ELECTROMAGNETIC PROPERTIES OF AGGREGATED SPHERES REVISITED

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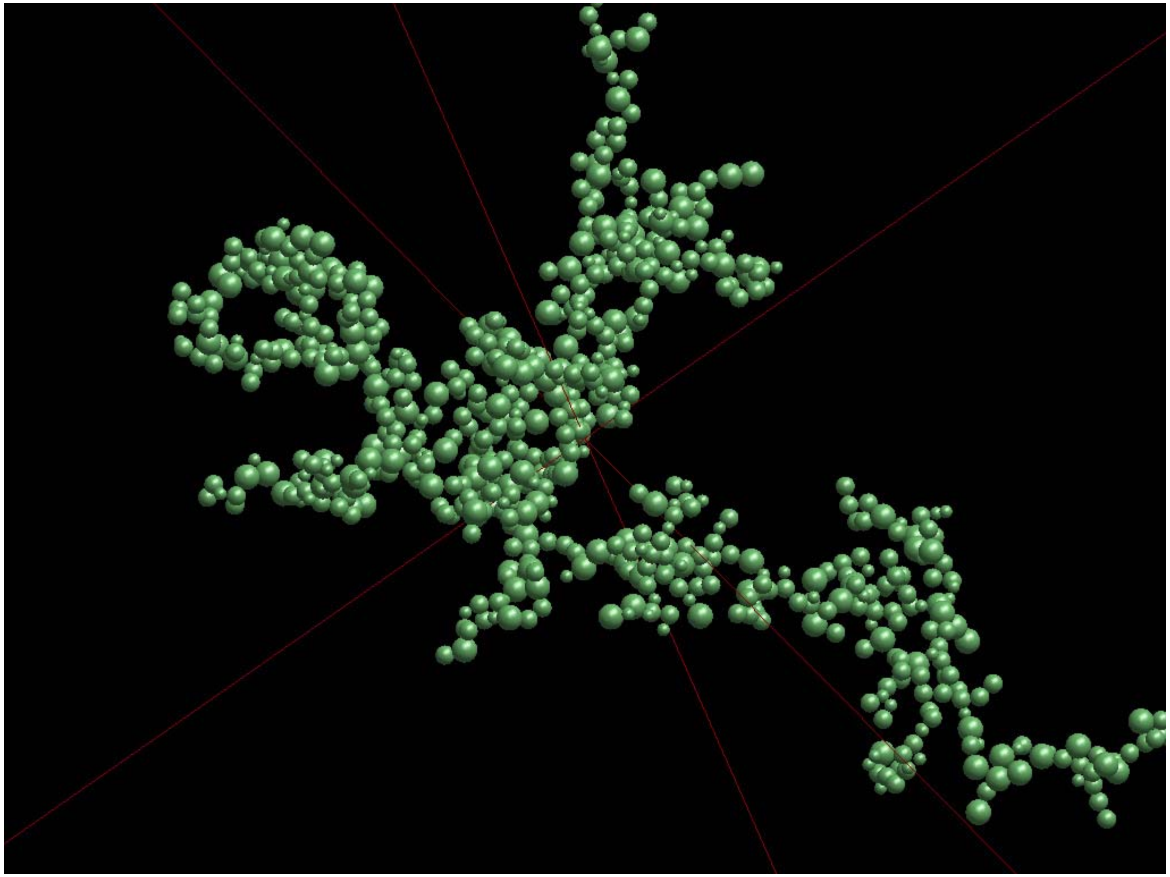
REFERENCES

- "*Electromagnetic Density of States and Absorption of Radiation by Aggregates of Nanosphereswith Multipole Interactions*," PRB 70, 54202 (2004).
- "*Local Anisotropy and Giant Enhancement of Local Electromagnetic Fields in Fractal Aggregates of Metal Nanoparticles*," preprint: physics/0507202 (2005).

Problem: calculate optical (more generally, electromagnetic) responses of large fractal aggregates of metal nanospheres.



MOTIVATION

- Giant enhancement of effective nonlinear optical susceptibilities
- Localization of electromagnetic energy
- Optical memory
- Soot particles often have fractal geometry (of interest in atmospheric optics).

Theoretical and Computational Approaches

1) Dipole approximation

- $3N$ equations (N – number of nanospheres)
- Easy to generalize beyond quasistatics
- Inacurate for touching spheres

2) Geometrical renormalization

- An approximation
- Corrects to some extent the deficiency of the dipole approximation
- Still $3N$ equations

3) Coupled multipoles

- $L(L+2)N$ equations (L – maximum order of multipole moment included in computations)
- Slow convergence with L for conducting spheres in close contact
- Computational complexity grows as L^6

General Approach (Extinction And DOS)

$$\varepsilon_{\mathrm{e}} = \frac{\sigma_{\mathrm{e}}}{V_{\mathrm{tot}}} = 4\pi k \,\mathrm{Im} \int \frac{\Gamma(w)dw}{z(\lambda) - w}$$

$$\int \Gamma(w)dw = 1$$

$$z(\lambda) = \frac{4\pi}{3} \frac{m^2(\lambda) + 2}{m^2(\lambda) - 1}$$

Definition of DOS

$$\Gamma(w) = \Sigma_\text{n} |c_n|^2 \delta(w - w_n)$$

$$W|n> = w_n|n>$$

Operator W is, in general, infinite-dimensional.

Dipole approximation: size $3N$

Truncated coupled multipoles: size $L(L+2)N$

Is W sparse? Yes, approximately. But scarcity factor is not that large and using sparse solvers (e.g., PARDISO) does not help much.

Numerical Methods of Calculating the Spectra

Calculation of spectra is based on different approximations for the expression

$$\theta(z) = \mathrm{Im}\int \frac{\Gamma(w)dw}{z-w}, \quad z = X - i\delta$$

In the limit $\delta \to 0$ this corresponds to direct calculation of $\Gamma(X)$ because

$$\lim_{\delta\to 0}[\theta(X,\delta)] = \pi\Gamma(X)$$

Numerical Methods of Calculating the Spectra (cont.)

Three approaches for calculating θ:

a) By expressing θ as a sum

$$\theta(z) = \sum \frac{c_n^2}{z - w_n}$$

b) By expressing θ as a continued fraction

$$\theta(z) = \frac{b_0^2}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - \ldots}}}$$

c) By choosing an analytical model for $\Gamma(w)$

Numerical Methods of Calculating the Spectra (cont.)

a) Expressing θ as a sum requires diagonalization of a matrix of the size $M = NL(L+2)$ where

N - number of spherical particles

L - maximum multipole order

(i) Numerical complexity: $\mathrm{O}(M^3)$

(ii) Memory requirement: $\mathrm{O}(M^2)$

(iii) Dipole approximation: $L = 1$

Numerical Methods of Calculating the Spectra (cont.)

b) Expressing θ as a continued fraction requires K matrix-vector multiplications for a matrix of the size $M = NL(L+2)$

(i) Numerical complexity: $O(KM^2)$

(ii) Memory requirement: $\ll M^2$

(iii) K-the order approximation $\Gamma_K(X)$ has ***exactly*** the same first K moments μ_n as the true density $\Gamma(X)$, where

$$\mu_n = \int X^n \Gamma(X) dX$$

Back to specific tasks

Sum Rules

Let $z = X - i\delta$

Then $\int \frac{\varepsilon_{\mathrm{e}}}{k} dX = 4\pi^2$ (for all materials/shapes)

$$\int_0^\infty \sigma(\lambda) d\lambda = 4\pi^3 \alpha_{zz}$$

α_{zz} - diagonal element of the electrostatic polarizability tensor

Spectral Variable $z=X-i\delta$ for Drudean Materials

For a Drudean material $$m^2 = 1 - \frac{\omega_\mathrm{p}^2}{\omega(\omega + i\gamma)}$$

$$X = \operatorname{Re} z = \frac{4\pi}{3}\left(1 - \frac{\omega^2}{\omega_\mathrm{F}^2}\right), \quad \text{where} \quad \omega_\mathrm{F} = \frac{\omega_\mathrm{p}}{\sqrt{3}}$$

If $\omega \approx \omega_\mathrm{F}$, then $X \approx \dfrac{8\pi}{3}\dfrac{\omega_\mathrm{F} - \omega}{\omega_\mathrm{F}}$

$$\delta \approx \frac{4\pi}{3}\frac{\gamma}{\omega_\mathrm{F}}$$

Long-Wavelength Limit

If $\lambda \to \infty \ (\omega \to 0)$,

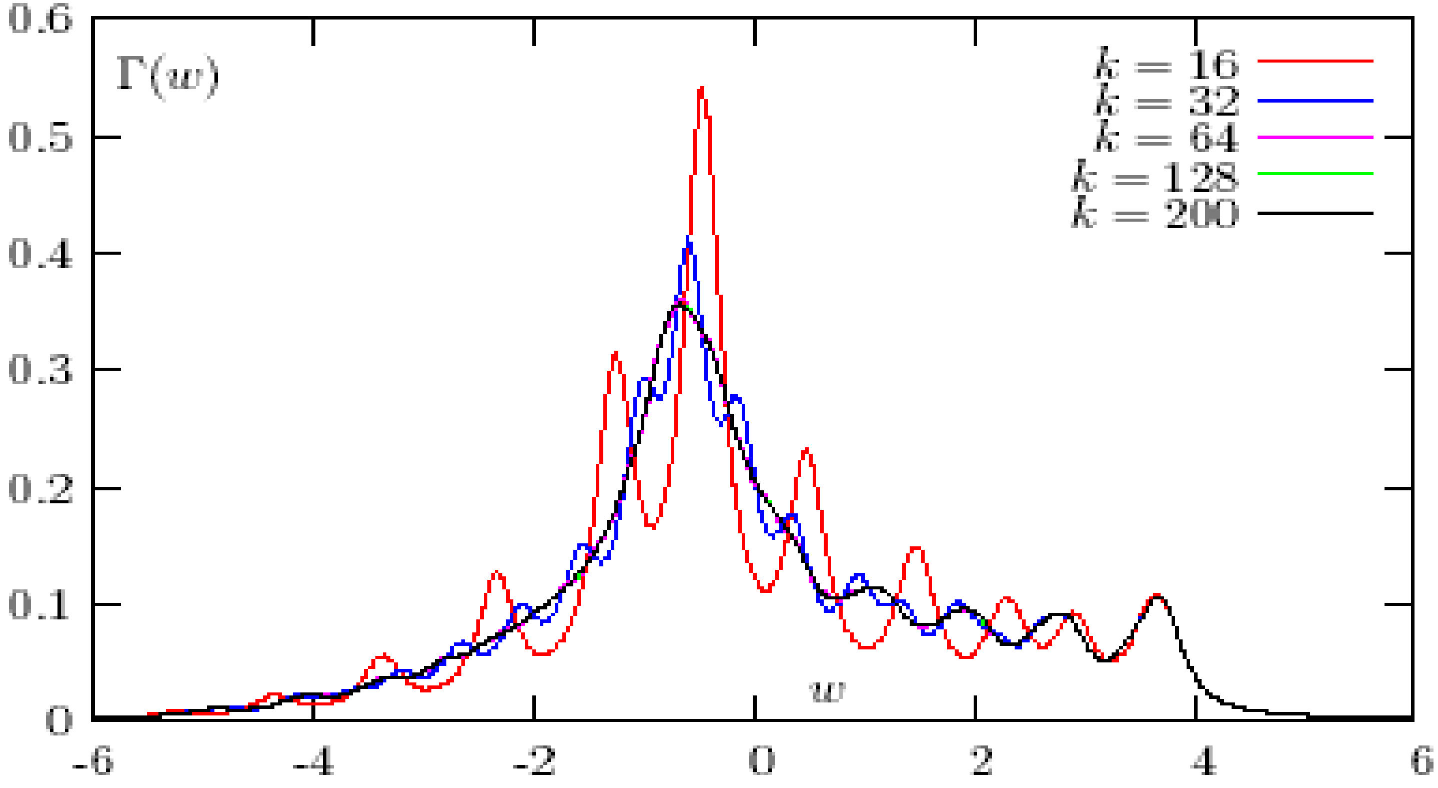
$$X \approx \frac{4\pi}{3}, \quad \delta \approx \frac{4\pi}{3}\frac{\omega\gamma}{\omega_F^2} = \frac{\omega}{\sigma} \to 0$$

