Moscow, 23.11.2011

Исследования неидеальной плазмы

SPATIALLY RESOLVED COLLECTIVE EXCITATIONS IN NANO-PLASMAS

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Introduction

Nanoplasmonics

- „optical phenomena in the nanoscale vicinity of metal surfaces“
- absorption and scattering of light from small particles

➔ resonant enhancement of specific frequencies

Lycurgus Cup (400 A.D.)

- wavelength >> nanoscale system
  (planar wave -> longwavelength limit)
- oscillator strength f
  (sum rule of absorption cross section)
- dependence on size/shape, composition/geometry, surrounding dielectric material

M. Stockman, Phys. today 64(2) 39 (2011), arXiv:0908.3559
S. Raza et al., arXiv:1106.2175
T. Sandu et al., arXiv:1104.5666
V.B. Gildenburg et al., Phys. Plasmas 18, 092101 (2011)

Equilibrium correlation functions and transport coefficients (fluctuation-dissipation theorem)

Generalized linear response

$$\epsilon(\vec{k},\omega) = 1 + \frac{i}{\epsilon_0 \omega}\sigma(\vec{k},\omega) = 1 - \frac{\omega_{\rm pl}^2}{\omega(\omega - i\nu(\vec{k},\omega))}$$

Reinholz, Ann. Phys. (Fr) 2005

- generalized statistical operator
- **Kubo** formula vs. generalized **Drude** formula

$$\sigma(\omega) \propto \langle \vec{j}; \vec{j} \rangle_{\omega+i\eta} \qquad \nu(\omega) \propto \langle \vec{F}; \vec{F} \rangle_{\omega+i\eta}$$

dynamical conductivity — dynamical collision frequency

current-current correlation function — force-force correlation function

Zubarev, Morozov, Röpke, *Stat. Mech. of Non-Equilibrium Processes* (1996)

MD simulations, homogeneous plasmas

- bilocal dynamical structure factor, Fourier transform
- wave vector *k* to characterize collective excitations

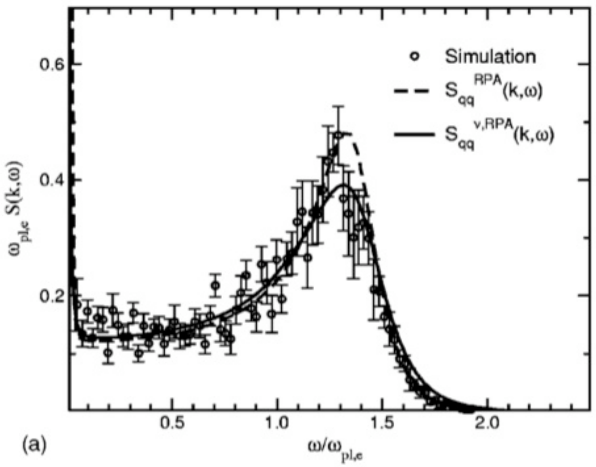
$$S(\vec{k},\omega) = \frac{1}{\pi\, V(k)}\ \frac{1}{\mathrm{e}^{-\beta\hbar\omega}-1}\ \mathrm{Im}\epsilon_l^{-1}(\vec{k},\omega)$$

different auto-correlation functions (ACF):
current-current, force-force, density-density

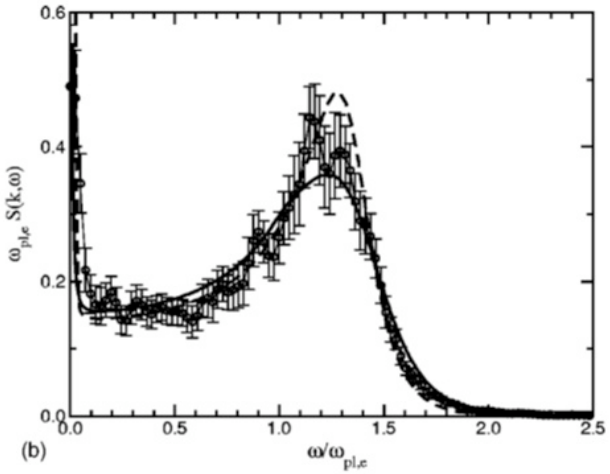
$$\varepsilon_l^{-1}(k,\omega) \propto \frac{1}{\omega}\left\langle j_k^z; j_k^z \right\rangle_{\omega+i\eta} \propto \frac{\omega}{k^2}\left\langle \delta n_k; \delta n_k \right\rangle_{\omega+i\eta}$$

Dynamical structure factor for H plasmas

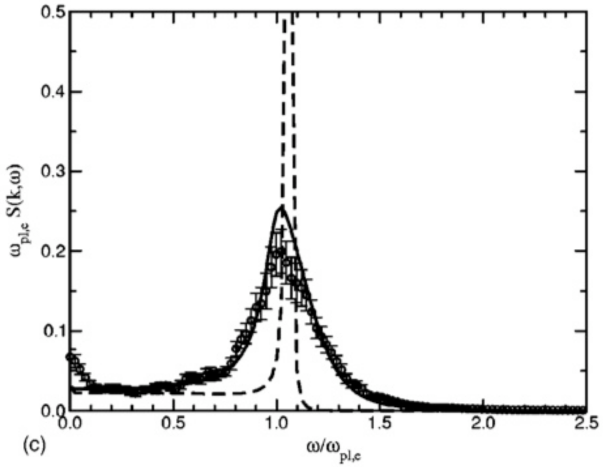
Γ=0.5
k/κ=0.51



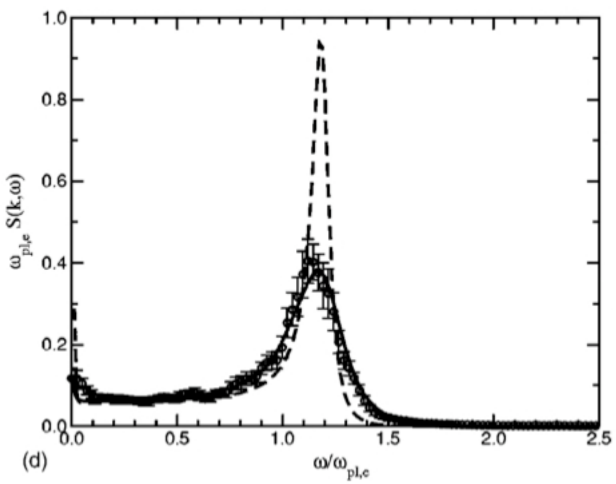
Γ=1
k/κ=0.51



Γ=2
k/κ=0.25



Γ=1
k/κ=0.36



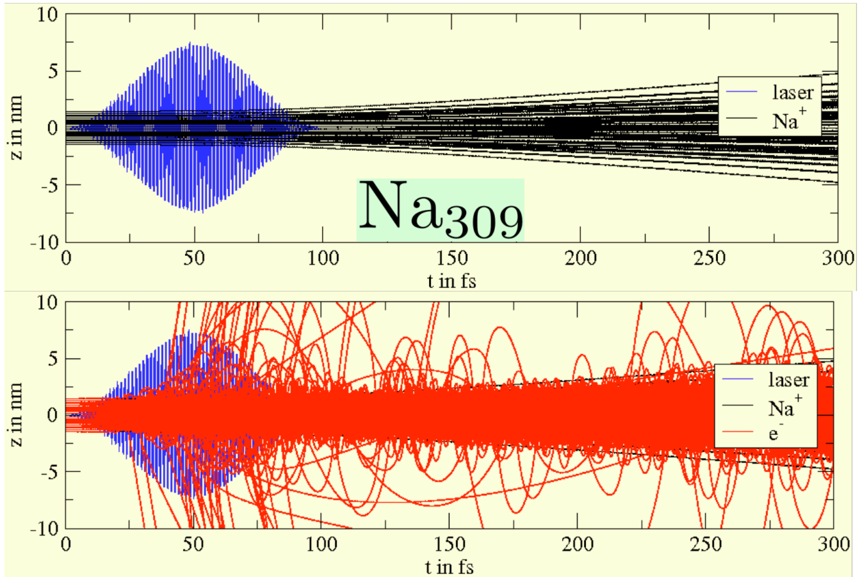
A. Selchow et al., Phys. Rev. E 64, 056410 (2001)

Finite size plasmas

Nanoplasma in laser excited clusters

sodium as exemplary system

- initial conditions: room temperature, solid density (2.8 10^{22} cm^{-3})
- isocahedral structure (Na_{55}, Na_{147}, Na_{309}) and randomly distributed (Na_{309},Na_{1000})
- intense short pulse laser (λ=436 nm, Δt =50fs, I=10^{12} W cm^{-2})



time evolution investigated via
MD simulations:
inner ionization, charging of cluster, density, temperature

correlation functions -> optical properties

Raitza et al, IJMPB 21 (2007) 2460; PRE 84, 214048 (2011)

