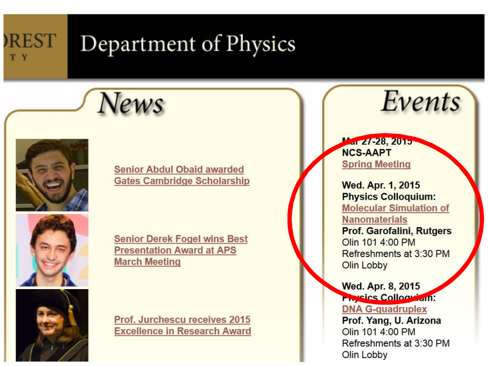
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 27:

- Chap. 20 in Marder
  - Models of dielectric response of materials

Some of the lecture materials are from slides prepared by Marder

20	Mon: 03/16/2015		Review Mid-term exam	#19	03/18/2015
21	Wed: 03/18/2015	Chap. 16	Electron Transport	#20	03/20/2015
22	Fri: 03/20/2015	Chap. 16	Electron Transport	#21	03/23/2015
23	Mon: 03/23/2015	Chap. 17	Electron Transport	#22	03/25/2015
24	Wed: 03/25/2015	Chap. 17 & 18	Electron Transport		
25	Fri: 03/27/2015	Chap. 18	Microscopic picture of transport	#23	03/30/2015
26	Mon: 03/30/2015	Chap. 19	Semiconductor devices	#24	04/01/2015
27	Wed: 04/01/2015	Chap. 20	Models of dielectric functions	#25	04/06/2015
	Fri: 04/03/2015	Good Friday	No class		
28	Mon: 04/06/2015				04/08/2015
29	Wed: 04/08/2015				04/10/2015
30	Fri: 04/10/2015				04/13/2015
31	Mon: 04/13/2015				04/15/2015
32	Wed: 04/15/2015				04/17/2015
33	Fri: 04/17/2015				04/20/2015
34	Mon: 04/20/2015				
35	Wed: 04/22/2015				
36	Fri: 04/24/2015				
	Mon: 04/27/2015		Presentations I		
	Wed: 04/29/2015		Presentations II		
	Fri: 05/01/2015		Presentations III & Take home exam		



WFU Physics Colloquium

TITLE: Molecular Simulations of Nanoscale Materials: Applications in Conversion Materials for Advanced Batteries and Nanoconfined Water and Proton Transport

SPEAKER: Professor Stephen H. Garofalini ,

Interfacial Molecular Science Laboratory
Department of Materials Science and Engineering
Rutgers University

TIME: Wednesday April 1, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

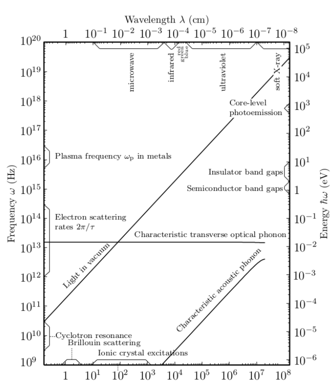
ABSTRACT

We have applied molecular dynamics simulations to study two important, but diverse topics, involving behavior at the nanoscale: (a) a nanoscale metal fluoride, FeF_2, used as a conversion material in advanced high capacity Li-ion batteries and (b) the behavior of nanoconfined water and water reactions and proton transport on oxide surfaces. In the first, exposure of FeF_2 to Li^+ causes a conversion reaction that forms nanocrystals of LiF and Fe-metal, enabling access to the multiple valence states of the iron cation. While these resultant nanocrystals are observed in post-reaction HRTEM, (high resolution transmission electron microscopy) the atomistic mechanisms and the reaction pathways in conversion

Drude model for unbound electrons in presence of electric field having pure time harmonic frequency ω:

$$m\dot{\vec{v}} = -e\vec{E} - m\frac{\vec{v}}{\tau},$$

$$\begin{aligned} -i\omega m\vec{v} &= -e\vec{E} - m\frac{\vec{v}}{\tau} \\ \Rightarrow \vec{j} &= -ne\vec{v} = \frac{ne^2\tau/m}{1-i\omega\tau}\vec{E} \\ \Rightarrow \sigma(\omega) &= \frac{ne^2\tau/m}{1-i\omega\tau}. \end{aligned}$$