(σ - electrostatic conductivity)

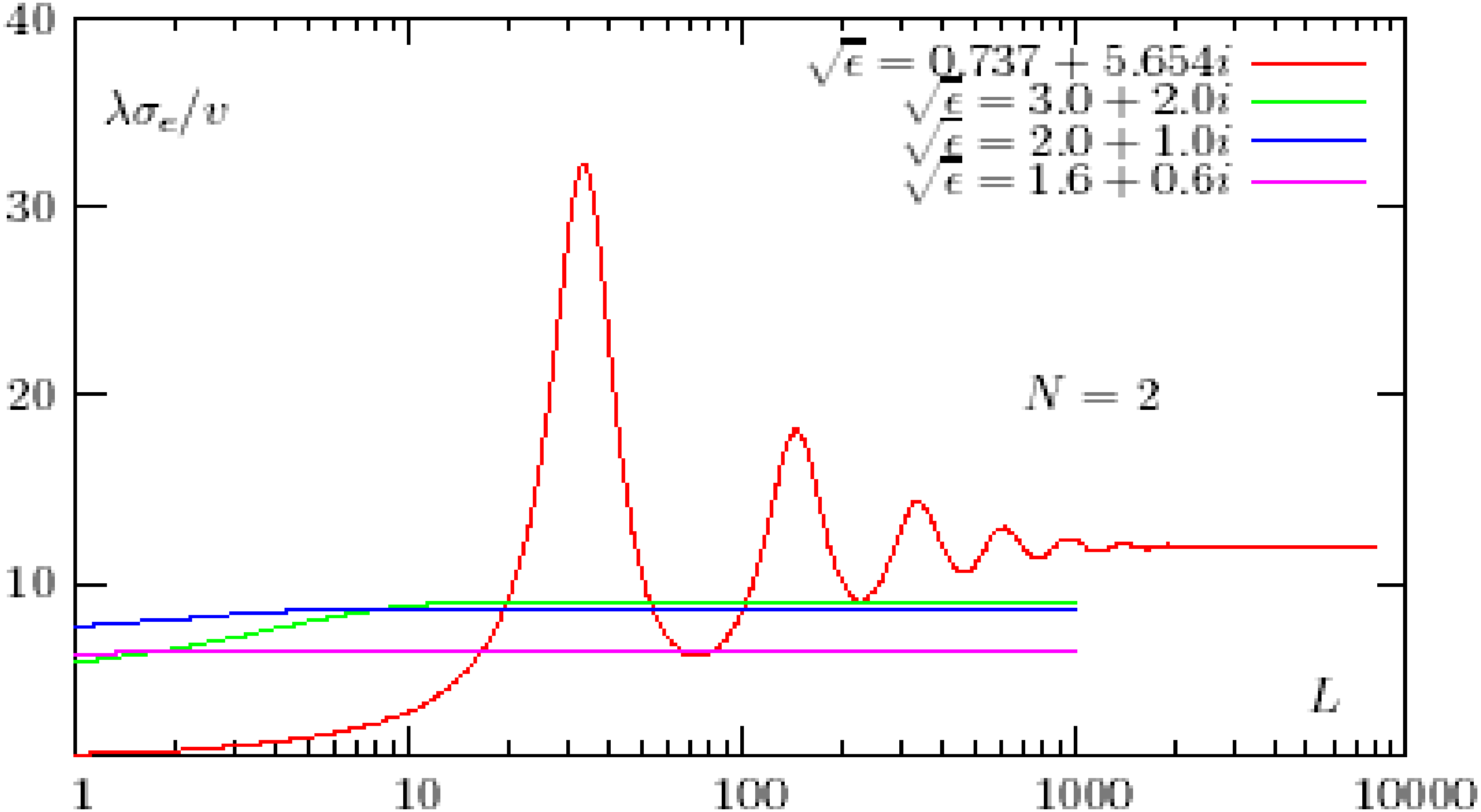
In this limit

$$\varepsilon_e = 4\pi^2 k \Gamma_\delta \left(\frac{4\pi}{3}\right) \propto \begin{cases} 1/\lambda, \text{ if } 4\pi/3 \in \text{"band"} \\ 1/\lambda^2, \text{ if } 4\pi/3 \notin \text{"band"} \end{cases}$$

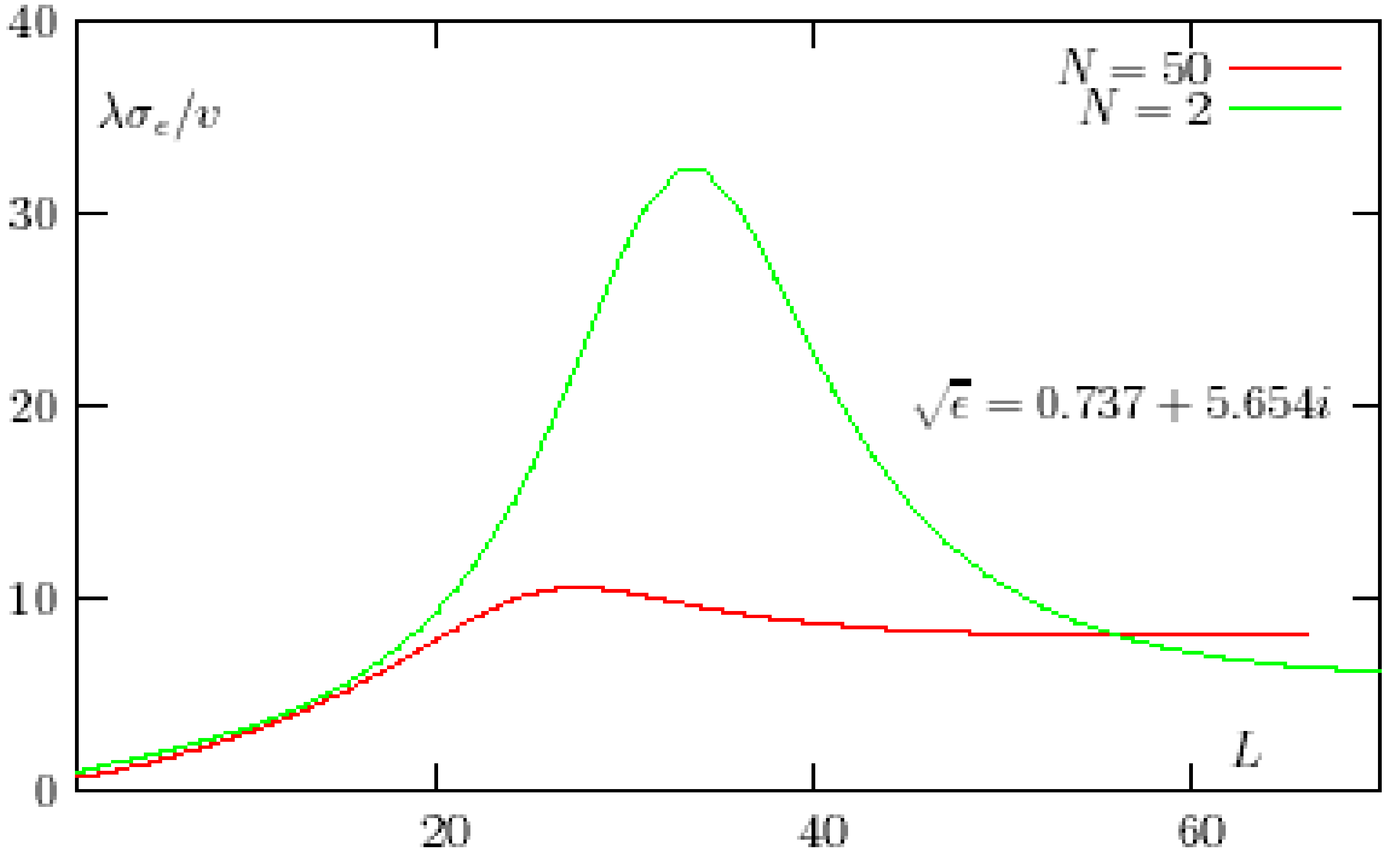
Convergence with CF order (*N*=50)



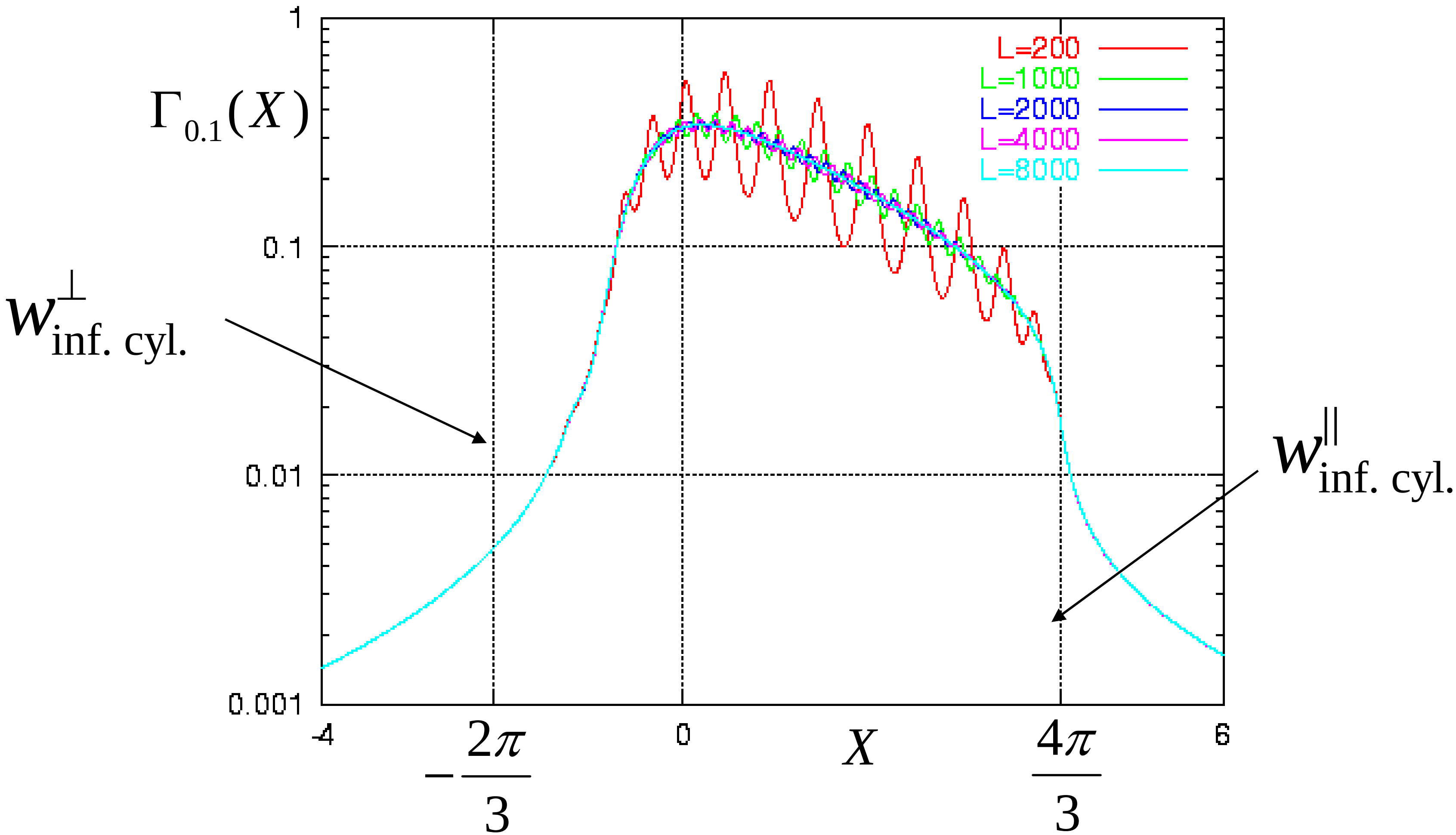
Convergence of Extinction Cross Section with *L* (*N*=2)



