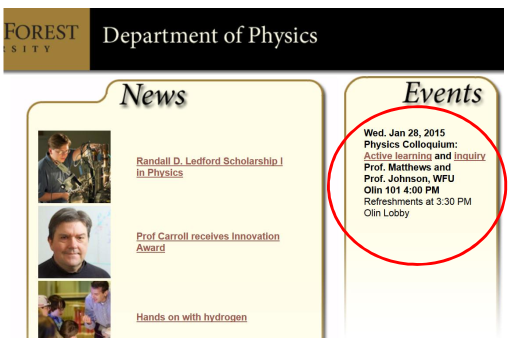
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 6:

Reading: Chapter 6 in MPM; Electronic Structure

1. Independent electron models
2. Free electron gas
3. Densities of states
4. Statistical mechanics of non-interacting electrons



Course schedule for Spring 2015

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015

Quantum Theory of materials

Exact Schrödinger equation:

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = E_{\alpha\nu}\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Electronic coordinates

Atomic coordinates

where

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Born-Oppenheimer approximation

Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)

Approximate factorization:

$$\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Quantum Theory of materials -- continued

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_{\alpha}(\{\mathbf{R}^a\})\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Nuclear Hamiltonian: (Often treated classically)

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right)X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = W_{\alpha\nu}X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right) = \sum_a \frac{\mathbf{P}^{a2}}{2M^a} + U_{\alpha}(\{\mathbf{R}^a\})$$

Effective nuclear interaction provided by electrons

Terms neglected in Born-Oppenheimer approximation

Correction terms

$$\mathcal{H}^{\text{Correction}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) =$$

$$\sum_a \frac{1}{M_a}\left(P_a X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})\right)\left(P_a \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right) +$$

$$\sum_a \frac{1}{2M_a} X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})\left(P_a^2 \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right)$$

First consider electronic Hamiltonian

Electronic Schrödinger equation:

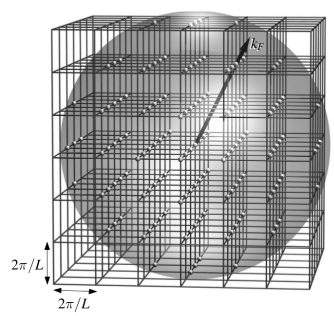
$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Replace by "jellium"

Independent electron contributions

Treatment of each electron (Fermi particle) in the jellium model



$$\psi_{\vec{k}} = \frac{1}{\sqrt{\mathcal{V}}}e^{i\vec{k}\cdot\vec{r}}$$

$$\vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z).$$

$$\mathcal{E}^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$$

Note: This and following slides taken from Marder's text

Enumerating the independent electron states by summing over *k*:

$$\sum_{\vec{k}} F_{\vec{k}},$$

$$\int d\vec{k}\, F_{\vec{k}} = \sum_{\vec{k}} \left(\frac{2\pi}{L}\right)^3 F_{\vec{k}}$$

$$\Rightarrow \sum_{\vec{k}} F_{\vec{k}} = \frac{\mathcal{V}}{(2\pi)^3}\int d\vec{k}\, F_{\vec{k}}.$$

$$\delta_{\vec{k}\vec{q}} \to \frac{(2\pi)^3}{\mathcal{V}}\delta(\vec{k}-\vec{q}).$$

Enumerating the independent electron states by summing over *k* – continued:

Note: Each spatial state has a spin degeneracy of 2.

$$D_{\vec{k}} = 2\frac{1}{(2\pi)^3},$$

$$\int [d\vec{k}] \equiv \frac{2}{\mathcal{V}}\sum_{\vec{k}} = \int d\vec{k}\, D_{\vec{k}} = \frac{2}{(2\pi)^3}\int d\vec{k}$$

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) = \mathcal{V}\int d\mathcal{E}\, D(\mathcal{E}) F(\mathcal{E}) \quad .$$

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) = \mathcal{V}\int [d\vec{k}]\, F(\mathcal{E}_{\vec{k}})$$

$$= \mathcal{V}\int d\mathcal{E}\int [d\vec{k}]\,\delta(\mathcal{E}-\mathcal{E}_{\vec{k}}) F(\mathcal{E})$$

$$\Rightarrow D(\mathcal{E}) = \int [d\vec{k}]\,\delta(\mathcal{E}-\mathcal{E}_{\vec{k}}) \quad .$$

