PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 10:

Reading: Chap. 4 in GGGPP;

Free electron theory of metals

1. **Density of states for free-electron model**
2. **Fermi-Dirac statistics**
3. **Chemical potential and electronic specific heat**

PHY 752 Solid State Physics

MWF 11 AM-11:50 PM | OPL 103 | http://www.wfu.edu/~natalie/f15phy752/

Instructor: Natalie Holzwarth | Phone:758-5510 | Office:300 OPL | e-mail:natalie@wfu.edu

Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1.1-1.2	Electrons in a periodic one-dimensional potential	#1
2	Fri, 8/28/2015	Chap. 1.3	Electrons in a periodic one-dimensional potential	#2
3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015			

News

Research Labs Tour Part I

Congratulations to Dr. Greg Smith, recent Ph.D. Recipient

Congratulations to Dr. Jie Liu, recent Ph.D. Recipient

Events

Wed. Sept. 16, 2015
Breaking down (and reintegrating) the role of cell and matrix mechanics in cell-matrix interactions
Professor Nicholas A. Kurniawan, Eindhoven University of Technology
Olin 101, 4:00 PM
Refreshments at 3:30 PM Olin Lobby

Fri. Sept. 18, 2015
Thesis Presentation
Solid Electrolytes
Nicholas Lepley, WFU
Olin 101 at 2:30 PM

WFU Physics Colloquium

TITLE: Breaking down (and reintegrating) the role of cell and matrix mechanics in cell-matrix interactions

SPEAKER: Professor Nicholas A. Kurniawan,

Department of Biomedical Engineering,
Eindhoven University of Technology

TIME: Wednesday September 16, 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

In recent years it has been increasingly realized that physical and mechanical interactions between the cell and the matrix are key determinants of a wide variety of physiological functions and pathological processes. In this talk, I will present our recent efforts to unravel (1) the underlying principles behind the fascinating nonlinear mechanical properties of protein networks such as the cytoskeleton and extracellular matrix like fibrin and collagen; and (2) the manifestations of the dynamic mechanical cell-matrix interactions during 3D cell

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:

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

Quantum Theory of materials -- continued

Electronic Schrödinger equation:

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

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

Nuclear Hamiltonian: (Often treated classically)

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

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

Effective nuclear interaction provided by electrons

Terms neglected in Born-Oppenheimer approximation

Correction terms

$$\mathcal{H}^{\text{Correction}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})X^{\text{Nuclei}}_{\alpha\nu}(\{\mathbf{R}^a\})\Upsilon^{\text{Electrons}}_{\alpha}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) =$$
$$\sum_a \frac{1}{M_a}\left(P_a X^{\text{Nuclei}}_{\alpha\nu}(\{\mathbf{R}^a\})\right)\left(P_a \Upsilon^{\text{Electrons}}_{\alpha}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right) +$$
$$\sum_a \frac{1}{2M_a} X^{\text{Nuclei}}_{\alpha\nu}(\{\mathbf{R}^a\})\left(P_a^2 \Upsilon^{\text{Electrons}}_{\alpha}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right)$$

First consider electronic Hamiltonian

Electronic Schrödinger equation:

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

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

Independent electron contributions

Jellium model of metals

- Nuclear potential represented by a uniform background of positive charge with charge density $n_0=Z/V$ (V representing volume per atom)
- Electrons represented as independent free electrons occupying free-electron states $E(k) = \frac{\hbar^2 k^2}{2m}$ for $0 \le k \le k_F$

Figure from GGGPP

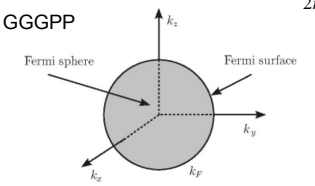


Figure 3.2 Schematic representation in the **k**-space of the Fermi sphere of occupied states and of the Fermi surface of the free-electron gas. At $T = 0$ each state of wavevector **k**, with $k < k_F$, is occupied by two electrons of either spin.

Determination of Fermi radius in terms of electron density $n=N/V$ where $N=Z$ Note: in practice only valence electrons are included in this model and the compensating nuclear background charge is adjusted accordingly.