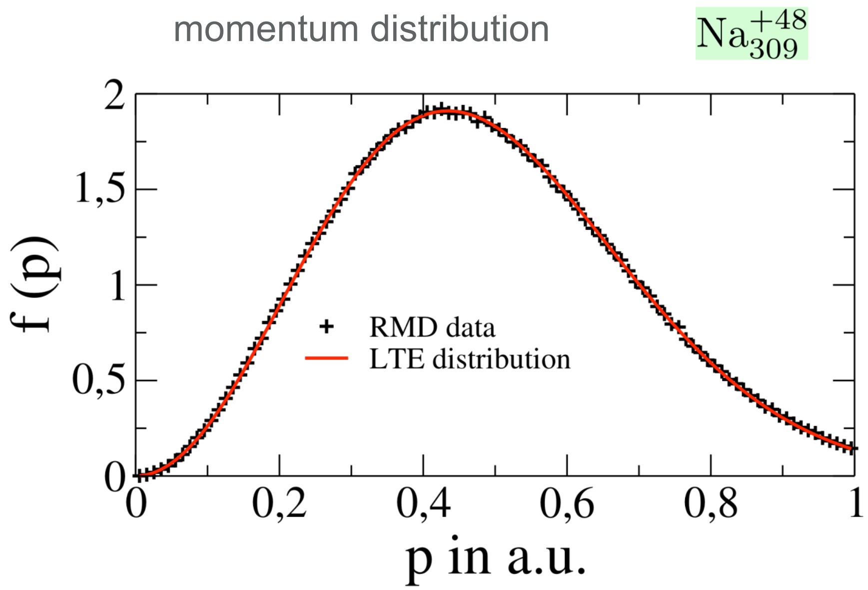
Two-time distributions: RMD

Restricted MD simulation scheme

- observed local thermal equilibrium justifies restricted MD (RMD)

ensemble average ➔ time average of trajectories for frozen ion configuration at fixed time

T= 6.35 eV (parameters for t=100 fs)



- auto correlation functions
- bi-local correlation matrix

➔

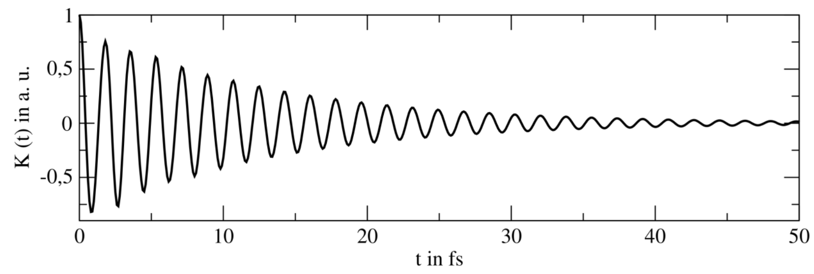
correlation effects

- collective excitations
- collisional damping

Raitza et al, CPP 49 (2009) 498

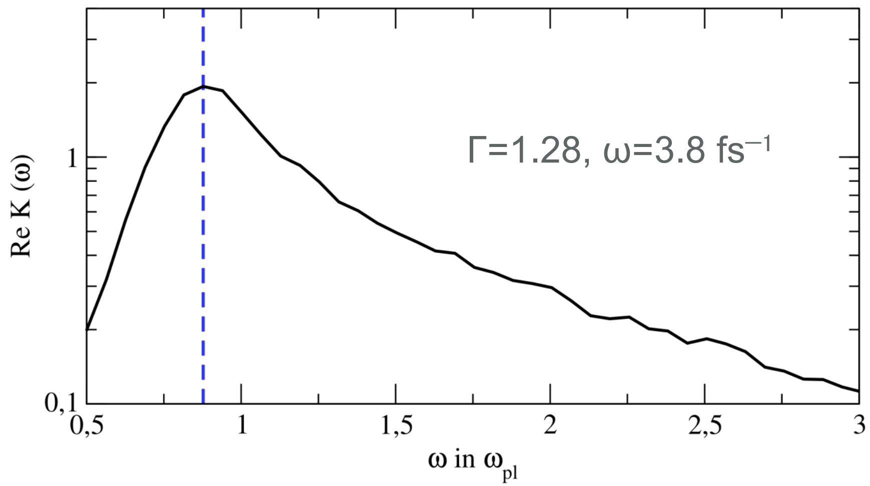
Frequency spectrum of correlation functions

$$K(t) = \frac{1}{\langle J^2 \rangle} \frac{1}{\delta} \int_0^\delta d\tau \, J^z(t+\tau) J^z(\tau)$$

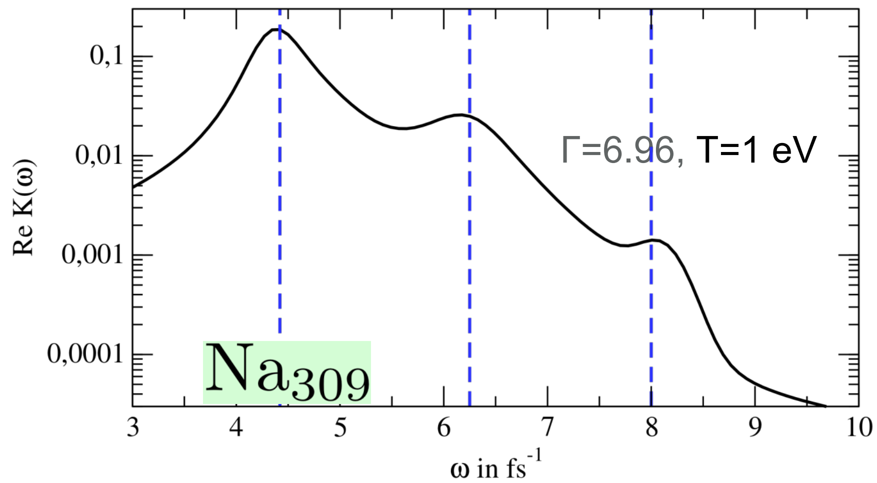


- Laplace transform *K(ω)* of total current density auto-correlation functions

bulk MD



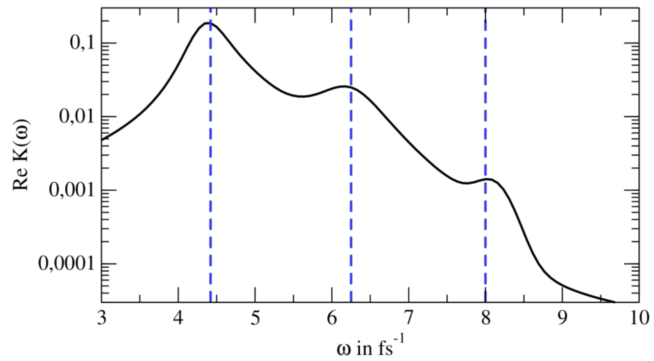
RMD cluster



H. Reinholz et al., PRE 69 (2004)

T. Raitza et al., JPA 42 (2009)

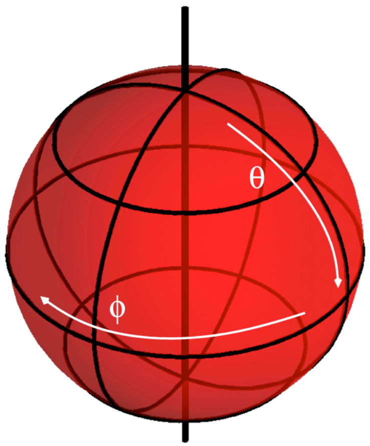
Plasma excitations



Resonances in finite systems

- multiple resonance structure obtained from RMD
- decomposition into spatially resolved correlations functions in order to find cross correlations

$$K(\vec{r},\vec{r}',t) = \frac{1}{N_\tau}\sum_{a=1}^{N_\tau} J(\vec{r},t+a\cdot\tau)\cdot J(\vec{r}',a\cdot\tau)$$



$$K(\omega) = \int\int \mathrm{d}^3\vec{r}\,\mathrm{d}^3\vec{r}'\, K(\vec{r},\vec{r}',\omega)$$

$$= \int\int \mathrm{d}^3\vec{r}\,\mathrm{d}^3\vec{r}'\, \sum_\nu \Psi_\nu(\vec{r},\omega)\, K_\nu(\omega)\, \Psi_\nu(\vec{r}',\omega)$$

- solving eigenproblem for resonance strength K_μ and spatial mode structure Ψ_μ

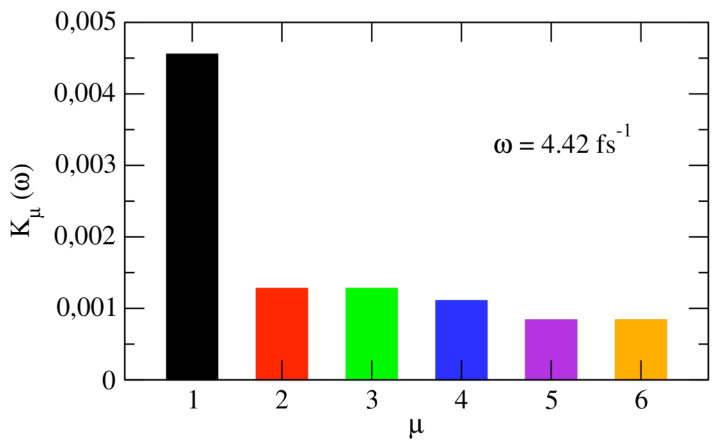
T. Raitza et al., JPA 42 (2009) 214048, T. Raitza et al., PRE 84, 036406 (2011)

