georgia State University
Atlanta, GA 30303-3083

CONCLUSIONS

1. At small distances (on order of a few nanometers), the conventional local electrodynamics is no more applicable.
2. Nonlocality of permittivity and Landau damping become important.
3. These effects limit the spatial resolution of the “perfect lens” to no better than 5 nm
4. Other resonant, plasmonic effects are also limited by these effects and die out at the scale of a few nanometers.