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

Plan for Lecture 29: Chap. 9 of GGGPP

Lattice dynamics of crystals

1. **Quantum treatment of lattice vibrations**
2. **Statistical mechanics of lattice vibrations**

Lecture notes prepared using materials from GGGPP text.

14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015	Chap. 6	Example electronic structures	#16
18	Mon, 10/05/2015	Chap. 6	Ionic and covalent crystals	#17
19	Wed, 10/07/2015	Chap. 6	More examples of electronic structures	#18
20	Fri, 10/09/2015	Chap. 1-6	Review	Start exam
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Exam due before 10/19/2015
	Fri, 10/16/2015		Fall break – no class	
21	Mon, 10/19/2015	Chap. 10	X-ray and neutron diffraction	#19
22	Wed, 10/21/2015	Chap. 10	Scattering of particles by crystals	#20
23	Fri, 10/23/2015	Chap. 11	Optical and transport properties of metals	#21
24	Mon, 10/26/2015	Chap. 11	Optical and transport properties of metals	#22
25	Wed, 10/28/2015	Chap. 11	Transport in metals	#23
26	Fri, 10/30/2015	Chap. 12	Optical properties of semiconductors and insulators	
27	Mon, 11/02/2015	Chap. 7 & 12	Excitons	#24
28	Wed, 11/04/2015	Chap. 9	Lattice vibrations	#25
29	Fri, 11/06/2015	Chap. 9	Lattice vibrations	#26
	Wed, 12/02/2015		Student presentations I	
	Fri, 12/04/2015		Student presentations II	
	Mon, 12/07/2015		Begin Take-home final	

Quantum treatment of one-dimensional harmonic crystal

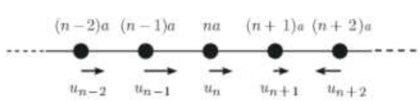

Figure 9.1 Longitudinal displacements in a one-dimensional monoatomic lattice. The equilibrium positions $t_n = na$ are indicated by circles; the displacements u_n at a given instant are indicated by arrows.

Hamiltonian:

$$H = \sum_n \frac{1}{2M} p_n^2 + \frac{1}{2} C \sum_n \left(2u_n^2 - u_n u_{n+1} - u_n u_{n-1}\right).$$

Commutation relations:

$$[u_n, p_{n'}] = i\hbar\delta_{n,n'}; \quad [u_n, u_{n'}] = [p_n, p_{n'}] = 0.$$

Fourier transformation relationships:

$$p_q = \frac{1}{\sqrt{N}} \sum_{t_n} e^{+iqt_n} p_n, \quad u_q = \frac{1}{\sqrt{N}} \sum_{t_n} e^{-iqt_n} u_n.$$

$$p_n = \frac{1}{\sqrt{N}} \sum_{q} e^{-iqt_n} p_q, \quad u_n = \frac{1}{\sqrt{N}} \sum_{q} e^{+iqt_n} u_q.$$

$$\frac{1}{N} \sum_{t_n} e^{-i(q-q')t_n} = \delta_{q,q'} \quad \text{and} \quad \frac{1}{N} \sum_{q} e^{-iq(t_n - t_{n'})} = \delta_{n,n'}.$$

$$[u_q, p_{q'}] = i\hbar\delta_{qq'}; \quad [u_q, u_{q'}] = [p_q, p_{q'}] = 0.$$

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Hamiltonian in terms of Fourier transformed variables

$$H = \sum_n \frac{1}{2M} p_n^2 + \frac{1}{2} C \sum_n \left(2u_n^2 - u_n u_{n+1} - u_n u_{n-1}\right).$$

$$\boxed{H = \sum_q \left[\frac{1}{2M} p_q p_{-q} + \frac{1}{2} M \omega_q^2 u_q u_{-q}\right]}.$$

where $\omega^2(q) = \frac{C}{M}(2 - e^{-iqa} - e^{iqa}) = \frac{4C}{M}\sin^2\frac{qa}{2}$

$$\sum_n u_n^2 = \frac{1}{N} \sum_n \sum_{qq'} e^{i(q+q')t_n} u_q u_{q'} = \sum_q u_q u_{-q}.$$

$$\sum_n u_n u_{n+1} = \frac{1}{N} \sum_n \sum_{qq'} e^{i(q+q')t_n + iq'a} u_q u_{q'} = \sum_q u_q u_{-q} e^{-iqa}$$

$$\sum_n p_n^2 = \sum_n p_q p_{-q}.$$

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Mathematical digression

Transformation to creation and annihilation operators -- Appendix A (one dimensional case)

$$H = \frac{1}{2}\hbar\omega \left[\frac{1}{M\hbar\omega} p_x^2 + \frac{M\omega}{\hbar} x^2\right]$$

Define $l_0^2 = \frac{\hbar}{M\omega}$.