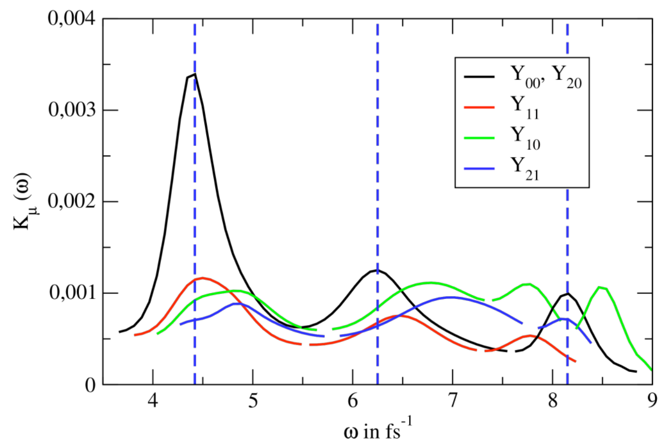
Plasma excitations

Eigenvalue spectrum

taking into account symmetries in bi-local correlation matrix

$$\int \mathrm{d}r' K(\vec{r},\vec{r}',\omega)\Psi_\mu(\vec{r}',\omega) = K_\mu(\omega)\Psi_\mu(\vec{r},\omega)$$





Na_{309} @ T_e=1.96 eV and n_e=5.2 10^{21} cm^{-3}

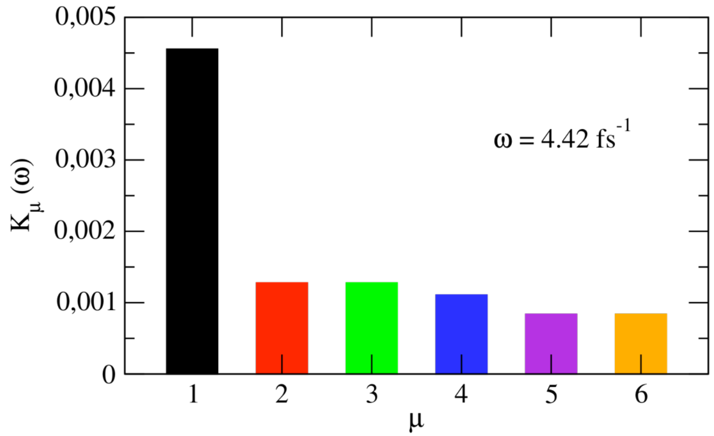
T. Raitza et al., PRE 84, 036406 (2011)

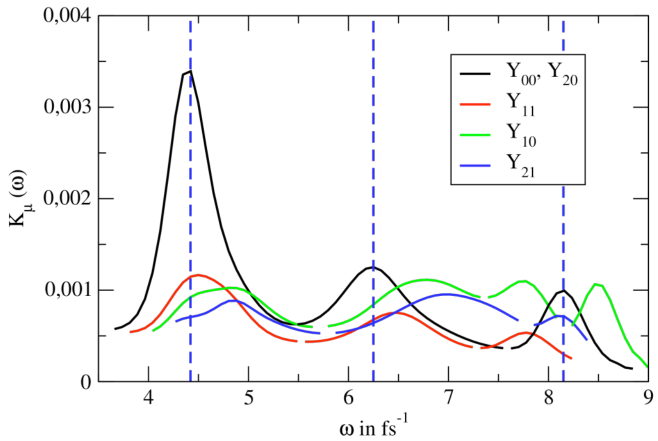
Plasma excitations

Eigenvalue spectrum

$$\int \mathrm{d}r' K(\vec{r},\vec{r}',\omega)\Psi_\mu(\vec{r}',\omega) = K_\mu(\omega)\Psi_\mu(\vec{r},\omega)$$

$$= K_\mu(\omega) \sum_{n=1}^{N_r} \sum_{l=0}^{N_\theta} \sum_{m=-l}^{l} S_{nlm}\, j_l(k_{nl} r)\, Y_{lm}(\theta,\phi)$$