Enumerating the independent electron states by summing over *k* – continued for $\mathcal{E}^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$:

$$\begin{aligned} D(\mathcal{E}) &= \int [d\vec{k}]\,\delta(\mathcal{E}-\mathcal{E}^0_{\vec{k}}) \\ &= 4\pi\frac{2}{(2\pi)^3}\int_0^\infty dk\, k^2\,\delta(\mathcal{E}-\mathcal{E}^0_{\vec{k}}) \\ &= \frac{1}{\pi^2}\int_0^\infty \frac{d\mathcal{E}^0}{|d\mathcal{E}^0/dk|}\frac{2m\mathcal{E}^0}{\hbar^2}\delta(\mathcal{E}-\mathcal{E}^0) \\ &= \frac{m}{\hbar^3\pi^2}\sqrt{2m\mathcal{E}} \\ &= 6.812\cdot 10^{21}\ \sqrt{\mathcal{E}/\mathrm{eV}}\ \mathrm{eV}^{-1}\ \mathrm{cm}^{-3}. \end{aligned}$$

Enumerating the independent electron states by summing over *k* – continued for $\mathcal{E}^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$:

$$\begin{aligned} N &= \sum_{\vec{k}\sigma} f_{\vec{k}} \\ &= \mathcal{V}\int [d\vec{k}] f_{\vec{k}}, \\ &= \mathcal{V}\int [d\vec{k}]\,\theta(k_F - k) \\ &= \frac{\mathcal{V}}{4\pi^3}\frac{4\pi}{3}k_F^3 = \frac{\mathcal{V}k_F^3}{3\pi^2}, \end{aligned}$$

$$k_F = (3\pi^2 n)^{1/3} = 3.09\ [n\cdot\text{Å}^3]^{1/3}\,\text{Å}^{-1}.$$

Enumerating the independent electron states by summing over *k* – continued for $\mathcal{E}_k^0 = \frac{\hbar^2 k^2}{2m}$:

$$\frac{4\pi}{3} r_s^3 \equiv \frac{\mathcal{V}}{N} \Rightarrow r_s = \left[\frac{3}{4\pi}\frac{\mathcal{V}}{N}\right]^{1/3}.$$

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} = 36.46\ [n \cdot \mathring{A}^3]^{2/3}\text{eV}.$$

$$v_F = \hbar k_F/m = 3.58\ [n \cdot \mathring{A}^3]^{1/3} \cdot 10^8\ \text{cm s}^{-1}.$$

$$D(\mathcal{E}_F) = \frac{3}{2}\frac{n}{\mathcal{E}_F} = 4.11 \cdot 10^{-2}\ [n \cdot \mathring{A}^3]\ \text{eV}^{-1}\ \mathring{A}^{-3}.$$

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Note: Previous results are special to a 3-dimensional jellium system where the electronic states are related to the wavevectors according to $\mathcal{E}_k^0 = \frac{\hbar^2 k^2}{2m}$

For your homework problem, you will consider a 2-dimensional jellium system with two different dispersions: *E(k)=Xk*^{2} and *E(k)=Xk.*

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Statistical mechanics of free Fermi gas in terms of "grand" partition function

$$Z_{\text{gr}} = \sum_{\text{states}} e^{\beta(\mu N - \mathcal{E})}$$
$$= \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\sum_{n_3=0}^{1}\cdots e^{\beta\sum_l n_l(\mu-\mathcal{E}_l)}$$
$$\sum_{n_1=0}^{N} \sum_{n_2=0}^{N}\cdots\sum_{n_M=0}^{N}\prod_{l=1}^{M} A_{n_l} = \prod_{l=1}^{M}\left\{\sum_{n_l=0}^{N} A_{n_l}\right\},$$
$$Z_{\text{gr}} = \prod_l \left\{\sum_{n_l=0}^{1} e^{\beta\, n_l[\mu-\mathcal{E}_l]}\right\}$$
$$= \prod_l \left[1 + e^{\beta[\mu-\mathcal{E}_l]}\right].$$

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"Grand" potential

$$\Pi \equiv -k_BT\ln Z_{gr}$$
$$= -k_BT\sum_l \ln\left[1+e^{\beta[\mu-\mathcal{E}_l]}\right].$$
$$= -k_BT\mathcal{V}\int d\mathcal{E}\,D(\mathcal{E})\ln\left[1+e^{\beta[\mu-\mathcal{E}]}\right].$$

$$N = -\frac{\partial\Pi}{\partial\mu}$$
$$= \mathcal{V}\int d\mathcal{E}'\,D(\mathcal{E}')\frac{e^{\beta\mu-\beta\mathcal{E}'}}{1+e^{\beta\mu-\beta\mathcal{E}'}}$$
$$\Rightarrow n = \frac{N}{\mathcal{V}} = \int d\mathcal{E}'\,D(\mathcal{E}')f(\mathcal{E}'),$$