$$\boxed{H = \frac{1}{2}\hbar\omega \left[\frac{l_0^2}{\hbar^2} p_x^2 + \frac{1}{l_0^2} x^2\right]}$$

Creation and annihilation operators

$$a = \frac{1}{\sqrt{2}}\left[\frac{1}{l_0} x + i\frac{l_0}{\hbar} p_x\right], \quad a^\dagger = \frac{1}{\sqrt{2}}\left[\frac{1}{l_0} x - i\frac{l_0}{\hbar} p_x\right]; \quad l_0 = \sqrt{\frac{\hbar}{M\omega}}.$$

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Inverse transformation

$$x = \frac{1}{\sqrt{2}} l_0 (a + a^\dagger), \quad p_x = \frac{-i}{\sqrt{2}} \frac{\hbar}{l_0} (a - a^\dagger).$$

Commutation relationships

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = 1.$$

$$aa^\dagger = a^\dagger a + 1, \quad aa^{\dagger 2} = (a^\dagger a + 1)a^\dagger = a^{\dagger 2} a + 2a^\dagger.$$

In general:

$$aa^{\dagger n} = a^{\dagger n} a + n a^{\dagger n-1}.$$

Normalized states

$$a|0\rangle = 0$$

$$|n\rangle = \frac{1}{\sqrt{n!}} a^{\dagger n} |0\rangle.$$

Properties of operators and states:

$$\langle 0|a^n a^{\dagger n}|0\rangle = \langle 0|a^{n-1} a a^{\dagger n}|0\rangle = n\langle 0|a^{n-1} a^{\dagger n-1}|0\rangle = n!$$

$$a^\dagger a|n\rangle = n|n\rangle.$$

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.$$

$$\langle n|a^{\dagger p} a^p|n\rangle = \langle n|a^{\dagger p}|n-p\rangle\langle n-p|a^p|n\rangle = (\sqrt{n-p+1}\cdots\cdots\sqrt{n})^2, \quad n \ge p.$$

$$\langle n|a^{\dagger p} a^p|n\rangle = \begin{cases} n!/(n-p)! & \text{if } n \ge p \\ 0 & \text{if } n < p \end{cases}$$

Hamiltonian

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

Eigenstates:

$$H|n\rangle = \epsilon_n|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle$$

Using creation and annhilation operators for operators in Fourier space

$$a_q = \sqrt{\frac{M\omega_q}{2\hbar}}\, u_q + i\sqrt{\frac{1}{2M\hbar\omega_q}}\, p_{-q},$$

$$a_q^\dagger = \sqrt{\frac{M\omega_q}{2\hbar}}\, u_{-q} - i\sqrt{\frac{1}{2M\hbar\omega_q}}\, p_q.$$

$$u_q = \sqrt{\frac{\hbar}{2M\omega_q}}\left(a_q + a_{-q}^\dagger\right) \quad \text{and} \quad p_q = (-i)\sqrt{\frac{M\hbar\omega_q}{2}}\left(a_{-q} - a_q^\dagger\right).$$

Commutation relations:

$$\left[a_q, a_{q'}^\dagger\right] = \delta_{qq'}; \quad \left[a_q, a_{q'}\right] = \left[a_q^\dagger, a_{q'}^\dagger\right] = 0.$$

In terms of site operators:

$$u_n = \frac{1}{\sqrt{N}} \sum_q e^{iqt_n} \sqrt{\frac{\hbar}{2M\omega_q}} \left(a_q + a_{-q}^\dagger\right).$$

$$p_n = \frac{1}{\sqrt{N}} \sum_q e^{-iqt_n} (-i) \sqrt{\frac{M\hbar\omega_q}{2}} \left(a_{-q} - a_q^\dagger\right).$$

Hamiltonian

$$\boxed{H = \sum_q \hbar\omega(q) \left(a_q^\dagger a_q + \frac{1}{2}\right)}.$$

Eigenstates for each q: $\left|n_q\right\rangle$

$$H\left|n_q\right\rangle = \epsilon_n \left|n_q\right\rangle = \hbar\omega_q \left(n_q + \frac{1}{2}\right)\left|n_q\right\rangle$$

Statistical mechanics treatment of vibrational motions at constant temperature T

Partition function: $Z(T) = \left\langle \psi \left| e^{-H/kT} \right| \psi \right\rangle = \prod_q \sum_{n_q=0}^{\infty} e^{-\hbar\omega_q\left(n_q+\frac{1}{2}\right)/kT}$

$$\equiv \prod_q Z_q$$

$$Z_q \equiv \sum_{n_q=0}^{\infty} e^{-\hbar\omega_q\left(n_q+\frac{1}{2}\right)/kT} = \frac{e^{-\hbar\omega_q/2kT}}{1-e^{-\hbar\omega_q/kT}}$$

Average vibrational energy: $U = -\frac{\partial \ln Z}{\partial \beta}$ where $\beta \equiv \frac{1}{kT}$