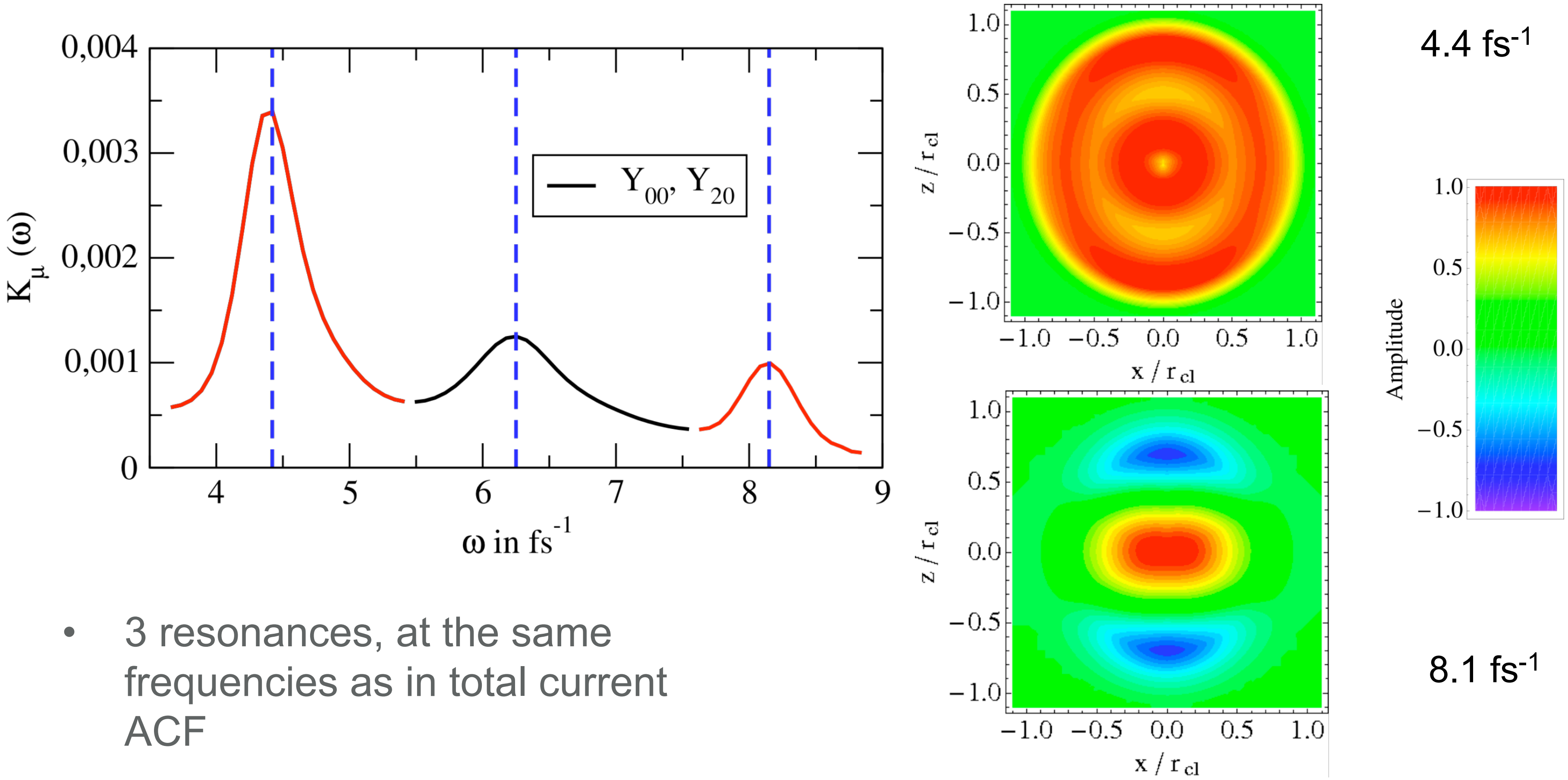


Na_{309} @ T_e=1.96 eV and n_e=5.2 10^{21} cm^{-3}

T. Raitza et al., PRE 84, 036406 (2011)

Plasma excitations

Fundamental dipole mode



4.4 fs^{-1}

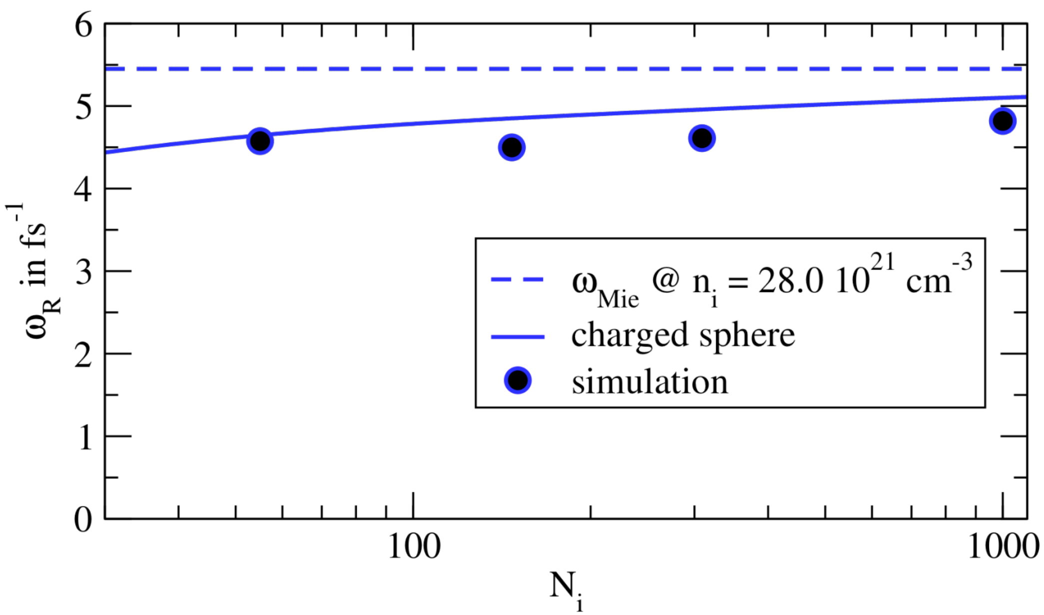
8.1 fs^{-1}

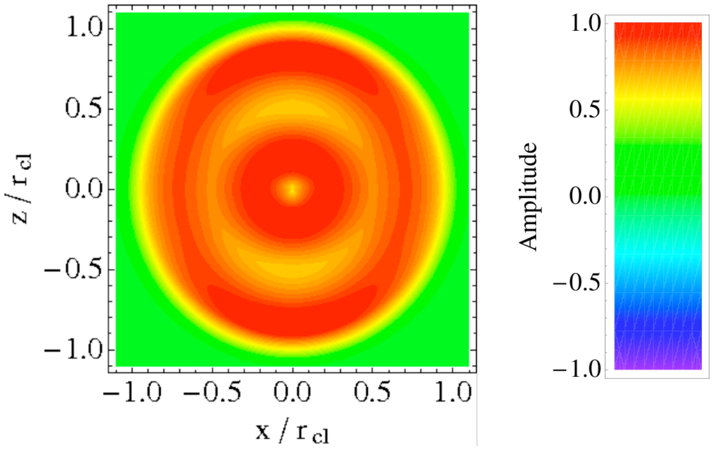
- 3 resonances, at the same frequencies as in total current ACF

T. Raitza et al., PRE 84, 036406 (2011)

Plasma excitations

Fundamental dipole resonance



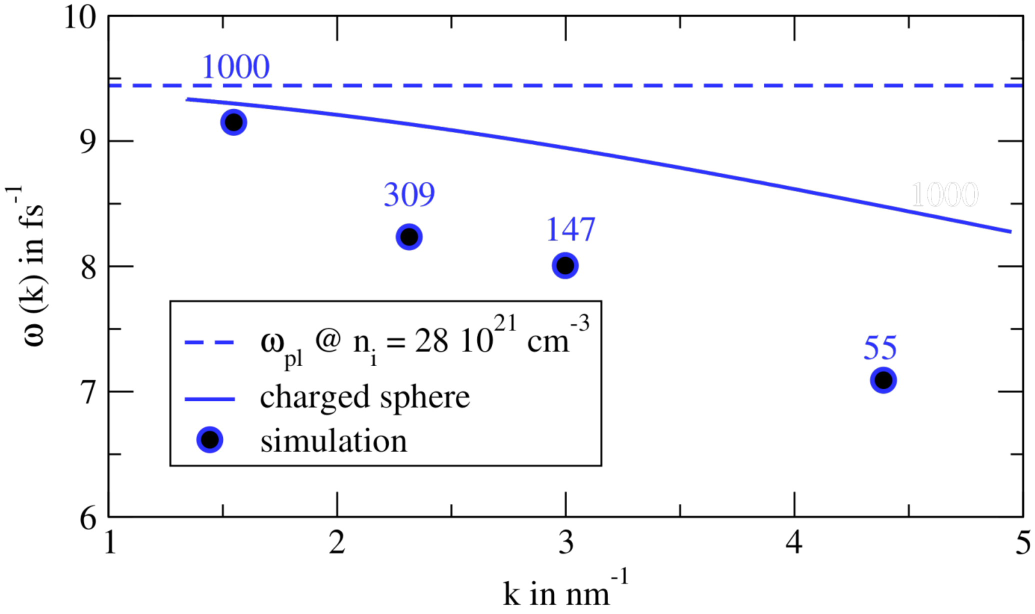


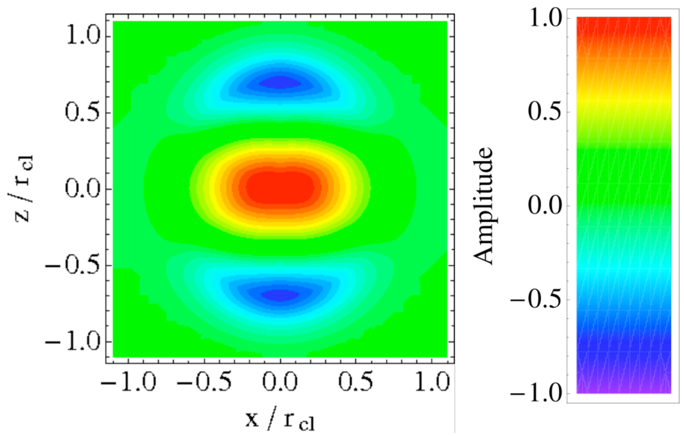
- rigid oscillation of electron density profile in external ion potential
- resonance of surface plasmon in analogy to Mie resonance

T. Raitza et al., PRE 84, 036406 (2011)

Plasma excitations

Dispersion of plane wave mode



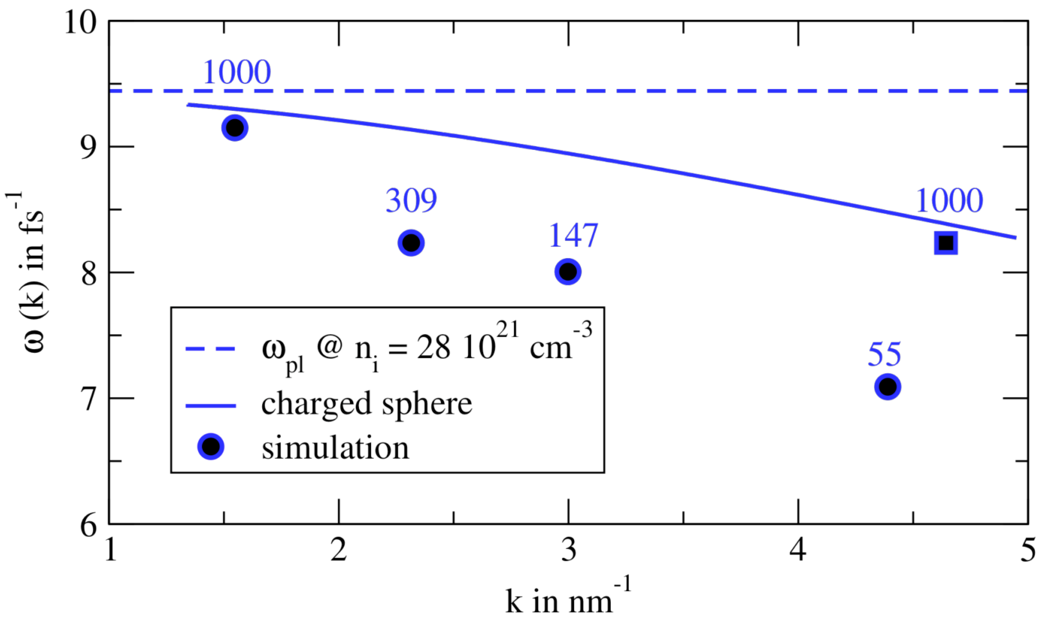


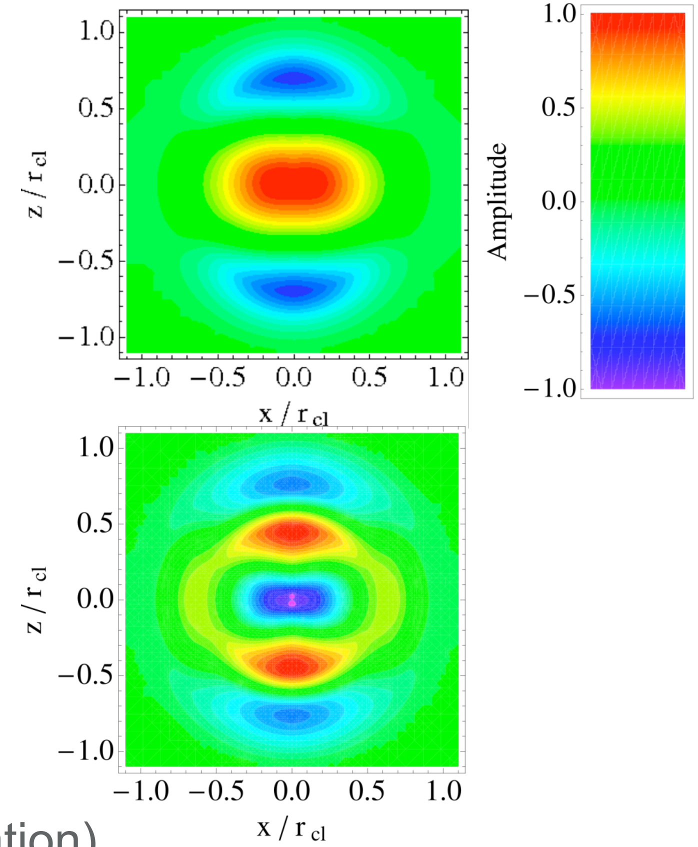
- analogy to volume plasmon resonance in bulk
- plane wave confined within sphere (Euler equation)