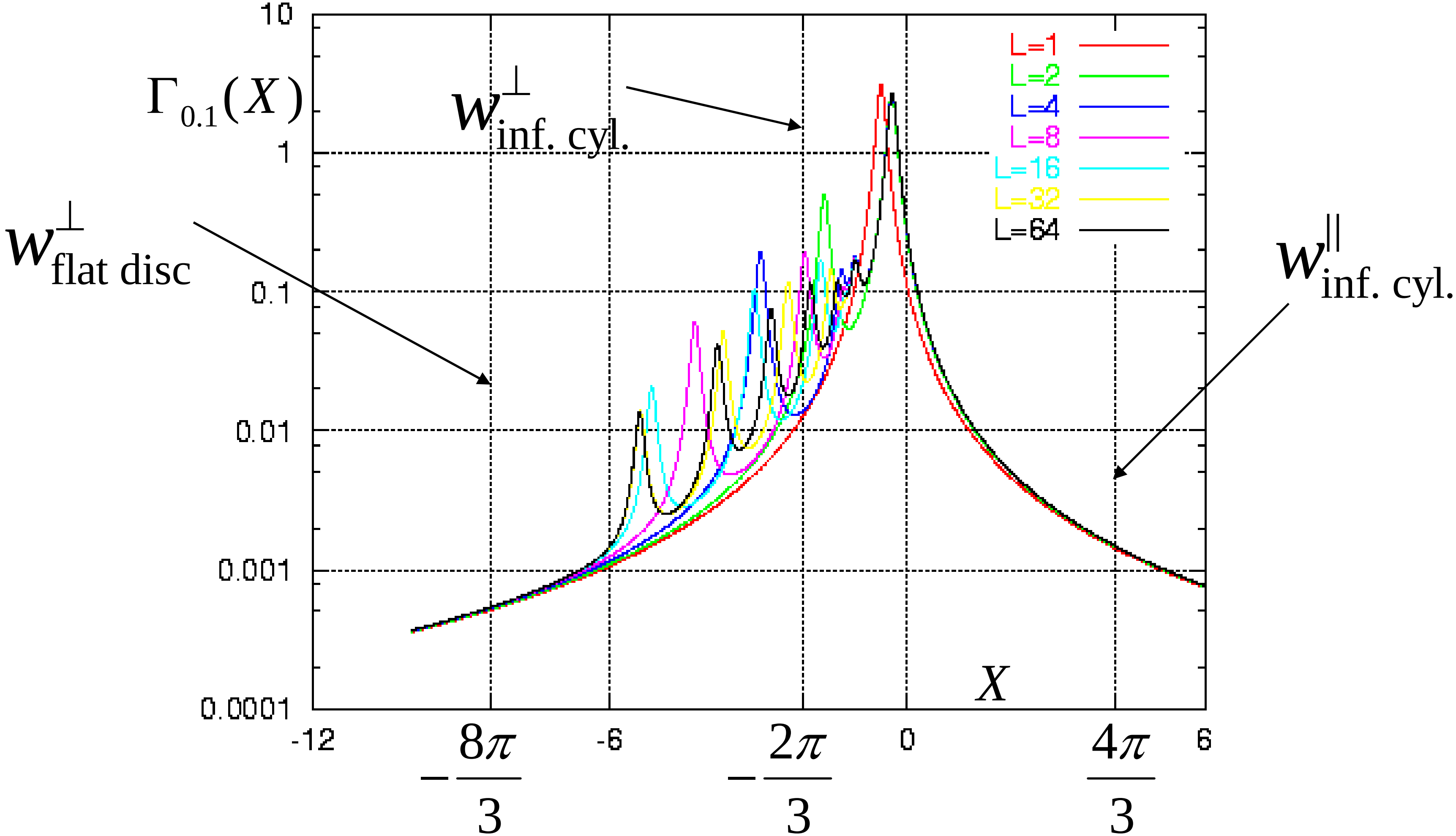
Convergence of Extinction Cross Section with L (N=50 vs N=2)



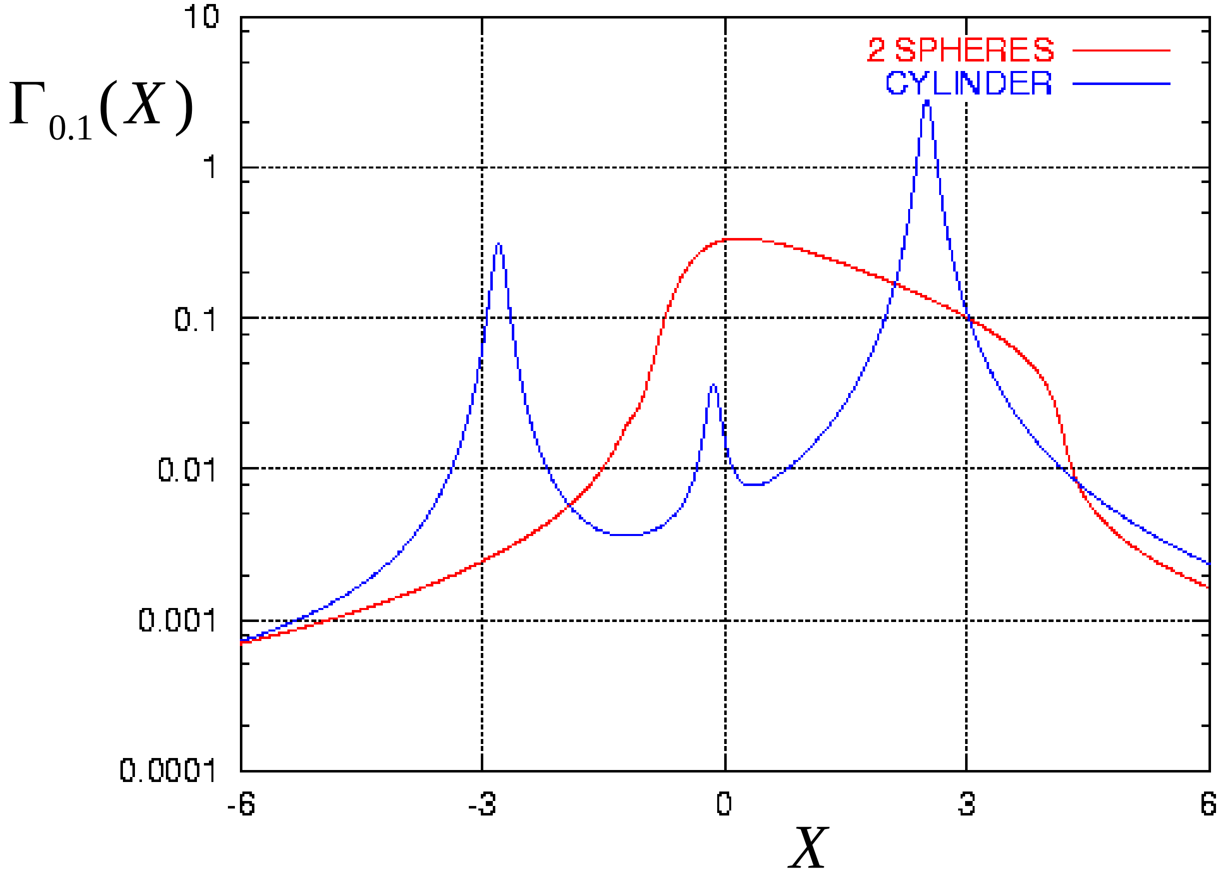
Convergence of DOS with *L*: (*N*=2, Parallel Polarization)