Statistical mechanics treatment of vibrational motions at constant temperature T

$$U_{\text{vibr}}(T) = \sum_{\mathbf{q}\,p} \left[\frac{\hbar\omega(\mathbf{q},p)}{e^{\hbar\omega(\mathbf{q},p)/k_BT} - 1} + \frac{1}{2}\hbar\omega(\mathbf{q},p)\right].$$

index for distinct modes (for each degree of freedom)

Specific heat

$$\boxed{C_V(T) = \frac{\partial U_{\text{vibr}}}{\partial T} = \frac{\partial}{\partial T} \sum_{\mathbf{q}p} \frac{\hbar\omega(\mathbf{q},p)}{e^{\hbar\omega(\mathbf{q},p)/k_BT} - 1}}.$$

$$= k \sum_{\mathbf{q},p} \left(\frac{\hbar\omega(\mathbf{q},p)}{kT}\right)^2 \frac{e^{\hbar\omega(\mathbf{q},p)/kT}}{\left(e^{\hbar\omega(\mathbf{q},p)/kT} - 1\right)^2}$$

Evaluation of summation over **q**:

$$\sum_{\mathbf{q},p} \Rightarrow \frac{V}{(2\pi)^3}\int d^3q\, d\omega \sum_p \delta(\omega-\omega(\mathbf{q},p)) = \int d\omega D(\omega)$$

Debye approximation to $D(\omega)$:

Assume: $\omega = v_s q$ for $0 \le q \le q_D$

where $\frac{4}{3}\pi q_D^3 = \frac{(2\pi)^3}{V}$

$$D(\omega) = \begin{cases} 3N\frac{\omega^2}{\omega_D^3} & 0 \le \omega \le \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

Debye approximation continued

$$U_{\text{vibr}}^{(\text{acoustic})}(T) = 9Nk_BT\left(\frac{T}{T_D}\right)^3\int_0^{x_D}\frac{x^3}{e^x-1}\,dx\,.$$

$$U_{\text{vibr}}^{(\text{acoustic})}(T) = \frac{3}{5}\pi^4Nk_B\frac{T^4}{T_D^3}, \quad T \ll T_D\,.$$

$$= 3NkT \quad \text{for} \quad T >> T_D$$

$$C_V(T) = \frac{12}{5}\pi^4Nk_B\frac{T^3}{T_D^3}, \quad T \ll T_D$$

$$= 3Nk \quad \text{for} \quad T >> T_D$$

Note that $T_D = \frac{\hbar v_s}{k}\left(\frac{6\pi^2}{V}\right)^{1/3}$

TABLE 1 Debye Temperature and Thermal Conductivity[a]

Low temperature limit of θ, in Kelvin
Thermal conductivity at 300 K, in W cm^{-1}K^{-1}

Li 344 0.85	Be 1440 2.00											B 0.27	C 2230 1.29	N	O	F	Ne 75
Na 158 1.41	Mg 400 1.56											Al 428 2.37	Si 645 1.48	P	S	Cl	Ar 92
K 91 1.02	Ca 230	Sc 360. 0.16	Ti 420 0.22	V 380 0.31	Cr 630 0.94	Mn 410 0.08	Fe 470 0.80	Co 445 1.00	Ni 450 0.91	Cu 343 4.01	Zn 327 1.16	Ga 320 0.41	Ge 374 0.60	As 282 0.50	Se 90 0.02	Br	Kr 72
Rb 56 0.58	Sr 147	Y 280 0.17	Zr 291 0.23	Nb 275 0.54	Mo 450 1.38	Tc 0.51	Ru 600 1.17	Rh 480 1.50	Pd 274 0.72	Ag 225 4.29	Cd 209 0.97	In 108 0.82	Sn α 200 0.67	Sb 211 0.24	Te 153 0.02	I	Xe 64
Cs 38 0.36	Ba 110	La β 142 0.14	Hf 252 0.23	Ta 240 0.58	W 400 1.74	Re 430 0.48	Os 500 0.88	Ir 420 1.47	Pt 240 0.72	Au 165 3.17	Hg 71.9	Tl 78.5 0.46	Pb 105 0.35	Bi 119 0.08	Po	At	Rn
Fr	Ra	Ac															

Ce 0.11	Pr 0.12	Nd 0.16	Pm	Sm 0.13	Eu	Gd 200 0.11	Tb 0.11	Dy 210 0.11	Ho 0.16	Er 0.14	Tm 0.17	Yb 120 0.35	Lu 210 0.16
Th 163 0.54	Pa	U 207 0.28	Np 0.06	Pu 0.07	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

[a] Most of the θ values were supplied by N. Pearlman; references are given the *A.I.P. Handbook*, 3rd ed. the thermal conductivity values are from R. W. Powell and Y. S. Touloukian, Science **181**, 999 (1973).