T. Raitza et al., PRE 84, 036406 (2011)

Plasma excitations

Dispersion of plane wave mode





- analogy to volume plasmon resonance in bulk
- plane wave confined within sphere (Euler equation)
- for large clusters bulk limit obtained

T. Raitza et al., PRE 84, 036406 (2011)

Some Applications

Collective excitations in metal clusters

- photoabsorption by excited clusters (pump-probe experiments)
- scattering of light
- electron spectra

Collective excitations in other finite many-particle systems

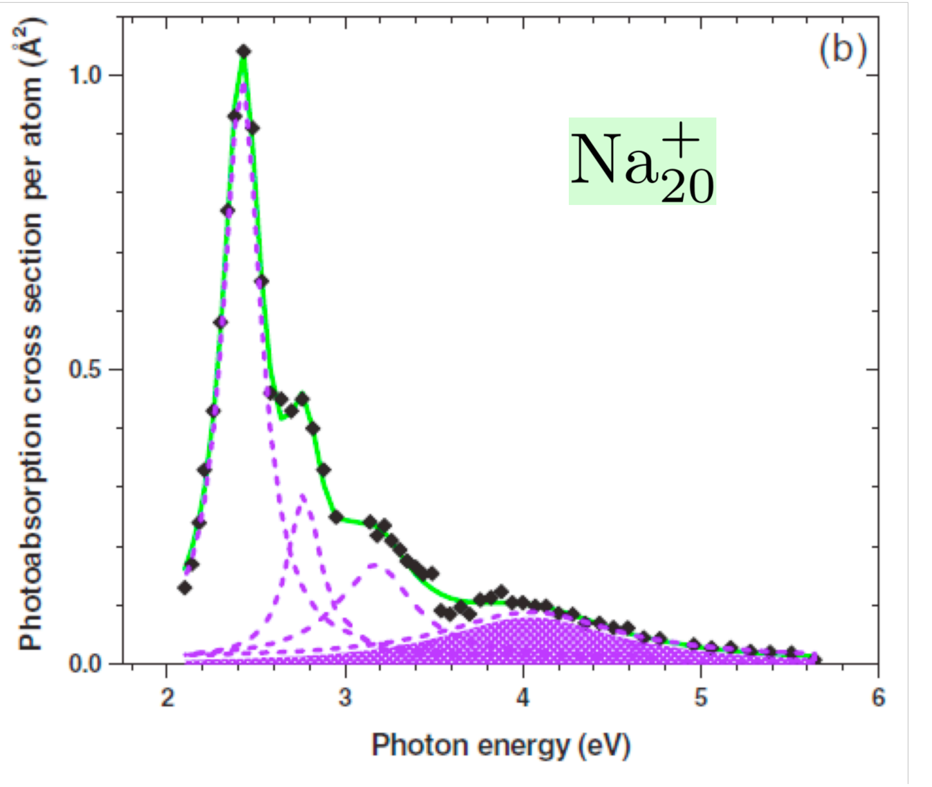
- atomic nuclei (giant dipole resonance, etc.)
- electrons in quantum dots
- dusty plasmas
- etc.

Experimental signatures

Na cluster

experiments on photodepletion absorption cross section:

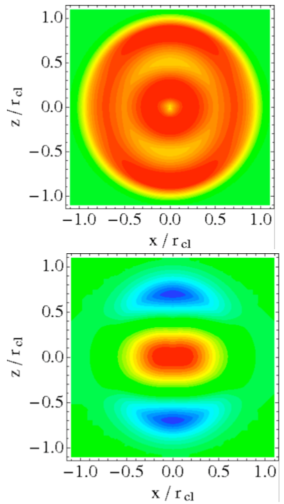
- multiple resonance structure for energies beyond Mie frequency
- fit by sum of Lorentzian profiles
- shaded area: volume plasmon (becomes dipole-active in finite systems)
- oscillator strength f=0.71



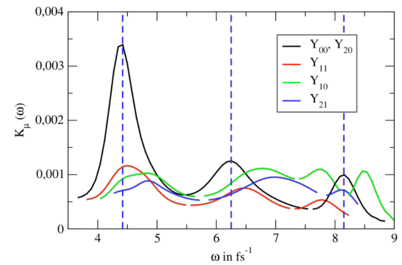
C. Xia,C. Yin, V.V. Kresin, PRL 102 (2009) 156802

Summary

- from bulk (wave vector *k*) to cluster (modes)
  - ✓ resonance modes beyond Mie/plasmon frequency
  - ✓ spatially resolved electron excitations
  - ✓ dependence on size, charge, density, temperature
  - ✓ change with cluster expansion (time evolution)



- damping behaviour of collective modes beyond Lorentzian fit and the relation to collision frequency
- discussion of higher modes, density vs. current (breathing modes, quadrupole modes, ..)
- some more technical issues
  - ✓ oscillator strength and link to experiments (electron- and photoabsorption spectroscopy)
  - ✓ going beyond non-degenerate systems (e.g. TD-LDA for electronic structure)
  - ✓ considering laser excitation processes for real systems



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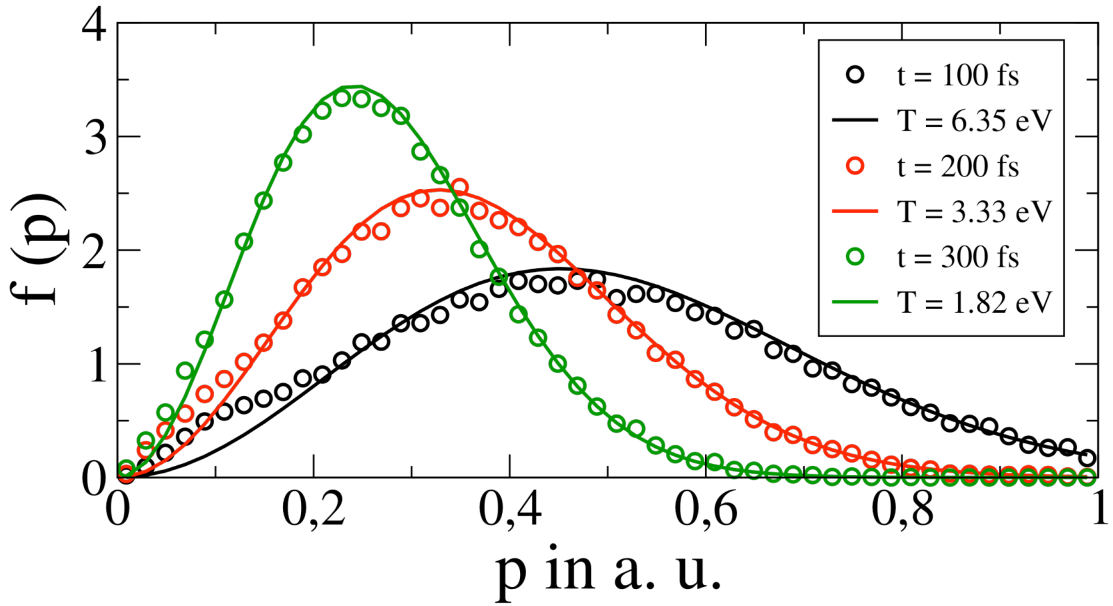
Finances: **SFB 652 (DFG)**

Single-time distributions: LTE

Momentum distribution



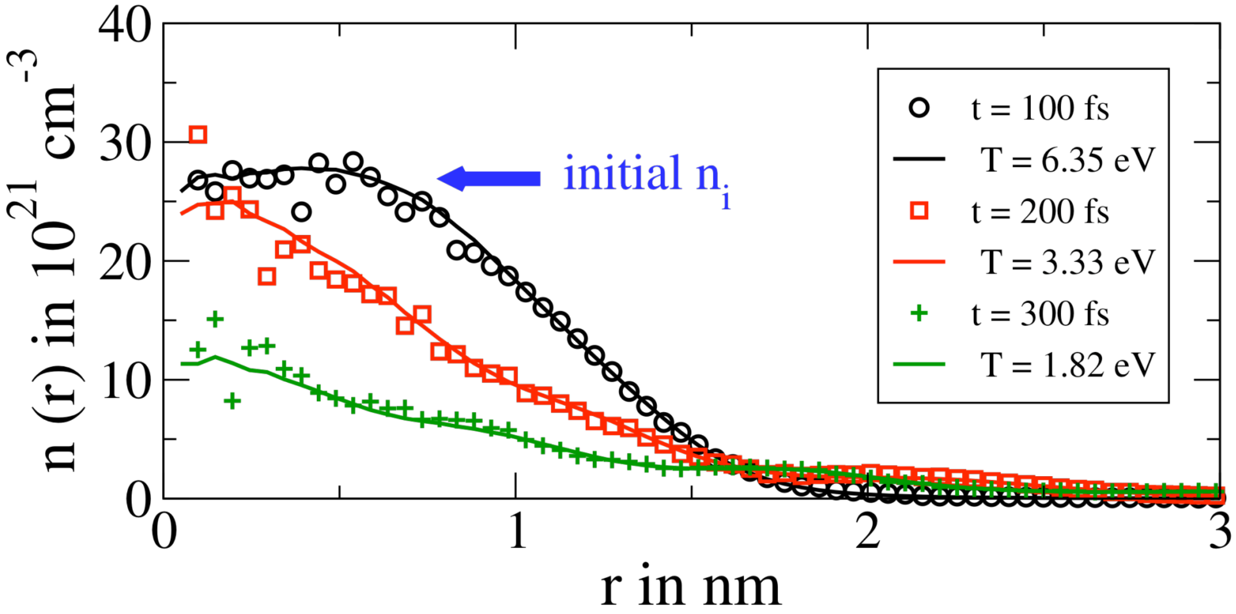
Na_{309}^{+48}

- isotropic distribution of inner free electrons observed
- agreement between temperatures due to mean kinetic energy $k_B T = \frac{3}{2} \langle E_{kin} \rangle$ and fit to Maxwell-Boltzmann distribution