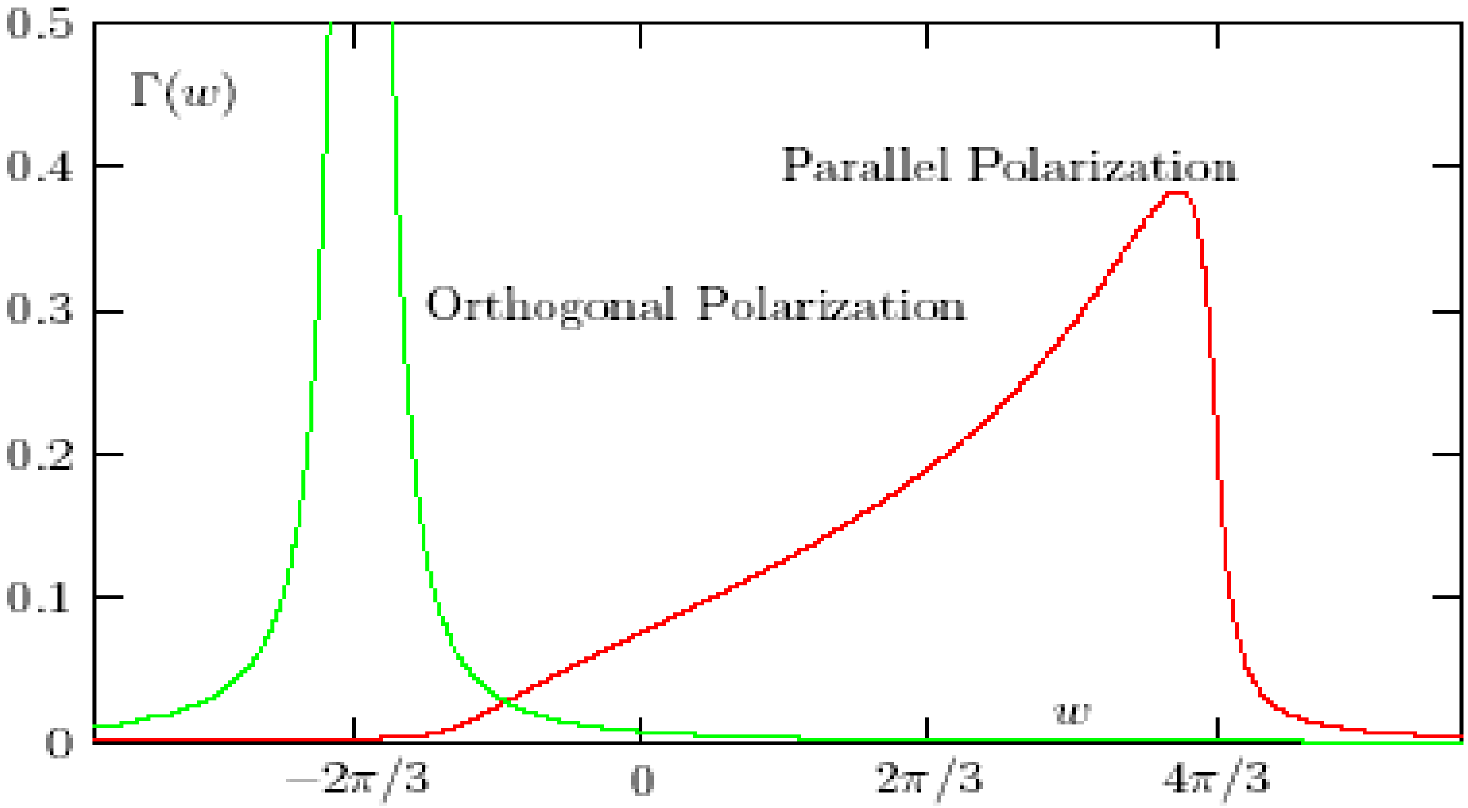
Convergence of DOS with *L*: (*N*=2, Parallel Polarization)



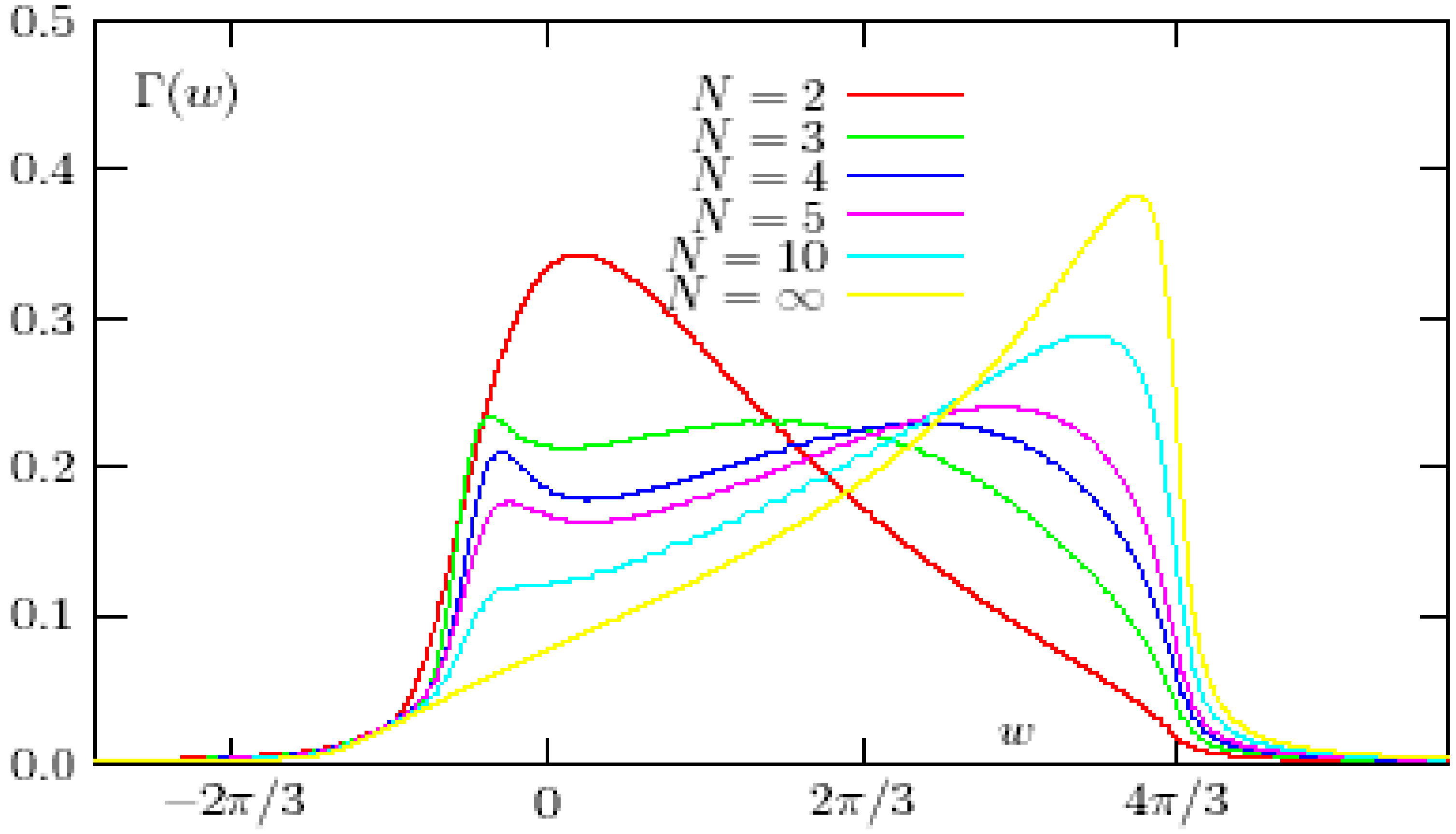
Comparison of DOS: Two Spheres and Cylinder (Parallel Polarization)