Wigner-Seitz radius $\frac{4}{3}\pi r_s^3 a_B^3 = \frac{1}{n} = \frac{V}{N}$,

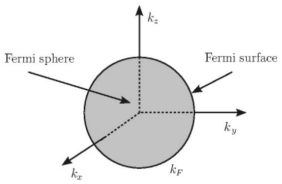
Bohr radius
0.529177 Angstroms

We evaluate r_s for alkali metals (for instance); Li, Na, K, Rb have bcc structure with cube edge a equal to 3.49 Å, 4.23 Å, 5.23 Å, and 5.59 Å, respectively. In the volume a^3 we have two atoms and two conduction electrons. From Eq. (3.2) we obtain

$$\frac{4}{3}\pi r_s^3 a_B^3 = \frac{a^3}{2} \quad \Longrightarrow \quad r_s = \frac{a}{a_B}\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/3} = 0.492\,\frac{a}{a_B};$$

the values for r_s are 3.25, 3.94, 4.87, and 5.20 for Li, Na, K, and Rb, respectively. A similar reasoning can be done for other crystals. For instance, the crystal structure of Al is fcc, with lattice constant $a = 4.05$ Å. In the volume a^3 we have four atoms and twelve conduction electrons; from Eq. (3.2) we have $(4/3)\pi r_s^3 a_B^3 = a^3/12$ and $r_s = 2.07$. Metallic densities of conduction electrons occur mostly in the range $2 < r_s < 6$.

Calculation of the Fermi level



$$N = \sum_{\mathbf{k}}^{k<k_F} 2 = 2\frac{V}{(2\pi)^3}\frac{4}{3}\pi k_F^3 = \frac{V}{3\pi^2}k_F^3 \quad \Longrightarrow \quad k_F^3 = 3\pi^2 n,$$

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
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

From Marder's text

Jellium analysis of some metals

Element	Z	n ($10^{22}\,\mathrm{cm}^{-3}$)	k_F ($10^8\,\mathrm{cm}^{-1}$)	$\mathcal{E}_F$ (eV)	T_F ($10^4\,\mathrm{K}$)	v_F ($10^8\,\mathrm{cm\,s}^{-1}$)	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

Density of states analysis of free electron gas

$$D(E) = 2\frac{V}{(2\pi)^3}\int \delta\left(E - \frac{\hbar^2k^2}{2m}\right)d\mathbf{k} = \frac{V}{4\pi^3}\int_0^\infty 4\pi k^2\,\delta\left(E - \frac{\hbar^2k^2}{2m}\right)dk.$$

The change of variable $\hbar^2k^2/2m = x$ gives

$$D(E) = \frac{V}{2\pi^2}\int_0^\infty \left(\frac{2m}{\hbar^2}\right)^{3/2} x^{1/2}\,\delta(E-x)\,dx = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}, \quad E > 0. \tag{3.8a}$$

$$D(E) = \frac{3}{2}\frac{N}{E_F}\left(\frac{E}{E_F}\right)^{1/2},$$

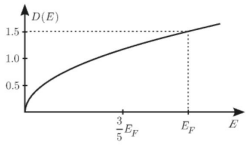


Figure 3.3 Density-of-states, in units of N/E_F, for a free-electron gas; the average electron energy (3/5) E_F is also indicated.

Temperature dependence of the Free-electron gas – Fermi-Dirac distribution

$$f(E,\mu,T) = \frac{1}{e^{(E-\mu)/k_BT} + 1},$$

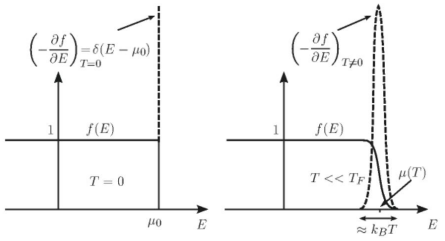


Figure 3.4 The Fermi-Dirac distribution function $f(E)$ and energy derivative $(-\partial f/\partial E)$ at $T = 0$ and at a finite temperature T, with $T \ll T_F$; μ_0 denotes the chemical potential $\mu(T)$ at $T = 0$.

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

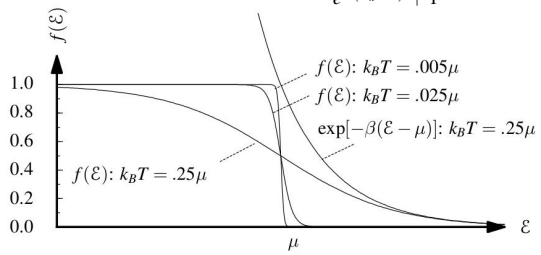


Figure 6.3: Sketch of the Fermi function $f(\mathcal{E})$ for various values of k_BT.