T. Raitza et al., JPA 42 (2009) 214048

Single-time distributions: LTE

Radial electron density profile



Na_{309}^{+48}

$n_i = 28\ 10^{21}\ cm^{-3}$

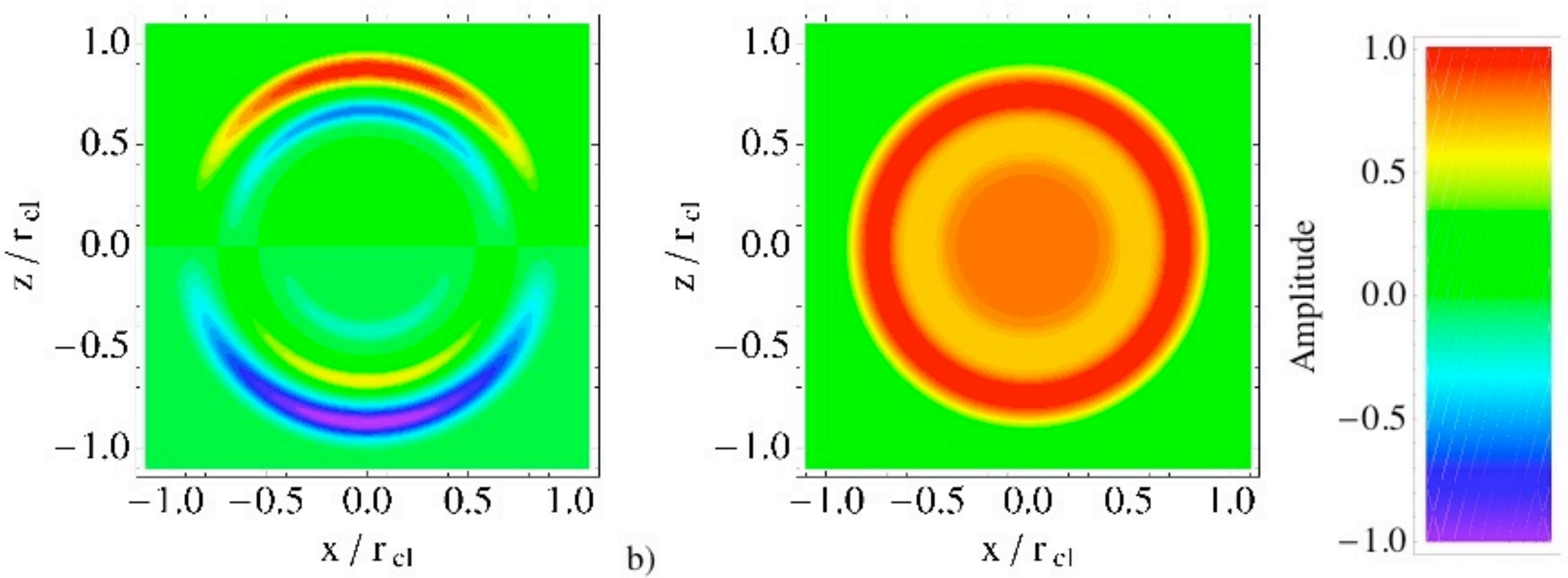
- simulation data can be interpreted as spatially distributed according to mean field *U(r)* due to forces on electron at radial distance r from ions and electrons

$$n(r) = n_0 \exp\left\{-\frac{U(r)}{k_B T}\right\}$$

T. Raitza et a.l, CPP 49 (2009) 498

Bilocal density and current ACF

- Transformation from density AFC to curl-free current AFC

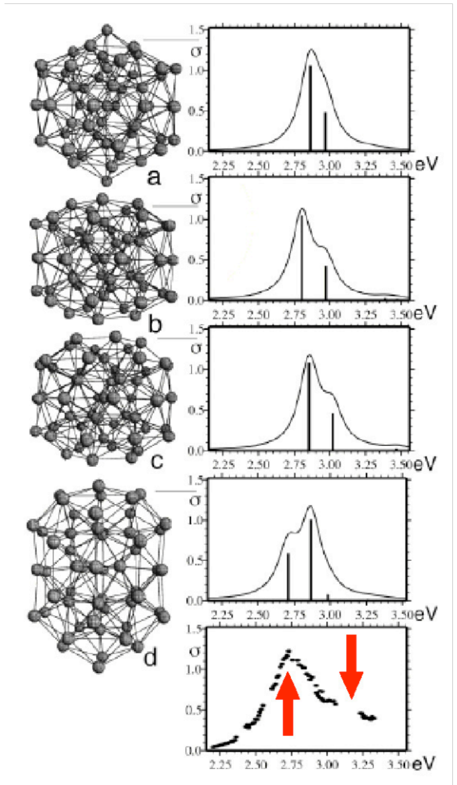


T. Raitza et al., CPP submitted

Experimental signatures

Na cluster

Na_{55}^{+}



close to icosahedral core for E_{min} [1]

small to medium size at low temperatures

- vibrationally broadened electronic transitions
- onset of plasmon peak @ higher energies for R↑

photoabsorption for sphere of radius R [2]

$$\alpha(\omega) \propto R^3 \mathrm{Im} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}$$

resonance frequeny:

$$\omega_{\mathrm{exp}} = 3.27\mathrm{eV}$$ [3]

homogeneous charge distribution

$$\omega_{\mathrm{Mie}} = 3.41\mathrm{eV}$$

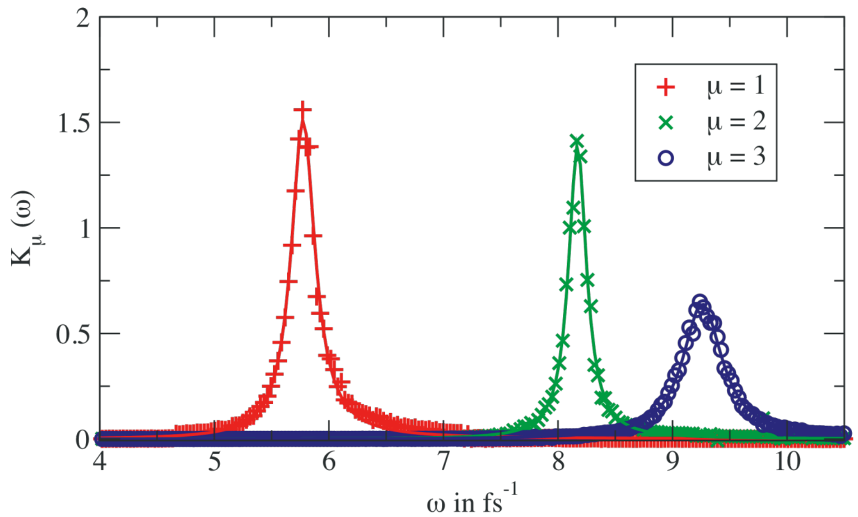
$$\omega_{\mathrm{pl}} = \sqrt{3}\omega_{\mathrm{Mie}} = 5.66\mathrm{eV}$$

[1] Kümmel et al, PRB 62 (2000) 7602,

[2] Haberland, in: *Metal Clusters* (ed. Ekardt, 1999)

[3] Smith PR 183 (1969) 634

Broadening of collective excitations



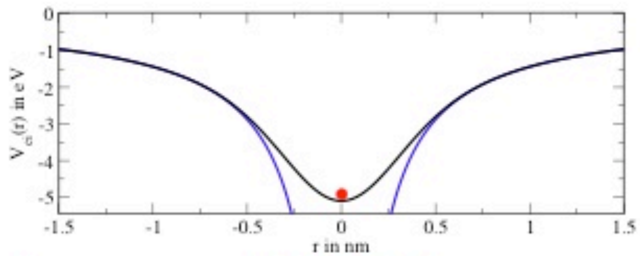
example:
1-d chain with 55 ions

- eigenmode spectra can be considered separately
- Lorentz fit to each mode (resonance)