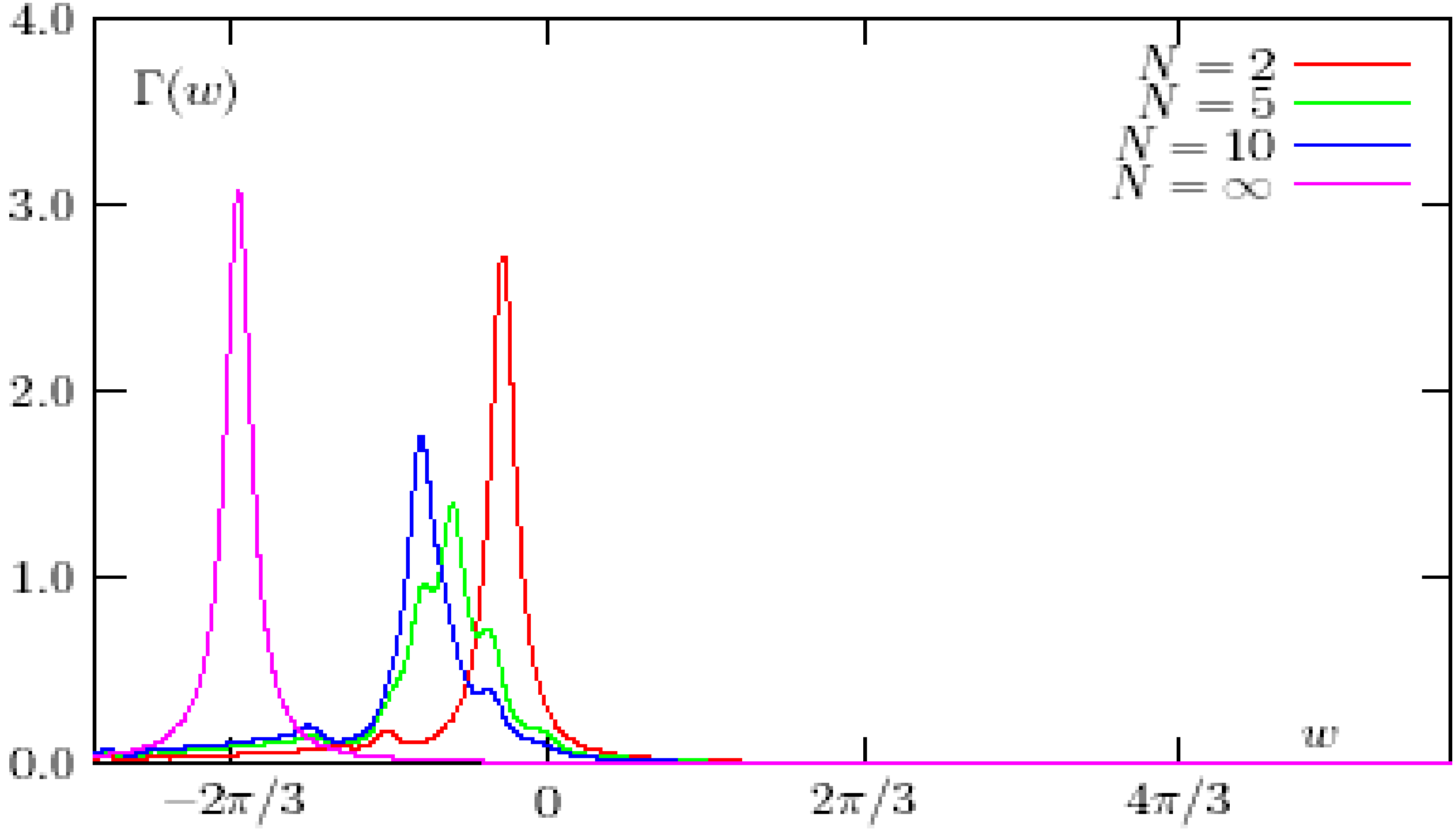
DOS for an Infinite Linear Chain



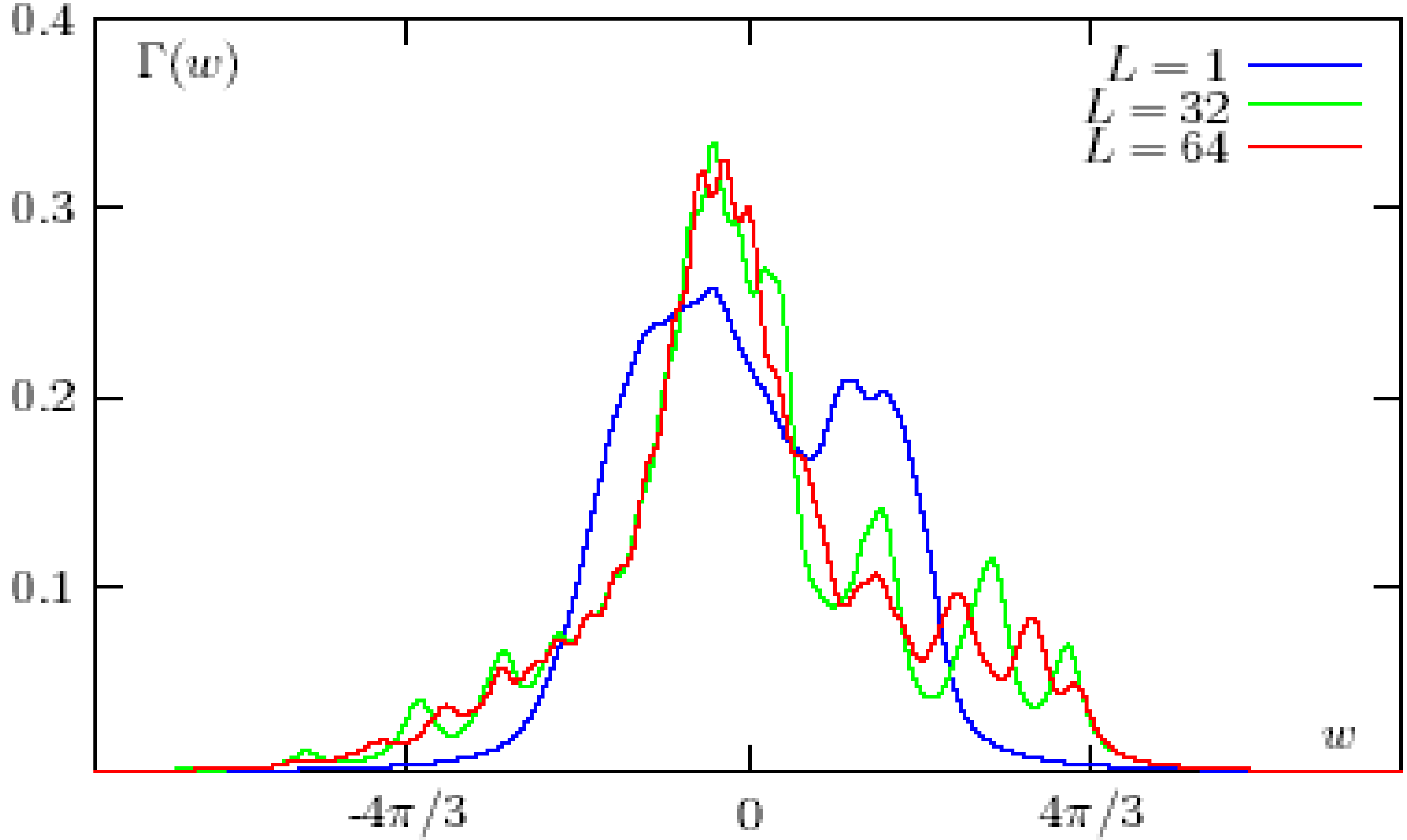
DOS for Linear Chains of Different Length (Parallel Polarization)



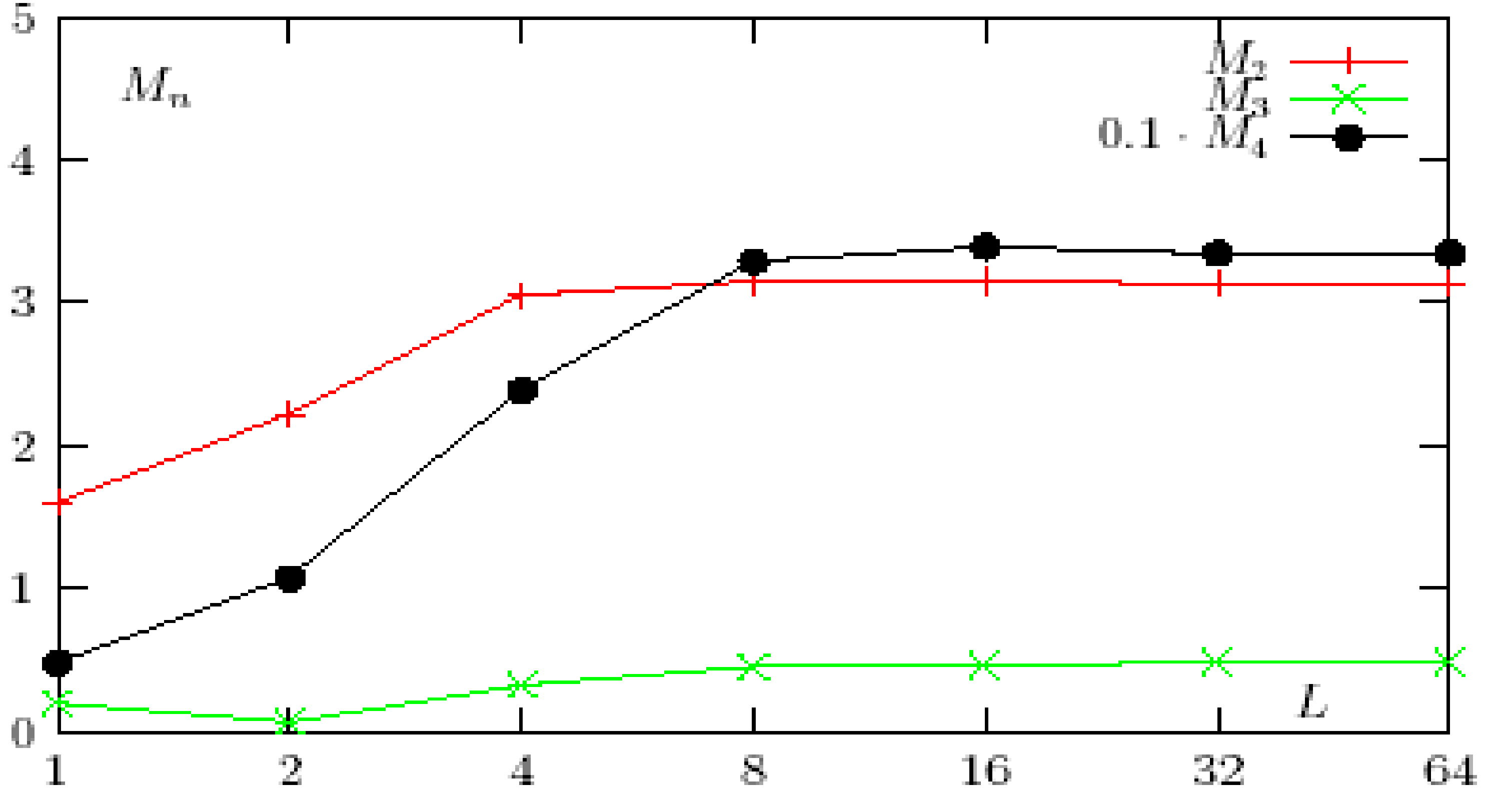
DOS for Linear Chains of Different Length (Orthogonal Polarization)



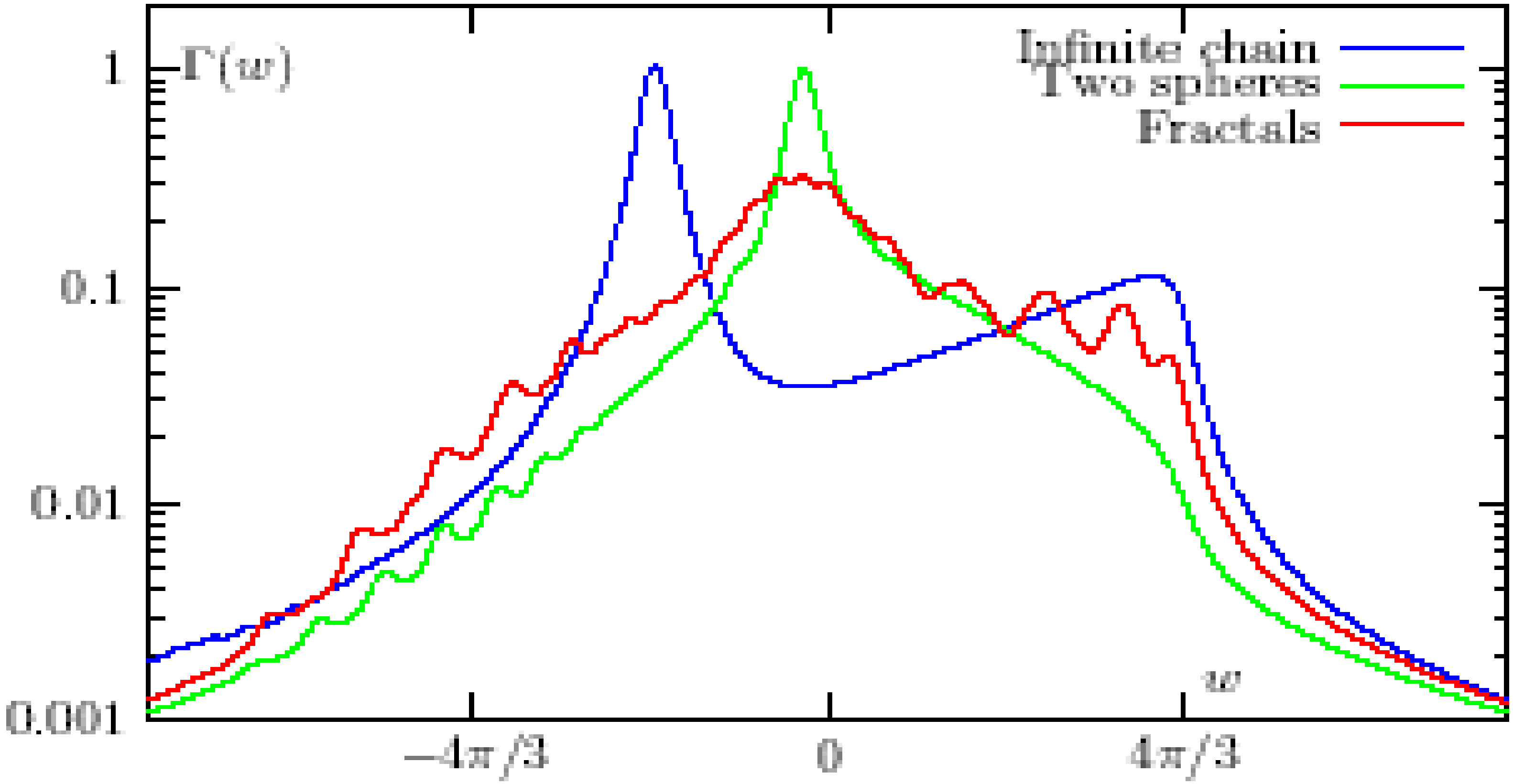
DOS for a lattice CCA cluster for Different *L* (*D*=1.8)