$$f(\mathcal{E}) = \frac{1}{e^{\beta(\mathcal{E}-\mu)}+1}$$

$$f_{\vec{k}} = \frac{1}{e^{\beta(\mathcal{E}_{\vec{k}}-\mu)}+1}.$$

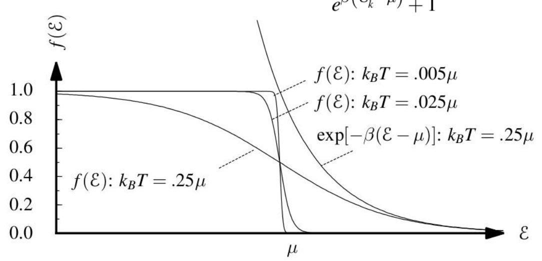

Figure 6.3: Sketch of the Fermi function $f(\mathcal{E})$ for various values of k_BT.

Element	Z	n ($10^{22}\,\mathrm{cm}^{-3}$)	k_F ($10^8\,\mathrm{cm}^{-1}$)	$\mathcal{E}_F$ (eV)	T_F (10^4 K)	v_F ($10^8\,\mathrm{cm\,s}^{-1}$)	r_s/a_0
Li	1	4.60	1.11	4.68	5.43	1.28	3.27
Na	1	2.54	0.91	3.15	3.66	1.05	3.99
K	1	1.32	0.73	2.04	2.37	0.85	4.95
Rb	1	1.08	0.68	1.78	2.06	0.79	5.30
Cs	1	0.85	0.63	1.52	1.76	0.73	5.75
Cu	1	8.49	1.36	7.04	8.17	1.57	2.67
Ag	1	5.86	1.20	5.50	6.38	1.39	3.02
Au	1	5.90	1.20	5.53	6.42	1.39	3.01
Be	2	24.72	1.94	14.36	16.67	2.25	1.87
Mg	2	8.62	1.37	7.11	8.26	1.58	2.65
Ca	2	4.66	1.11	4.72	5.48	1.29	3.26
Sr	2	3.49	1.01	3.89	4.52	1.17	3.59
Ba	2	3.15	0.98	3.64	4.22	1.13	3.71
Zn	2	13.13	1.57	9.42	10.93	1.82	2.31
Cd	2	9.26	1.40	7.47	8.66	1.62	2.59
Hg	2	16.22	1.69	10.84	12.59	1.95	2.15

Jellium analysis of some metals

Element	Z	n (10^{22} cm^{-3})	k_F (10^8 cm^{-1})	$\mathcal{E}_F$ (eV)	T_F (10^4 K)	v_F (10^8 cm s^{-1})	r_s/a_0
Al	3	18.07	1.75	11.66	13.53	2.02	2.07
Ga	3	15.31	1.65	10.44	12.11	1.92	2.19
In	3	11.50	1.50	8.62	10.01	1.74	2.41
Sn	4	14.83	1.64	10.22	11.86	1.89	2.22
Pb	4	13.19	1.57	9.45	10.97	1.82	2.30
Sb	5	16.54	1.70	10.99	12.75	1.97	2.14
Bi	5	14.04	1.61	9.85	11.43	1.86	2.26
Mn	4	32.61	2.13	17.28	20.05	2.46	1.70
Fe	2	16.90	1.71	11.15	12.94	1.98	2.12
Co	2	18.18	1.75	11.70	13.58	2.03	2.07
Ni	2	18.26	1.76	11.74	13.62	2.03	2.07

How well does the jellium model work – analysis of electronic contribution to specific heat

First consider the following trick:

$$\langle H \rangle = \int_{-\infty}^{\infty} d\mathcal{E}\, H(\mathcal{E}) f(\mathcal{E}).$$

$$\langle H \rangle = \int_{-\infty}^{\infty} d\mathcal{E} \left[\int_{-\infty}^{\mathcal{E}} d\mathcal{E}' H(\mathcal{E}') \right] \left[\frac{\partial f}{\partial \mu} \right].$$

$$\langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \sum_{n=1}^{\infty} [\frac{d^{2n-1}}{d\mu^{2n-1}} H(\mu)] \int_{-\infty}^{\infty} d\mathcal{E}\, \frac{(\mathcal{E}-\mu)^{2n}}{(2n)!} \left[\frac{\partial f}{\partial \mu} \right]$$

$$= \int_{-\infty}^{\mu} d\mathcal{E} H(\mathcal{E}) + \sum_{n=1}^{\infty} a_n [k_B T]^{2n} \frac{d^{2n-1}}{d\mu^{2n-1}} H(\mu)$$