Maxwell's equations including "internal" charges and currents

$$\vec{\nabla}\cdot\vec{E} = -4\pi e n \qquad \vec{\nabla}\cdot\vec{B}=0$$
$$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{B}=\frac{4\pi\vec{j}}{c}+\frac{1}{c}\frac{\partial\vec{E}}{\partial t}.$$

$$\vec{P}=\int^{t} dt'\vec{j}_{\rm int}(t').$$

$$-e\frac{\partial n_{\rm int}}{\partial t} = -\vec{\nabla}\cdot\vec{j}_{\rm int}$$
$$\Rightarrow e n_{\rm int} = \vec{\nabla}\cdot\vec{P},$$
$$\vec{D} = \vec{E}+4\pi\vec{P}.$$

Maxwell's equations including both internal and "external" charges and currents

$$\vec{\nabla}\cdot\vec{D} = -4\pi e n_{\rm ext} \qquad \vec{\nabla}\cdot\vec{B}=0$$
$$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{B}=\frac{4\pi\vec{j}_{\rm ext}}{c}+\frac{1}{c}\frac{\partial\vec{D}}{\partial t}.$$

Relationship between current, conductivity and electric field:

$$\vec{j}(\vec{r},t) = \int dt'd\vec{r}'\sigma(\vec{r}-\vec{r}',t-t')\vec{E}(\vec{r}',t')$$

In Fourier space:

$$\vec{j}(\vec{q},\omega)=\sigma(\vec{q},\omega)\vec{E}(\vec{q},\omega).$$

$$\vec{D}(\vec{r},t)=\epsilon*\vec{E}(\vec{r},t)\Rightarrow\vec{D}(\vec{q},\omega)=\epsilon(\vec{q},\omega)\vec{E}(\vec{q},\omega).$$

$$\epsilon(\vec{q},\omega)=1+\frac{4\pi i}{\omega}\sigma(\vec{q},\omega).$$

Electromagnetic waves within media

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\times\vec{B}=-\frac{1}{c^2}\frac{\partial^2\epsilon*\vec{E}}{\partial t^2}$$
$$\Rightarrow q^2\vec{E}-\vec{q}(\vec{q}\cdot\vec{E}) = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E}.$$

Transverse mode:

$$q^2\vec{E} = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E}$$
$$\Rightarrow q = \omega\tilde{n}/c; \quad \tilde{n}(\vec{q},\omega)=\sqrt{\epsilon(\vec{q},\omega)},$$

Real and imaginary parts of refractive index

$$\epsilon_1 = \bar{n}^2 - \kappa^2$$
$$\epsilon_2 = 4\pi \mathrm{Re}[\sigma]/\omega = 2\bar{n}\kappa.$$

Absorption coefficient

$$\alpha = \frac{2\omega}{c}\kappa = \frac{\omega\epsilon_2}{\bar{n}c}.$$

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Drude model with bound oscillators

$$\vec{E}(\vec{r},t) = \vec{E}e^{-i\omega t},$$

$$m_l\ddot{\vec{r}} = -m_l\omega_l^2\vec{r} - m_l\dot{\vec{r}}/\tau_l - e\vec{E}(\vec{r},t)$$
$$\Rightarrow \vec{r}(\omega) = -\frac{e\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}$$

$$\vec{j}(\omega) = \frac{-i\omega n_l e^2\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)},$$

$$\sigma(\omega) = \frac{-i\omega n_l e^2}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}.$$

$$\epsilon(\omega) = 1 + \sum_l \frac{4\pi n_l e^2/m_l}{\omega_l^2 - \omega^2 - i\omega/\tau_l}.$$