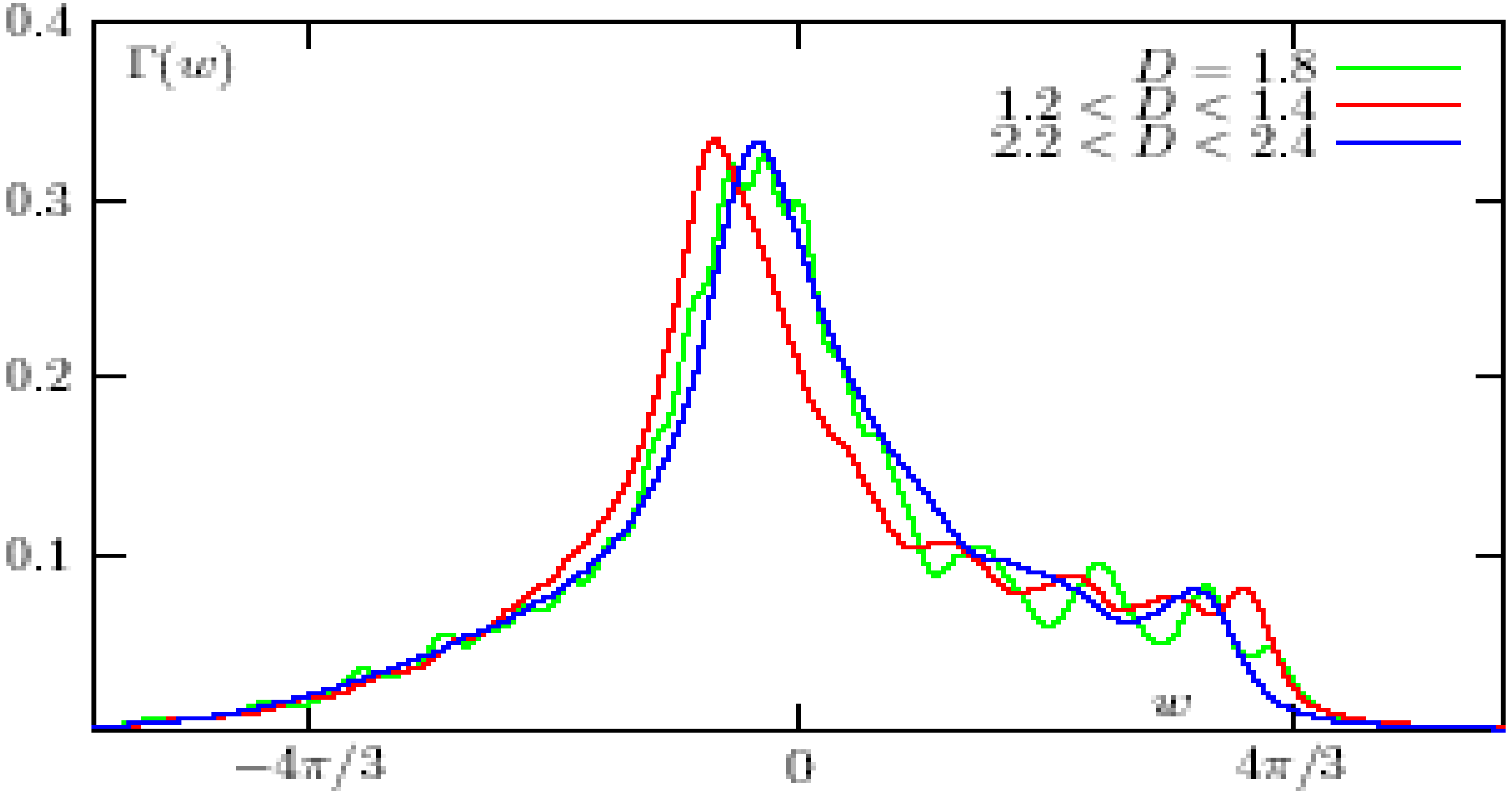
Convergence of the First few Moments of DOS with *L*



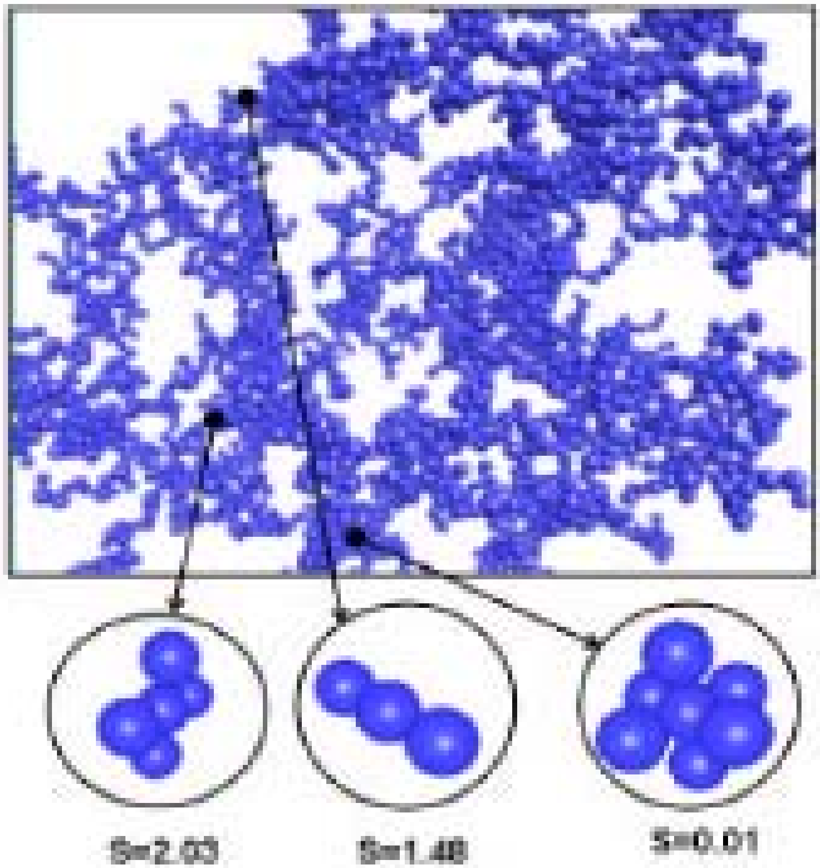
Rotationally Averaged DOS for Different Types of Aggregates



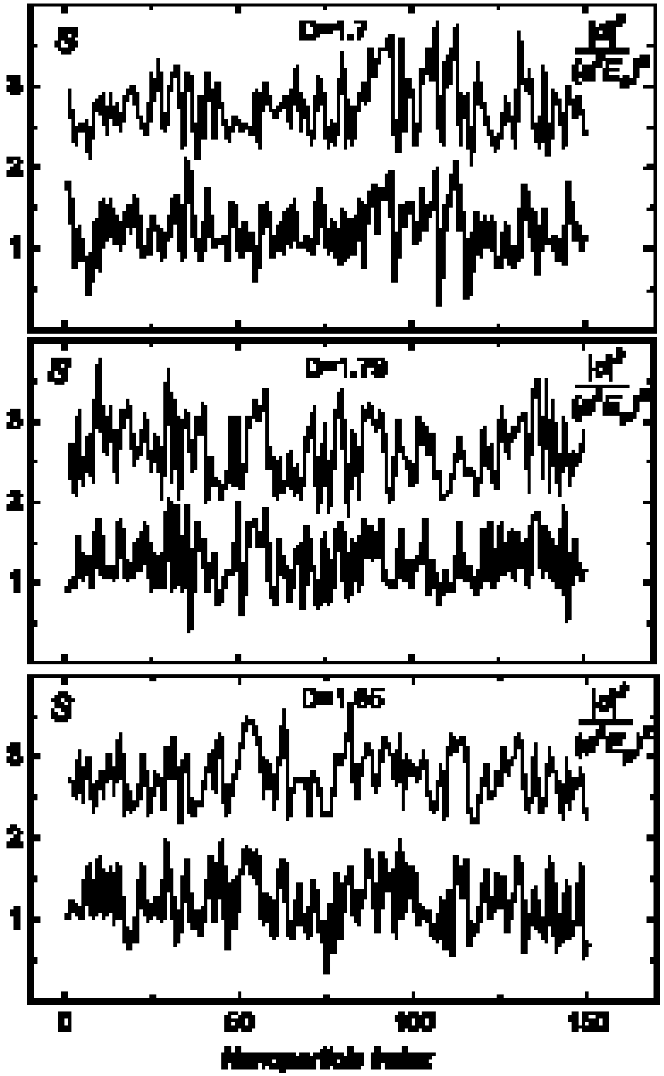
Rotationally Averaged DOS for Offlattice Fractal Aggregates with Different *D*



Local Anisotrropy Factor



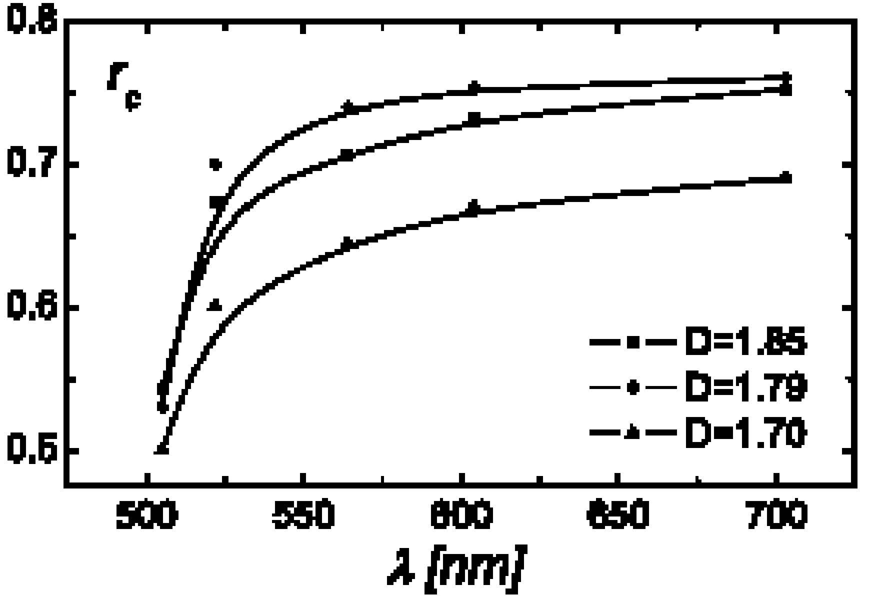
Local Dipole Moments vs. Local Anisotropy Factor



L=16

h = 0.05*R* (surface layer)