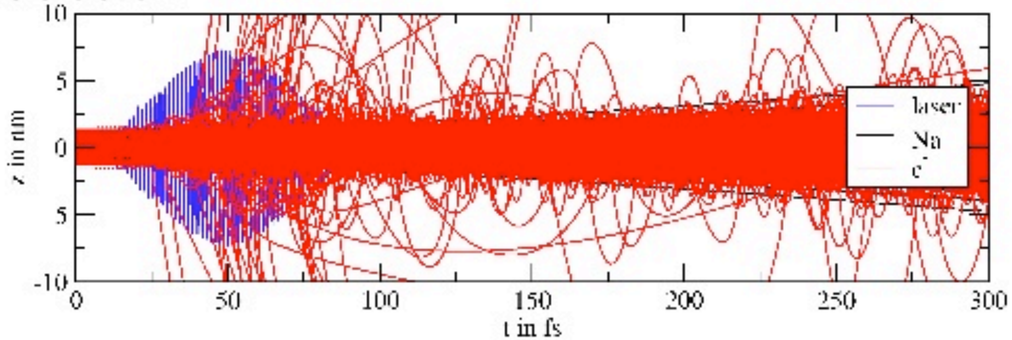
$$K_\mu(\omega) = K_0 \frac{{\omega_\mu}^2 \omega}{\nu_\mu \omega - \mathrm{i}(\omega^2 - {\omega_\mu}^2)}$$

T. Raitza et al., JPA 42 (2009) 214048

- clusters up to 1000 atoms
  - different ion structures
  - one electron per singly charged ion
  - initially electrons on top of ions
- error function potential:
  $V^{\mathrm{erf}}(r) = -\frac{Ze^2}{r}\mathrm{erf}\left(\frac{r}{\sigma}\right)$

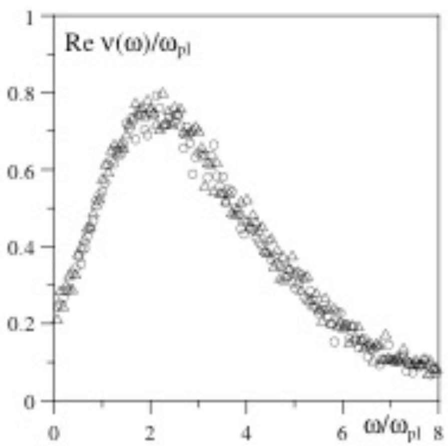


- time evolution:



- total current-density: $j_k(t) = \frac{1}{V}\frac{e}{m}\sum_i p_{i,k}(t)$
- current-density auto-correlation function (ACF):

$$K(k,t) = (j_k(t); j_k(0)) = \lim_{N_\tau \to \infty} \frac{1}{N_\tau} \sum_{i=0}^{N_\tau} j_k(t + \tau \cdot i) \cdot j_k(\tau \cdot i)$$



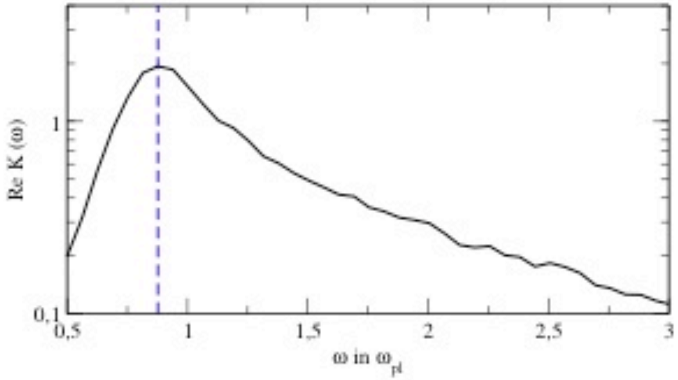
$\Gamma = 1.27$, $T = 3$ eV
Reinholz *et al.*; *PRE* **62**, 066412 (2004)

- generalized Drude expression in long wavelength limit for bulk

$$K(\omega) = \frac{\omega}{\nu(\omega)\omega - \mathrm{i}\left(\omega^2 - \omega_{\mathrm{pl}}^2\right)}$$

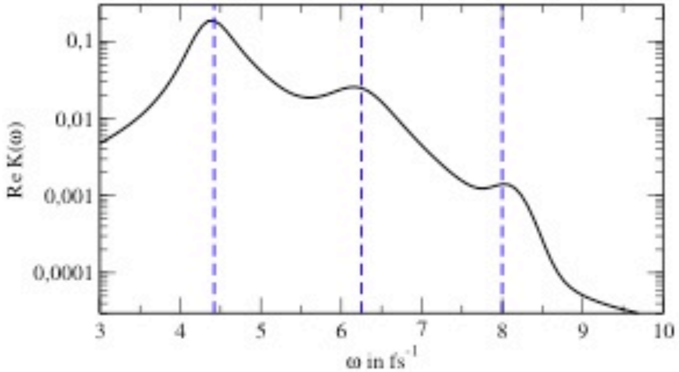
- related to dynamical collision frequency $\nu(\omega)$ (see figure) total current of:

bulk system ($\Gamma = 1.28$, $\omega_{\rm pl} = 3.8$ fs^{-1})



H. Reinholz, *et al.*; *PRE* **69**, 066412 (2004)

Na_{309} ($\Gamma = 6.96$, $T = 1$ eV)



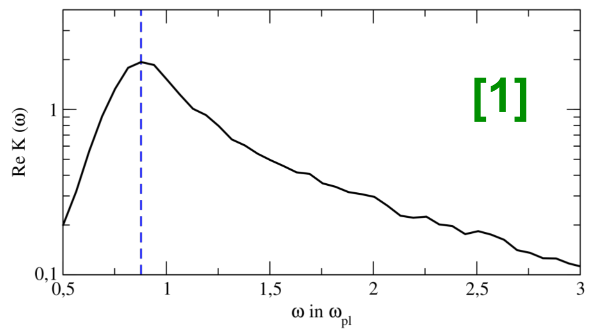
T. Raitza, *et al.*; *JPA* **42**, 214048 (2009)

- bulk: single resonance described by generalized Drude model ($k = 0$):

$$K(\omega) = \frac{\omega}{\nu(\omega)\omega - \mathrm{i}\left(\omega^2 - \omega_{\rm pl}^2\right)}, \quad \omega_{\rm pl}^2 = \frac{n_{\rm e} e^2}{\varepsilon_0 m_{\rm e}}$$

- finite system: multiple resonances

Plasmon resonance in bulk



- single resonance described by

generalized Drude formula (linear response) [2]

$$K(\omega) = \frac{1}{\nu(\omega) - \mathrm{i}\left(\omega - \frac{\omega_{pl}^2}{\omega}\right)},$$

- width of resonance peak due to collisional broadening described by

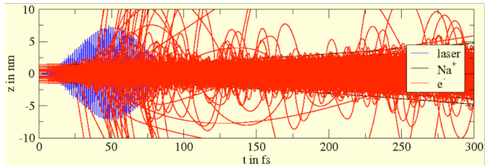
dynamical collision frequency $\nu(\omega)$

- couples to longitudinal field, but not to transversal field (light)

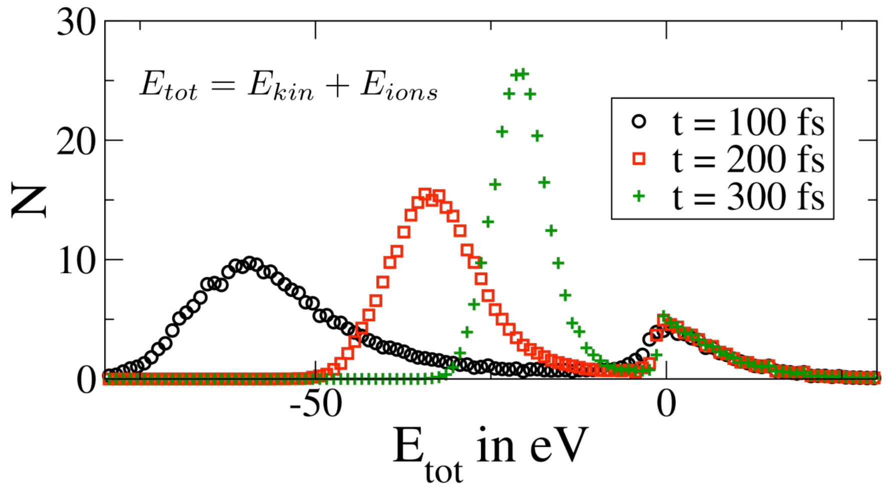
[1] Reinholz et al., PRE 69 (2004), [2] Reinholz et al, PRE 62 (2000)

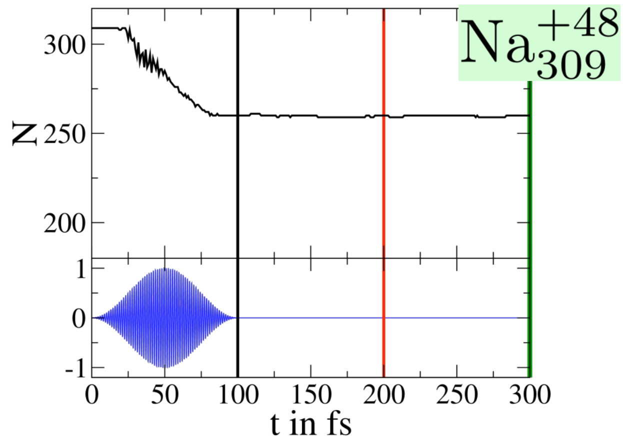
Cluster parameters

Total energy of electrons



- cluster expansion process analyzed via ensemble average





- electrons with $E_{tot} < 0$ found in local thermal equilbrium distribution

$$f(r,p) = \frac{4\pi p^2}{Z} \exp\left\{ -\frac{1}{k_B T}\left(\frac{p^2}{2m} + U(r) \right) \right\}$$