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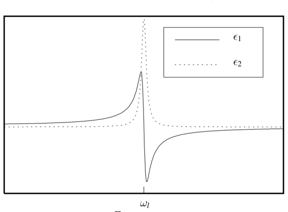
Real and imaginary parts of dielectric function for Drude model

$$\epsilon_1(\omega) = \mathrm{Re}[\epsilon(\omega)] = 1 + \sum_l \frac{4\pi n_l e^2(\omega_l^2 - \omega^2)/m_l}{(\omega_l^2-\omega^2)^2 + (\omega/\tau_l)^2}$$
$$\epsilon_2(\omega) = \mathrm{Im}[\epsilon(\omega)] = \sum_l \frac{4\pi n_l e^2\omega/(\tau_l m_l)}{(\omega_l^2-\omega^2)^2 + (\omega/\tau_l)^2},$$



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Analytic properties of dielectric function

$$\epsilon(t) = 0 \text{ for } t < 0.$$

$$\epsilon(\omega) = \int_0^\infty dt\, e^{i\omega t} \epsilon(t).$$

$$\epsilon(\omega) = \oint \frac{d\omega'}{2\pi i} \frac{\epsilon(\omega')}{\omega' - \omega - i\eta}.$$

$$\epsilon(\omega) - \epsilon^\infty = \oint \frac{d\omega'}{2\pi i} \frac{\epsilon(\omega') - \epsilon^\infty}{\omega' - \omega - i\eta}.$$

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$$\epsilon(\omega) - \epsilon^\infty = \oint \frac{d\omega'}{2\pi i} \frac{\epsilon(\omega') - \epsilon^\infty}{\omega' - \omega - i\eta}.$$

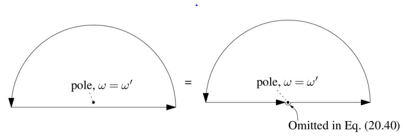

Figure 20.3: The integral at distance η above the real axis can be deformed into a contour integral on the real axis, with a contribution from a half-circuit around the pole at $\omega = \omega'$.

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In terms of principle parts integral over negative and positive frequencies

$$\epsilon(\omega) - \epsilon^\infty = \mathcal{P} \int \frac{d\omega'}{\pi i} \frac{\epsilon(\omega') - \epsilon^\infty}{\omega' - \omega}$$

$$\begin{aligned} \mathrm{Re}[\epsilon(\omega) - \epsilon^\infty] &= \mathcal{P} \int \frac{d\omega'}{\pi} \frac{\mathrm{Im}[\epsilon(\omega') - \epsilon^\infty]}{\omega' - \omega} \\ \mathrm{Im}[\epsilon(\omega) - \epsilon^\infty] &= -\mathcal{P} \int \frac{d\omega'}{\pi} \frac{\mathrm{Re}[\epsilon(\omega') - \epsilon^\infty]}{\omega' - \omega}. \end{aligned}$$

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In terms of positive frequencies only

$$\epsilon_1(\omega)-\epsilon^{\infty} = \mathcal{P}\int_0^{\infty}\frac{2\omega' d\omega'}{\pi}\frac{\epsilon_2(\omega')}{\omega'^2-\omega^2}$$
$$\epsilon_2(\omega) = -\mathcal{P}\int_0^{\infty}\frac{2\omega d\omega'}{\pi}\frac{\epsilon_1(\omega')-\epsilon^{\infty}}{\omega'^2-\omega^2}.$$

Analysis of reflectivity data

$$\tilde{r} = \frac{\tilde{n}-1}{\tilde{n}+1} \equiv \rho e^{i\theta}.$$

$$\ln(\frac{\tilde{r}(\omega)}{\tilde{r}(0)}) = \ln(\rho(\omega)/\rho(0)) + i(\theta(\omega)-\theta(0)),$$

$$\theta(\omega)-\theta(0) = -\frac{1}{\pi}\mathcal{P}\int d\omega' \ln\left[\frac{\rho(\omega')}{\rho(0)}\right][\frac{1}{\omega'-\omega}-\frac{1}{\omega'}]$$
$$\Rightarrow \theta(\omega) = -\frac{2\omega}{\pi}\mathcal{P}\int_0^{\infty} d\omega' \frac{\ln\rho(\omega')}{\omega'^2-\omega^2}.$$