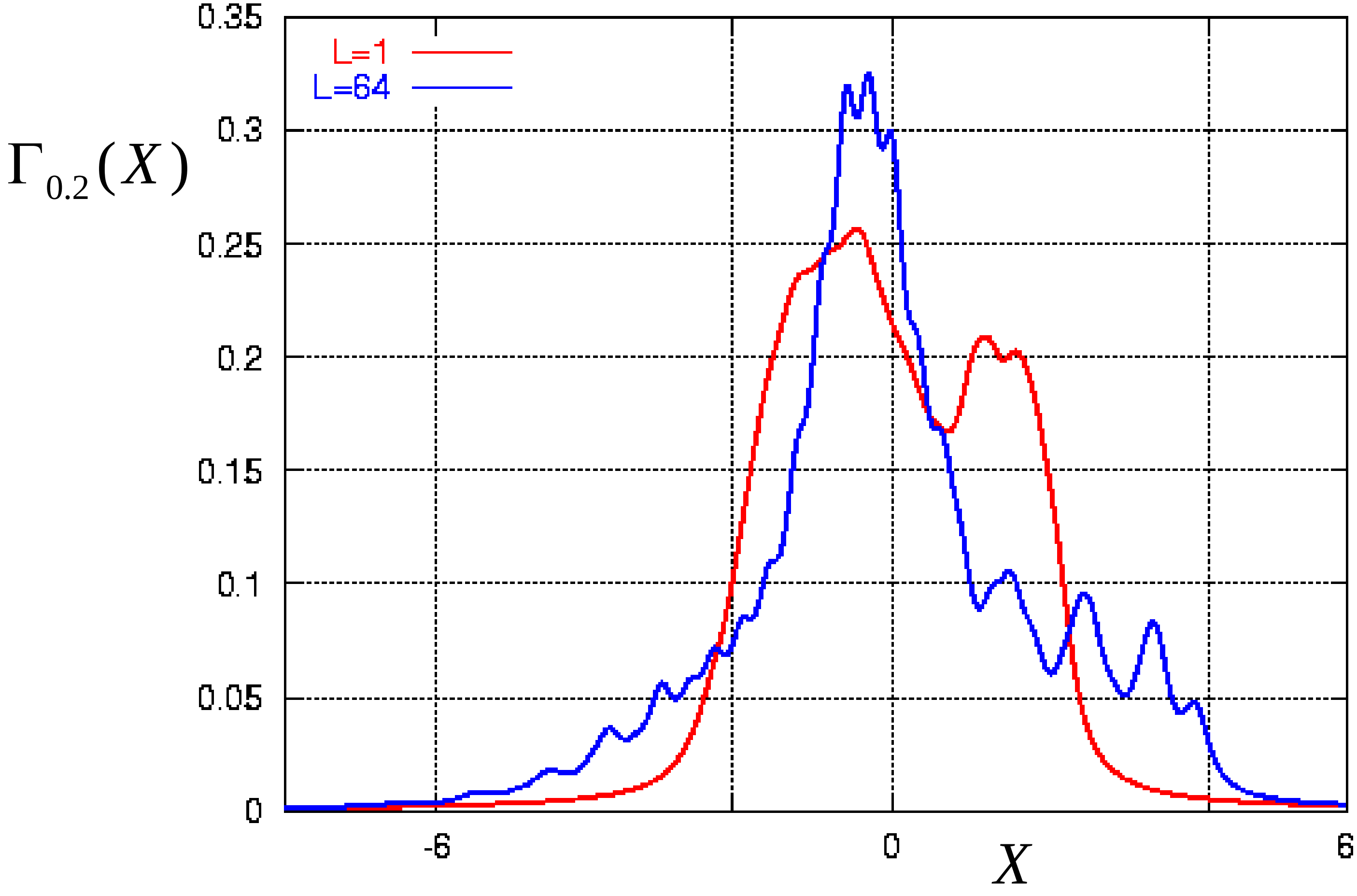
Correlation of Local Dipole Moments and Local Anisotropy Factors



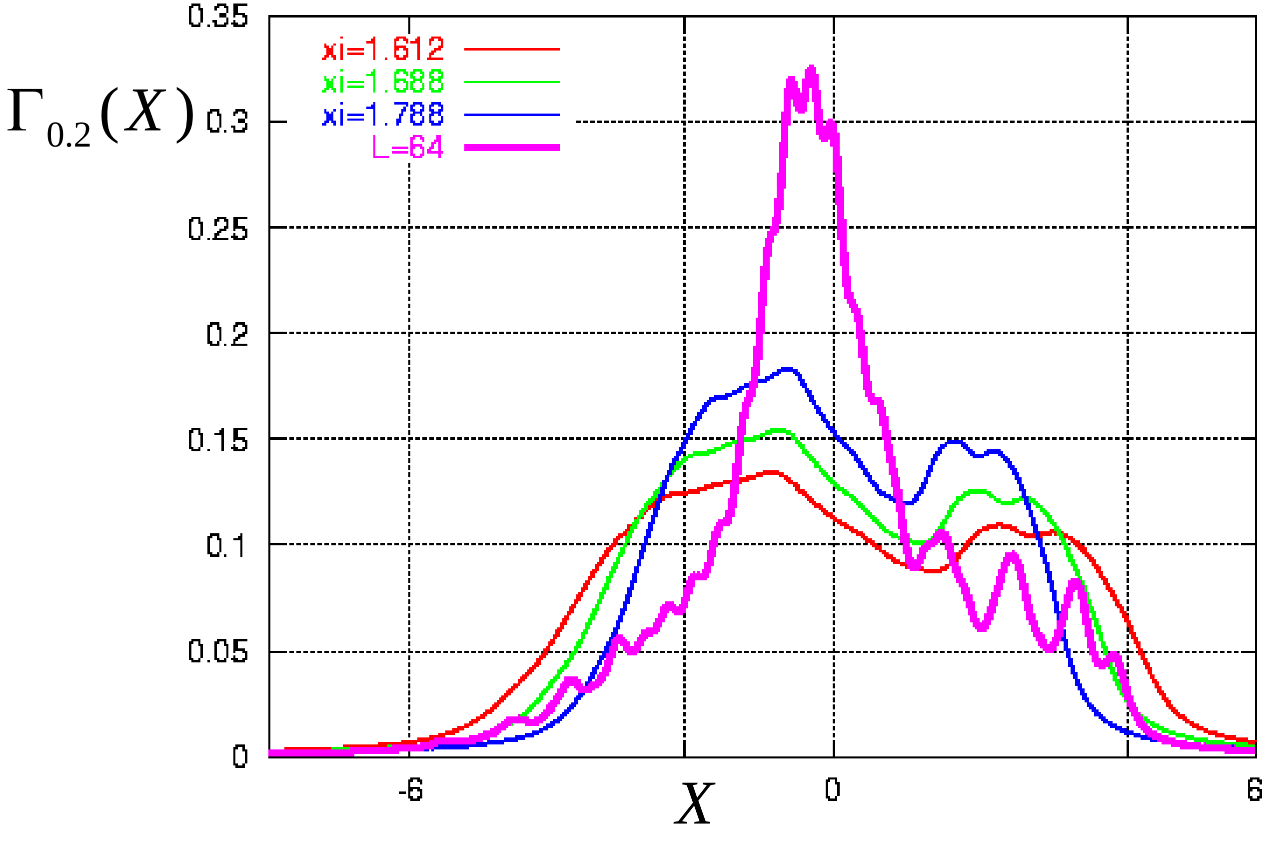
CONCLUSIONS

- For touching metal spheres, very high orders of multipole meoments must be taken into account
- Correspondingly, internal fields inside the nanospheres is highly inhomogeneous
- This has important consequences for nonlinear susceptibilities (more work must be done)
- Optical properties of large fractal aggregates are much more determined by local geometry than previously thought. Large scale structure plays, perhaps, a minor role.
- Lattice and off-lattice fractal aggregates have similar electromagnetic properties after rotationalo averaging.

Fractals: Dipole approximation vs *L*=64



Renormalized Dipole Approximation DOS vs *L*=64 DOS



From analogy with DDA:

ξ=1.612

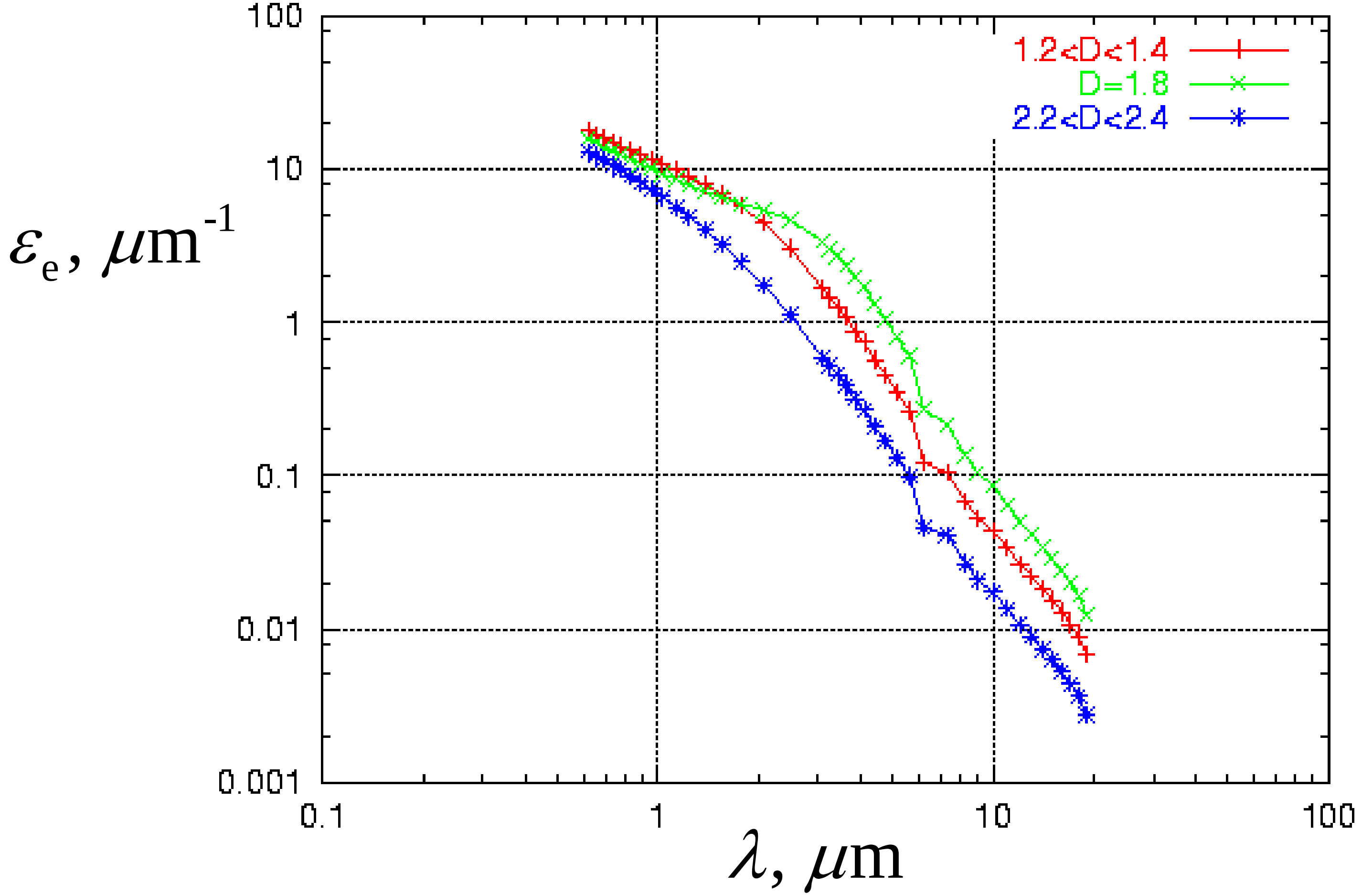
From requirement that a chain of spheres has the same depolarization coefficients as an infinite cylinder:

ξ=1.688

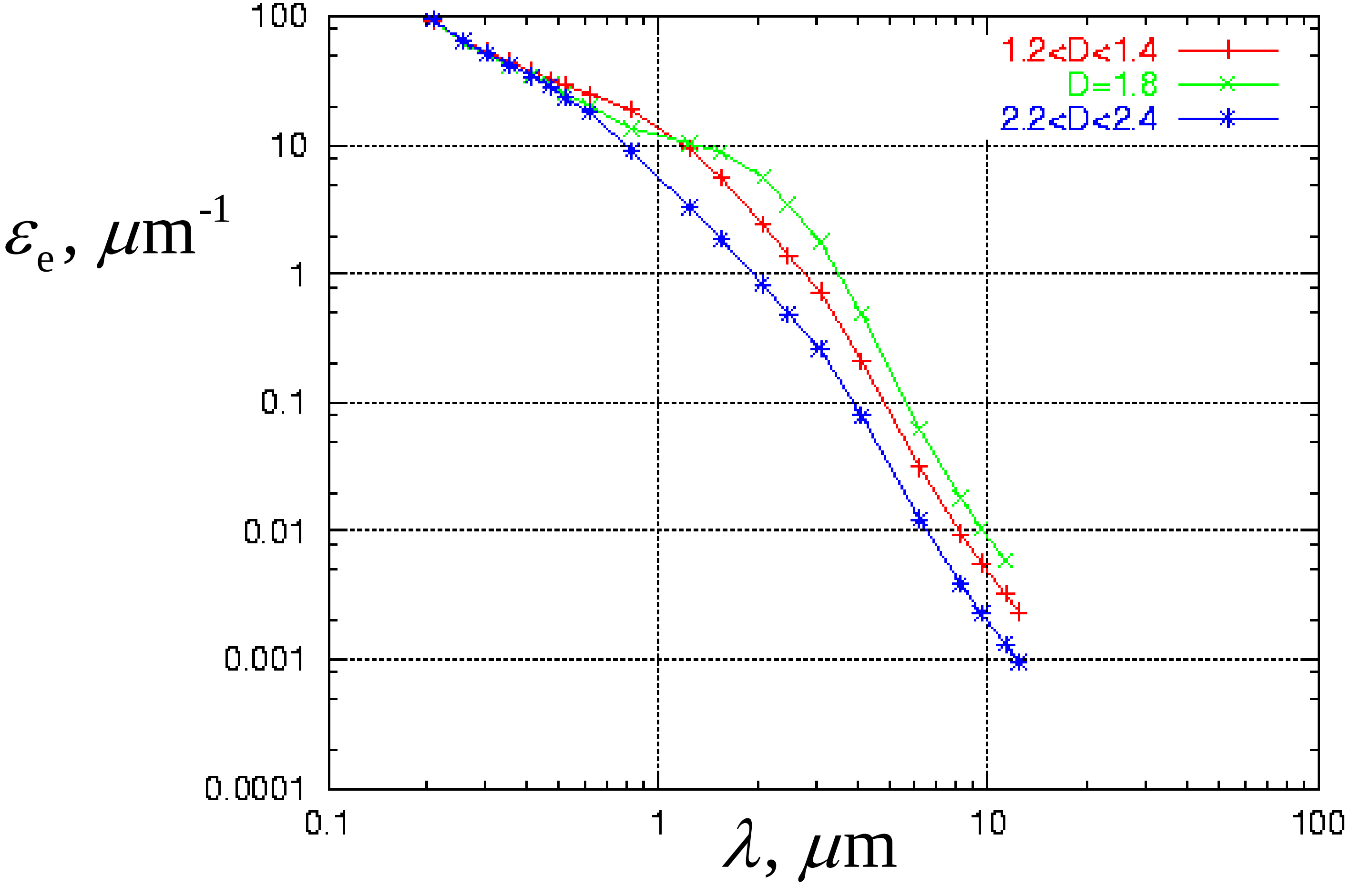
From conservation of the second moment of DOS:

ξ=1.788

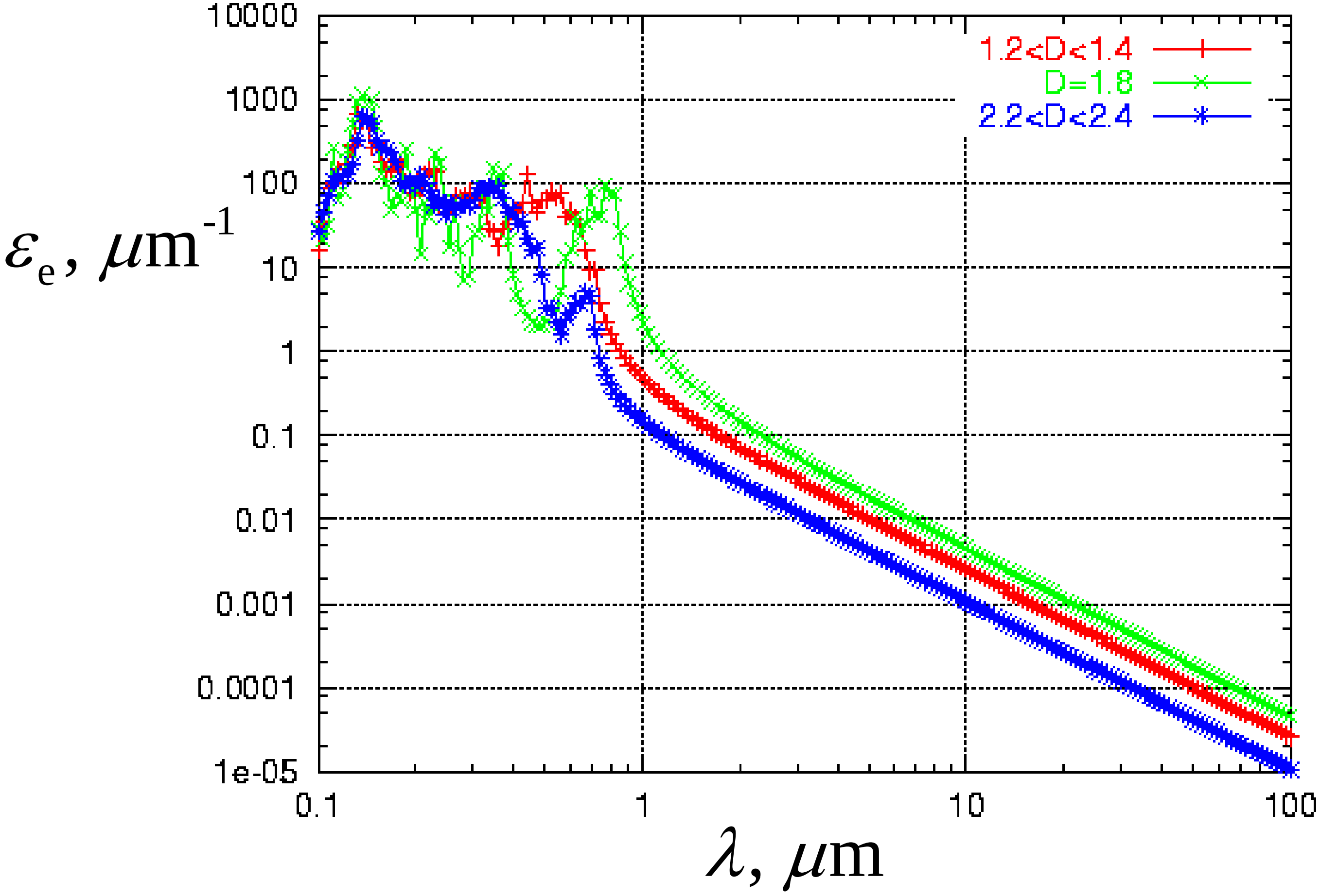
Wavelength Dependence: Clusters with different *D:* Fe



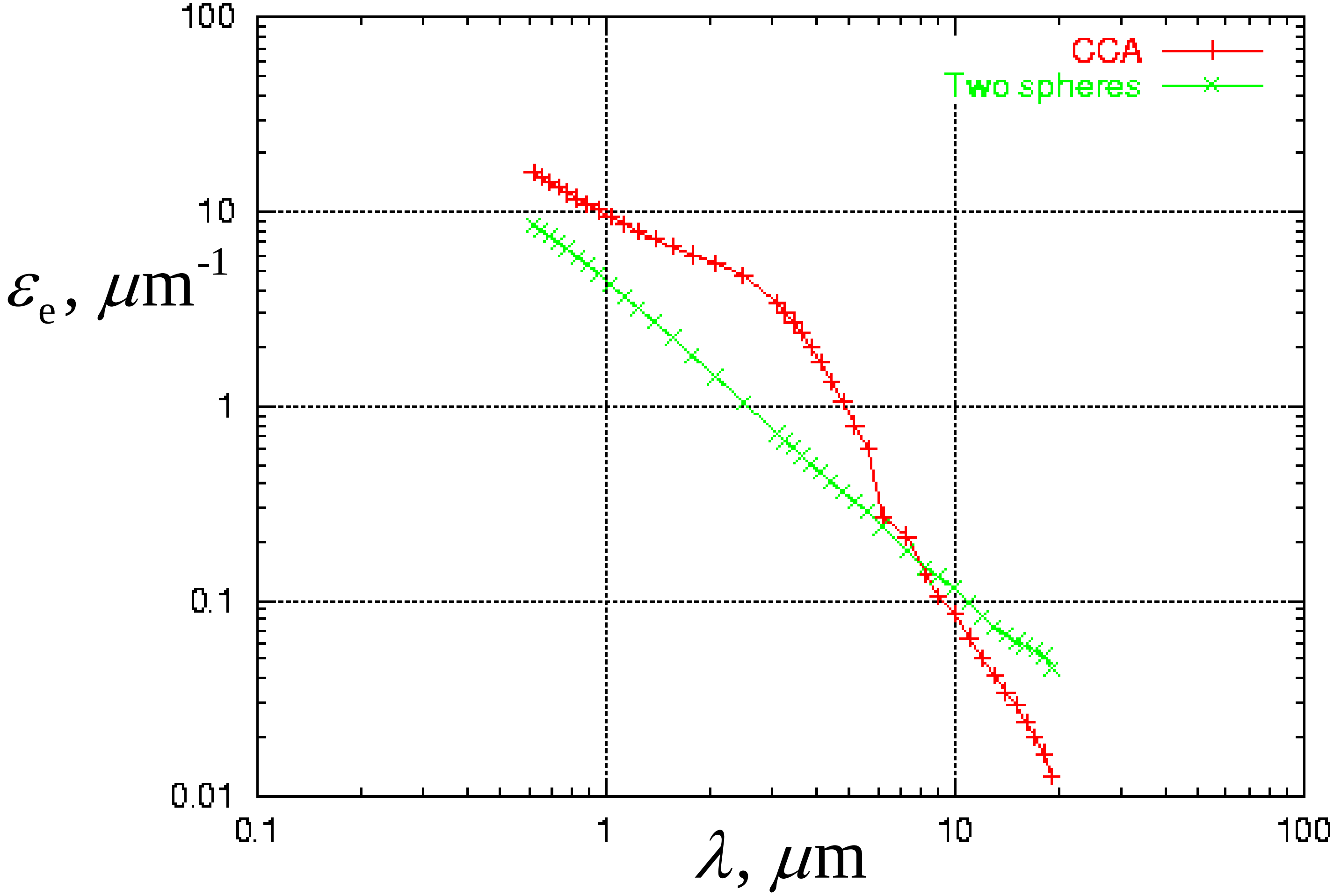
Wavelength Dependence: Clusters with different *D:* Pd



Wavelength Dependence: Clusters with different *D:* Al



CCA Cluster vs. Two Spheres: Fe



CCA Cluster vs. Two Spheres: Pd