Raitza et al, CPP 49 (2009) 496

Some Applications

- reflectivity *Morozov, Raitza, HR et al. 2005*
- optical line shapes (H, He^{+}, Li^{2+}) *Omar, Lorenzen, Wierling, HR et al. 2008, 2009*

VUV to X-ray necessary for diagnostics of warm dense matter

$$\omega > \omega_{\rm pl} = \sqrt{\frac{e^2 n_e}{\epsilon_0 m_e}}$$

- Thomson scattering *Thiele, HR et al. PRE 78 (2008); Fäustlin, HR et al. 2009*
- bremsstrahlung *Zastrau, HR et al. PRE 78 (2008), Fortmann, HR et al. 2006, 2009*
- X-ray emission lines (K_α, K_β) *Sengebusch, HR et al. 2008, 2009*

Optical Properties

Dielectric function, homogeneous systems: wave vector *k*

$$\epsilon(\vec{k},\omega) = 1 - \frac{1}{\epsilon_0 k^2}\left(\Pi_1(\vec{k},\omega) + \Pi_2(\vec{k},\omega) + \ldots\right)$$

cluster expansion of polarization function:
contributions of free electrons Π_1 and bound states Π_2

- optical information: reflection, absorption

$$\lim_{k\to 0} \epsilon_t(\vec{k},\omega) = \left(n(\omega) + \frac{ic}{2\omega}\alpha(\omega)\right)^2$$

- dynamical structure factor (Thomson scattering)

$$S(\vec{k},\omega) = \frac{1}{\pi V(k)} \frac{1}{e^{-\beta\hbar\omega}-1} \operatorname{Im}\epsilon_l^{-1}(\vec{k},\omega)$$

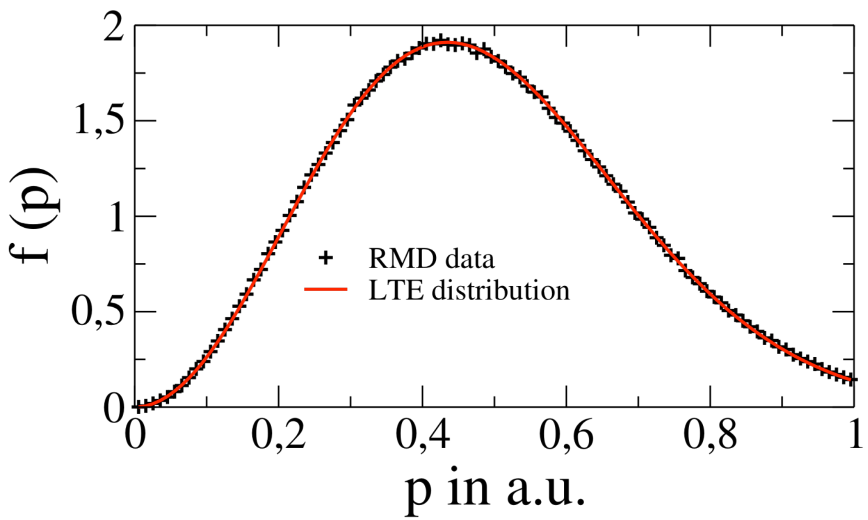
Two-time distributions: RMD

Restricted MD simulation scheme

- observed local thermal equilibrium justifies restricted MD (RMD)

ensemble average ➔ time average of trajectories for
frozen ion configuration at fixed time

momentum distribution



Na_{309}^{+48}

@ T= 6.35 eV (parameters for t=100 fs)

Raitza et al, CPP 49 (2009) 498

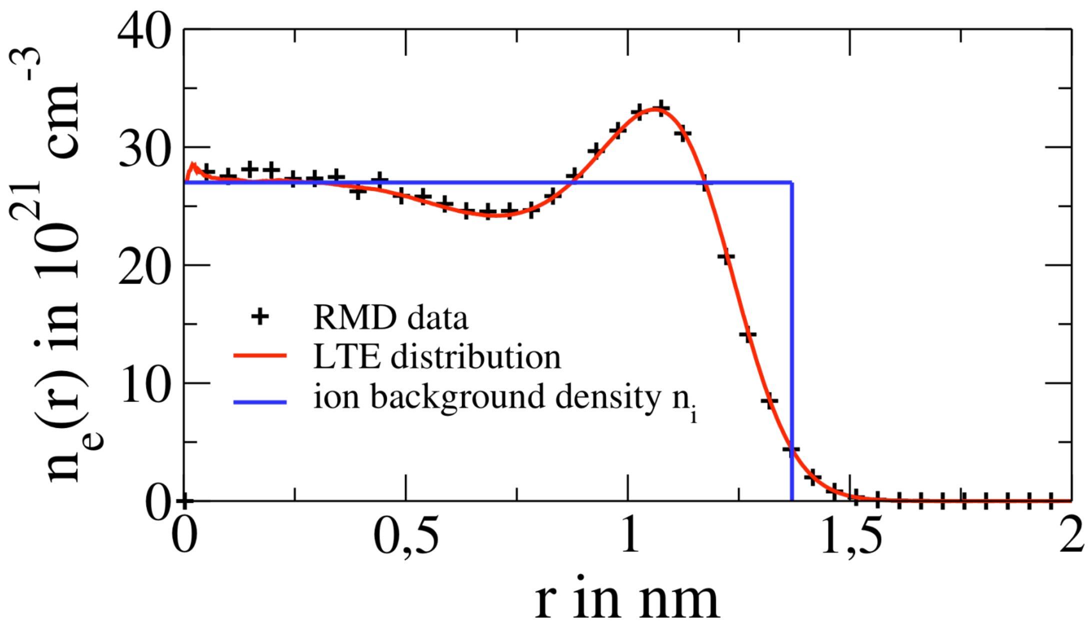
Two-time distributions: RMD

Restricted MD simulation scheme

- observed local thermal equilibrium justifies restricted MD (RMD)

ensemble average ➔ time average of trajectories for frozen ion configuration at fixed time

spatial distribution



Na_{309}^{+48}

@ T= 6.35 eV (parameters for t=100 fs)

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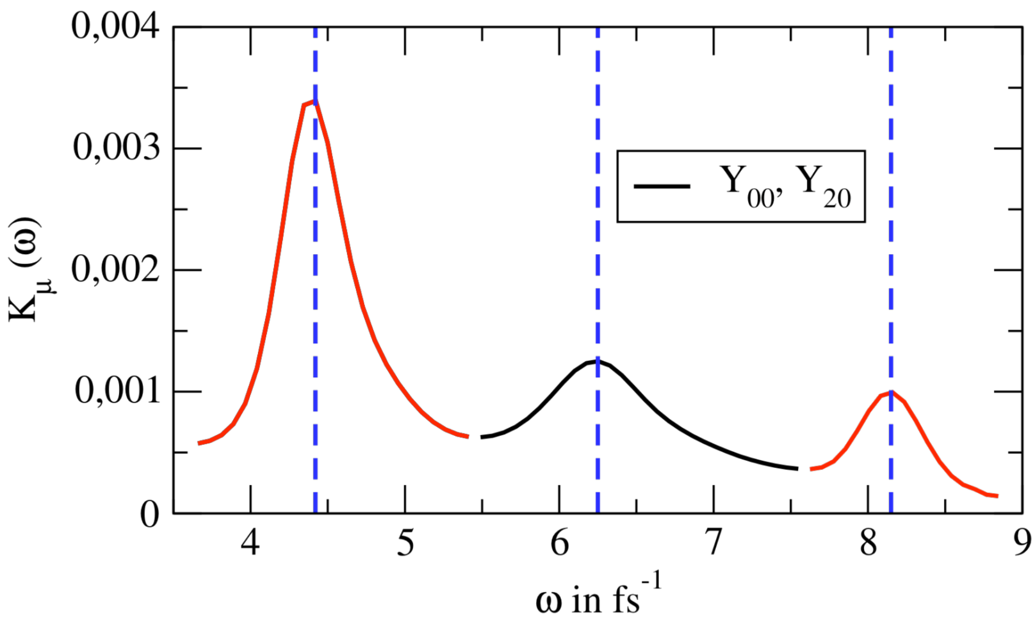
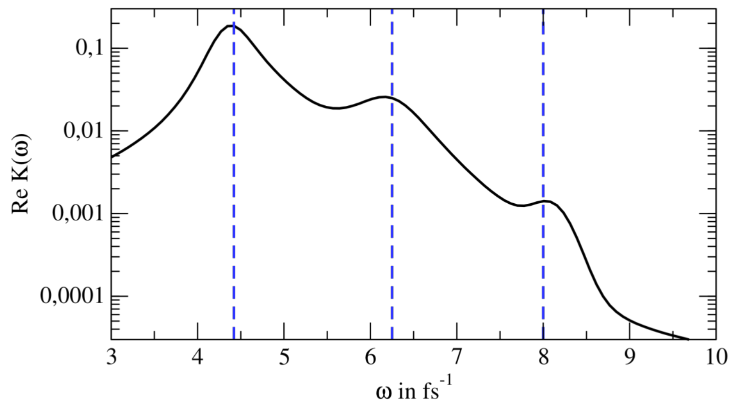
Plasma excitations

Fundamental dipole mode (μ=1)



- 3 resonances, at the same frequencies as in total current ACF



T. Raitza et al., PRE 84, 036406 (2011)