$$a_n = \int_{-\infty}^{\infty} dx \left[-\frac{\partial}{\partial x} \frac{1}{e^x+1} \right] \frac{x^{2n}}{(2n)!}$$

$$= \frac{1}{(2n)!} \left(\frac{d}{db} \right)^{2n} \left[\frac{b\pi}{\sin b\pi} \right] \Big|_{b=0}$$

$$\Rightarrow \langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \frac{\pi^2}{6} [k_B T]^2 H'(\mu) + \frac{7\pi^4}{360} [k_B T]^4 H'''(\mu) + \ldots .$$

$$c_{\mathcal{V}} = \frac{1}{\mathcal{V}}\frac{\partial \mathcal{E}}{\partial T}\,|_{N\mathcal{V}}.$$

$$\begin{aligned}\frac{\mathcal{E}}{\mathcal{V}} &= \int d\mathcal{E}' f(\mathcal{E}')\mathcal{E}' D(\mathcal{E}') \\ &= \int_0^{\mu} d\mathcal{E}'\,\mathcal{E}' D(\mathcal{E}') + \frac{\pi^2}{6}(k_B T)^2 \frac{d(\mu D(\mu))}{d\mu}.\end{aligned}$$

$$\frac{\partial \mu}{\partial T}\,|_{N\mathcal{V}} = -\frac{\frac{\partial N}{\partial T}\,|_{\mu\mathcal{V}}}{\frac{\partial N}{\partial \mu}\,|_{T\mathcal{V}}}.$$

$$N = \mathcal{V}\int d\mathcal{E}' f(\mathcal{E}') D(\mathcal{E}') = \mathcal{V}\int_0^{\mu} d\mathcal{E}'\, D(\mathcal{E}') + \mathcal{V}\frac{\pi^2}{6}(k_B T)^2 D'(\mu),$$

$$\frac{\partial \mu}{\partial T}\,|_{N\mathcal{V}} = -\frac{\pi^2}{3}k_B^2 T \frac{D'(\mu)}{D(\mu)}.$$

$$\mu = \mathcal{E}_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(\mathcal{E}_F)}{D(\mathcal{E}_F)}.$$

$$\begin{aligned}\frac{\mathcal{E}}{\mathcal{V}} &= \int_0^{\mathcal{E}_F} d\mathcal{E}'\,\mathcal{E}' D(\mathcal{E}') + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \\ &\quad + \mathcal{E}_F\left\{(\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6}(k_B T)^2 D'(\mathcal{E}_F)\right\}\end{aligned}$$

$$\begin{aligned}\Rightarrow \frac{\mathcal{E}}{\mathcal{V}} &= \int_0^{\mathcal{E}_F} d\mathcal{E}\,\mathcal{E} D(\mathcal{E}) + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \\ \Rightarrow c_{\mathcal{V}} &= \frac{\pi^2}{3}k_B^2 T D(\mathcal{E}_F).\end{aligned}$$

$$c_{\mathcal{V}} = \frac{1}{\mathcal{V}}\left.\frac{\partial \mathcal{E}}{\partial T}\right|_{N\mathcal{V}}$$

$$\gamma \equiv \frac{c_{\mathcal{V}}}{T} = \frac{\pi^2}{2}\left(\frac{k_B}{\mathcal{E}_F}\right) n k_B.$$

Specific heat table from Marder's text:

Metal	Z	γ (mJ mole^{-1} K^{-2}) Expt.	Eq. (6.78)	Metal	Z	γ (mJ mole^{-1} K^{-2}) Expt.	Eq. (6.78)
Li	1	1.65	0.74	Al	3	1 .35	0.91
Na	1	1.38	1.09	Ga	3	0 .60	1.02
K	1	2.08	1.67	In	3	1 .66	1.23
Rb	1	2.63	1.90	Sn	4	1 .78	1.41
Cs	1	3.97	2.22	Pb	4	2 .99	1.50
Cu	1	0.69	0.50	Sb	5	0 .12	1.61
Ag	1	0.64	0.64	Bi	5	0 .008	1.79
Au	1	0.69	0.64	Mn	2	12 .8	1.10
Be	2	0.17	0.5	Fe	2	4 .90	1.06
Mg	2	1.6	0.99	UPt_3		450	
Ca	2	2.73	1.51	UBe_{13}		1100	
Sr	2	3.64	1.79				
Ba	2	2.7	1.92				
Zn	2	0.64	0.75				
Cd	2	0.69	0.95				