Temperature dependence of the chemical potential

$$N = \int_{-\infty}^{+\infty} D(E) f(E, \mu, T)\, dE;$$

$$N = \int_{-\infty}^{\mu} D(E)\, dE + \frac{\pi^2}{6} k_B^2 T^2 D'(\mu) + O(T^4),$$

Justification for this result; consider the following integral

$$I = \int_{-\infty}^{+\infty} G(E) \left(-\frac{\partial f}{\partial E}\right) dE,$$

Taylor's expansion

$$G(E) = G(\mu) + (E-\mu)\left(\frac{dG}{dE}\right)_{E=\mu} + \frac{1}{2}(E-\mu)^2 \left(\frac{d^2G}{dE^2}\right)_{E=\mu} + \cdots$$

Evaluating the integrals

$$\int_{-\infty}^{+\infty} G(E) \left(-\frac{\partial f}{\partial E}\right) dE = G(\mu) + \frac{1}{2} G''(\mu) \int_{-\infty}^{+\infty} (E-\mu)^2 \left(\frac{\partial f}{\partial E}\right) dE + \cdots$$

$$\begin{aligned}
&\frac{1}{2}\int_{-\infty}^{+\infty} (E-\mu)^2 \left(-\frac{\partial f}{\partial E}\right) dE \\
&= \int_{\mu}^{+\infty} (E-\mu)^2 \left(-\frac{\partial f}{\partial E}\right) dE \quad \text{[integrating by parts]} \\
&= 2\int_{\mu}^{+\infty} (E-\mu) f(E)\, dE \\
&= 2\int_{\mu}^{+\infty} \frac{E-\mu}{e^{(E-\mu)/k_BT}+1}\, dE \quad \left[\text{set } \frac{E-\mu}{k_BT} = x\right] \\
&= 2(k_BT)^2 \int_0^{+\infty} \frac{x}{e^x+1}\, dx = \frac{\pi^2}{6} k_B^2 T^2.
\end{aligned}$$

$$\int_0^{+\infty} \frac{x}{e^x+1} dx = \frac{1}{2}\Gamma(2)\,\zeta(2) = \frac{\pi^2}{12}$$

Evaluation of the integrals continued

$$\int_{-\infty}^{+\infty} \frac{dG(E)}{dE} f(E)\,dE \equiv G(\mu) + \frac{\pi^2}{6}(k_B T)^2 G''(\mu) + \cdots$$

Now suppose that $G(E) = \int_{-\infty}^{E} \Gamma(E')\,dE'.$

$$\boxed{\int_{-\infty}^{+\infty} \Gamma(E) f(E)\,dE = \int_{-\infty}^{\mu} \Gamma(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 \left(\frac{d\Gamma}{dE}\right)_{E=\mu} + O(T^4)},$$

$$N = \int_{-\infty}^{\mu} D(E)\,dE + \frac{\pi^2}{6} k_B^2 T^2 D'(\mu) + O(T^4),$$

Taking temperature derivative:

$$N = \int_{-\infty}^{\mu} D(E)\,dE + \frac{\pi^2}{6} k_B^2 T^2 D'(\mu) + O(T^4),$$

$$0 = D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3} k_B^2 T D'(\mu)$$

$$\frac{d\mu}{dT} = -\frac{\pi^2}{3} k_B^2 T \frac{D'(\mu)}{D(\mu)}.$$

For Free-electron gas:

$$\frac{d\mu}{dT} = -\frac{\pi^2}{6\mu} k_B^2 T$$

$$\mu(T) = \mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\mu_0}\right)^2\right] = \mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right].$$

Specific heat of Free electron gas

$$C_V = \left(\frac{dU}{dT}\right)_V.$$

$$U(T) = \int_{-\infty}^{+\infty} E\,D(E) f(E, \mu, T)\,dE$$

$$= \int_{-\infty}^{\mu} E\,D(E)\,dE + \frac{\pi^2}{6} k_B^2 T^2 [D(\mu) + \mu D'(\mu)] + O(T^4),$$

$$C_V = \left(\frac{dU}{dT}\right)_V = \mu D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3} k_B^2 T [D(\mu) + \mu D'(\mu)].$$

$$\boxed{C_V(T) = \frac{\pi^2}{3} k_B^2 T D(\mu_0)}.$$

$$c_V(T) = \frac{\pi^2}{3} k_B^2 T \frac{D(\mu_0)}{V} = \gamma T, \qquad \gamma = \frac{\pi^2}{3} k_B^2 \frac{D(\mu_0)}{V}.$$

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				