Size-dependent effects in the electron dynamics of metal clusters

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physics in San Sebastián
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clusters as crossroads

atoms and molecules

physics

solid state

chemistry
clusters vs. bulk

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lifetime of electronic excitations:
2PPE pump-probe experiments

a first (pump) laser pulse
populates an unoccupied state
and a second (probe) laser pulse
photoemits the electron.

two main channels compete in electron relaxation:
electron-electron scattering
electron-phonon interaction

competition between them determines photochemical activity, for instance
... but also energy transfer, electron transfer across interfaces, etc.
decay of excitations in a FEG: density of states vs. screening

density of states
more DOS
more phase space available
more probability for the process
shorter lifetimes

screening
more DOS
more screening
weaker interaction
longer lifetimes

Free electrons
Quinn (1962)

\[ \tau \approx \frac{263 \, r_s^{-5/2}}{(E-E_F)^2} \propto \frac{n^{5/6}}{(E-E_F)^2} \]
questions to solve:

how does the lifetime of electronic excitations change when moving from infinite to finite nano-sized systems?

which is the dependence with size of the electronic excitation lifetimes?
lifetimes in clusters vs. lifetimes in solids: DOS effects

discretization of levels

less phase space available

longer lifetimes

\( \tau_{\text{cluster}} > \tau_{\text{FEG}} \)?
lifetimes in clusters vs. lifetimes in solids: screening effects

- surface effects and less electron mobility
  - less screening
  - shorter lifetimes

- clusters

- FEG
  - no surface, free electrons
  - more screening
  - longer lifetimes

\[ \tau_{\text{cluster}} < \tau_{\text{FEG}} \]
experimental measurements of size-dependent electron dynamics

Ag nanoparticles

Voisin et al.,
Size-dependent electron-electron interactions in metal nanoparticles
PRL 85, 2200 (2000)

A sharp increase of the electron energy exchange rate is demonstrated for nanoparticles smaller than 5 nm. ... due to surface induced reduction of the Coulomb interaction screening.

\[ \tau_{ci} < \tau_{bulk} \]
experimental measurements of size-dependent electron dynamics

Ag 2nm nanoparticles

Merschdorf et al.,
Collective and single-particle dynamics in time-resolved two-photon photoemission
PRB 70, 193401 (2004)

Experiments performed with TR 2PPES on bulk Ag yield significantly lower lifetimes (‘as compared to clusters’).

\[ \tau_{cl} > \tau_{bulk} \]
**lifetimes in clusters vs. lifetimes in solids**

**screening arguments:** \( \tau_{\text{cluster}} < \tau_{\text{FEG}} \) ?

**DOS arguments:** \( \tau_{\text{cluster}} > \tau_{\text{FEG}} \) ?

\( \tau_{\text{cluster}} \leq \tau_{\text{FEG}} \) ?
1st step: DFT calculation of a jellium cluster

Cluster is described in the jellium model (a background of constant positive charge)

Kohn-Sham equations solved self-consistently

\[
\left\{-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r})\right\} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})
\]

\[
v_{\text{eff}}(\mathbf{r}) = v_{\text{jellium}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})
\]
lifetimes of electronic excitations in metal clusters

metallic clusters in excited electronic states

hv

( excited by incident laser light, for instance)

occupied states

decay of excitation through electron-electron interaction
2nd step: calculation of the linear response function \( \chi(r, r', \omega) \) and of the screened interaction \( W(r, r', \omega) \)

2a\textsuperscript{-} independent-particle response function \( \chi_0(r, r', \omega) \)

\[
\chi_0(r, r', \omega) = \sum_{\varphi_2 \in \text{occ.}} \sum_{\varphi_3 \notin \text{occ.}} \left[ \frac{\varphi_2^*(r) \varphi_2(r') \varphi_3^*(r') \varphi_3(r)}{\omega + \varepsilon_2 - \varepsilon_3 + i\delta} - \frac{\varphi_2(r) \varphi_2^*(r') \varphi_3(r') \varphi_3^*(r)}{\omega - \varepsilon_2 + \varepsilon_3 + i\delta} \right]
\]

2b\textsuperscript{-} self-consistent calculation of \( \chi(r, r', \omega) \) in real space (RPA)

\[
\chi(r, r', \omega) = \chi_0(r, r', \omega) + \int dr_1 dr_2 \chi_0(r, r_1, \omega) \left[ \frac{1}{|r_1 - r_2|} \right] \chi(r_2, r', \omega)
\]

2c\textsuperscript{-} calculation of the screened Coulomb interaction \( W(r, r', \omega) \)

\[
W(r, r', \omega) = \frac{1}{|r - r'|} + \int dr_1 dr_2 \left[ \frac{1}{|r - r_1|} \right] \chi(r_1, r_2, \omega) \left[ \frac{1}{|r_2 - r'|} \right]
\]
3rd step: calculation of the imaginary part of the self-energy
GW approximation

\[ \Gamma_i = -2 \sum_{f \notin \text{occ.}} \int dr dr' \phi_i^* (r) \phi_f^* (r') \text{Im} W(r, r', \omega) \phi_i (r') \phi_f (r) \]

\( \varphi_i (r) \) is a KS unoccupied wavefunction that represents the initial state in the decay
\( \varphi_f (r) \) is a KS unoccupied wavefunction that represents the final state in the decay

calculation of the decay rate \( \Gamma = \tau^{-1} \)
size-dependence of the decay rate for electrons excited ~1 eV above the Fermi level

we sum over all possible final states

Quijada et al., Nanotechnology 16, 176 (2005)
size-dependence of the decay rate for electrons excited \( \sim 1 \) eV above the Fermi level

\[ E_i - E_F = 1 \text{ eV} \]

lifetime \( \tau \) (fs)

cluster radius \( R \) (nm)

Electron lifetimes in clusters range between 3 and 30 fs for \( E \sim 1 \) eV

Order of magnitude is similar in a FEG

Oscillations due to the discretization of levels

\[ \tau_{\text{cluster}} < \tau_{\text{FEG}}! \]
size-dependence of the decay rate for electrons excited $\sim 2.6$ eV above the Fermi level

we sum over all possible final states

$E_i - E_F = 2.6$ eV

solid limit (Quinn-Ferrell)
size-dependence of the decay rate for electrons excited ~2.6 eV above the Fermi level

Electron lifetimes in clusters range are ~2fs for E~2.6eV (slightly longer than solids)

$$\tau_{\text{cluster}} > \tau_{\text{FEG}}$$
size-dependence of the decay rate for electrons

decay rate $\Gamma$ normalized to the solid (FEG) value

$\tau_{\text{cluster}} \lesssim \tau_{\text{FEG}}$?
Initial energy dependence of the decay rate

\[ \tau \approx \frac{263 \, r_s^{-5/2}}{(E-E_F)^2} \propto \frac{n^{5/6}}{(E-E_F)^2} \]
comparison of lifetimes in solids and nanosized clusters

**Theoretical calculation** for (gas-phase) Na clusters of ~ 4nm diameter

**Experimental measurements** for (supported) Ag clusters of ~ 2.2nm diameter

**electron lifetimes in metal nanoparticles: conclusions**

Electron lifetimes in metal clusters are of the order of few femtoseconds (not far from those in solids), for sufficiently large (nm) clusters.

Nevertheless, in this size range, there are apparent differences with respect to the free-electron gas: lifetimes can be either larger or shorter depending on the excitation energy.

There is not a clear winner in the screening versus DOS competition: the free-electron gas dependence $\tau \sim 1/(E-E_F)^2$ is broken!
thank you for your attention