

Phonons

5.1 Monatomic Lattice with Random Interactions

In a disordered material the periodicity of the solid is broken, and this affects the phonon spectrum. Various types of disorder are possible, including bond disorder, isotopic mass disorder, or a breaking of the lattice periodicity. In this section a simple model exhibiting bond disorder is studied: a monatomic lattice in one dimension with nearest-neighbor (NN) interactions but with random spring constants. These are assumed to have only two values, K_A or K_B , with probabilities p_A and $p_B = 1 - p_A$, respectively.

The squares of the mode frequencies, ω_μ^2 , are determined by finding the eigenvalues of the random matrix \mathbf{D} defined by

$$D_{n,n} = \frac{K_n + K_{n-1}}{M}, \quad D_{n,n+1} = -\frac{K_n}{M}, \quad D_{n,n-1} = -\frac{K_{n-1}}{M}, \quad (\text{W5.1})$$

where $n = 1, 2, \dots, N$ labels the atoms in the monatomic lattice (with the subscript convention $0 \rightarrow N$ and $N + 1 \rightarrow 1$). All other matrix elements are zero. Rapid numerical techniques are available for diagonalizing such matrices.

The density of states (per unit frequency) per atom,

$$\rho(\omega) = \frac{1}{N} \sum_{\mu} \delta(\omega - \omega_{\mu}), \quad (\text{W5.2})$$

will be compared with the corresponding function expected for the uniform lattice with an average spring constant $K = p_A K_A + p_B K_B$. The density of states per atom for the uniform lattice is obtained using the dispersion relation of the book,[†] Eq. (5.7). Thus

$$\begin{aligned} \rho(\omega) &= \frac{1}{N} \int_{-\pi/a}^{\pi/a} \frac{Ldk}{2\pi} \delta\left(\sqrt{\frac{4K}{M}} \left|\sin \frac{ka}{2}\right| - \omega\right) \\ &= \frac{2}{\pi} \frac{1}{\sqrt{(4K/M) - \omega^2}}, \end{aligned} \quad (\text{W5.3})$$

[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a “W”; cross-references to material in the textbook appear without the “W.”

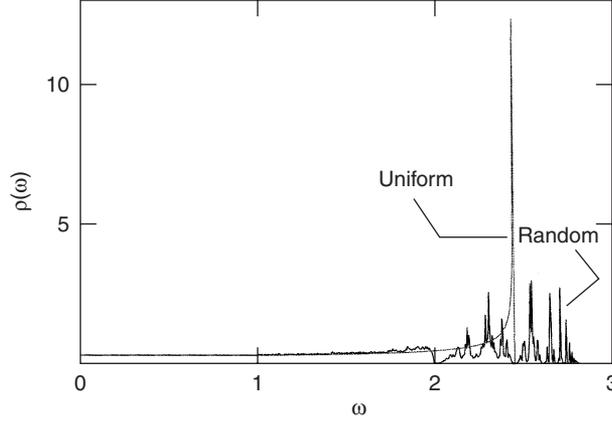


Figure W5.1. Phonon densities of states for random and uniform lattices. The calculation was performed with $N = 125$.

where $\omega^2 \leq 4K/M$. The results are presented in Fig. W5.1, where units are chosen so that $M = 1$, $K_A = 1$, $K_B = 2$, and $p_A = p_B = 0.5$. An $N = 125$ lattice was used and an ensemble average over different sets of random bonds was made. The frequencies corresponding to the pure K_A or pure K_B lattices are $\omega_A = 2(K_A/M)^{1/2}$ and $\omega_B = 2(K_B/M)^{1/2}$ (2 and 2.828 in the figure). The differences between the random and uniform lattice (with $K = 0.5K_A + 0.5K_B = 1.5$) are striking. At low frequencies the density of states follows the trend expected for the infinite uniform lattice. In the high-frequency region ($\omega_A < \omega < \omega_B$) there is an irregular structure for the density of states. It is found that as N increases, the high-frequency structure remains basically unchanged, except for the appearance of finer irregular features.

W5.2 Debye–Waller Factor

In this section the derivation of the Debye–Waller factor is sketched. For the sake of simplicity consider a monatomic lattice of atoms with mass M . Let the instantaneous position of the atom be denoted by $\mathbf{R} + \mathbf{u}(\mathbf{R}, t)$. The electron density is

$$n(\mathbf{r}, t) = n_{\text{atom}}(\mathbf{r} - \mathbf{R} - \mathbf{u}(\mathbf{R}, t)). \quad (\text{W5.4})$$

The analysis proceeds as in Chapter 3. The scattering amplitude $F(\mathbf{q}, t)$ is

$$F(\mathbf{q}, t) = f_{\text{atom}}(\mathbf{q}) \sum_{\mathbf{R}} \exp[-i\mathbf{q} \cdot (\mathbf{R} + \mathbf{u}(\mathbf{R}, t))] = f_{\text{atom}}(\mathbf{q})S(\mathbf{q}, t). \quad (\text{W5.5})$$

When evaluated at a reciprocal lattice vector $\mathbf{q} = \mathbf{G}$, the geometric structure factor becomes

$$S(\mathbf{G}, t) = \sum_{\mathbf{R}} \exp[-i\mathbf{G} \cdot \mathbf{u}(\mathbf{R}, t)]. \quad (\text{W5.6})$$

The strength of the coherent x-ray scattering is proportional to the absolute square of $S(\mathbf{G})$. It is useful to work in the *interaction representation* of quantum mechanics, in

which the operators are not time dependent. Begin by writing

$$|S(\mathbf{G})|^2 = \sum_{\mathbf{R}\mathbf{R}'} \exp[i\mathbf{G} \cdot (\mathbf{u}(\mathbf{R}') - \mathbf{u}(\mathbf{R}))]. \quad (\text{W5.7})$$

In the absence of fluctuations, this would be N^2 . In the presence of fluctuations, expand the displacements as a sum of phonon modes [see Eq. (W5A.5)]:

$$\mathbf{u}(\mathbf{R}) = \sqrt{\frac{1}{N}} \sum_{\hat{\mathbf{Q}}} \hat{\epsilon}_{\mathbf{Q}} [u_{\mathbf{Q}} \exp(i\mathbf{Q} \cdot \mathbf{R}) + u_{\mathbf{Q}}^\dagger \exp(-i\mathbf{Q} \cdot \mathbf{R})], \quad (\text{W5.8})$$

where $u_{\mathbf{Q}}$ and $\hat{\epsilon}_{\mathbf{Q}}$ are the amplitude and polarization of a phonon with wave vector \mathbf{Q} and frequency $\omega_{\mathbf{Q}}$. It follows that

$$|S(\mathbf{G})|^2 = \sum_{\mathbf{R}\mathbf{R}'} \prod_{\mathbf{Q}} \exp\left(\frac{i}{\sqrt{N}} \mathbf{G} \cdot \hat{\epsilon}_{\mathbf{Q}} \{u_{\mathbf{Q}} [\exp(i\mathbf{Q} \cdot \mathbf{R}') - \exp(i\mathbf{Q} \cdot \mathbf{R})] + \text{h.c.}\}\right), \quad (\text{W5.9})$$

where h.c. is the Hermitian conjugate of the first term. This must be averaged over a thermal distribution of phonons. The exponential is expanded into a power series. Note that $u_{\mathbf{Q}}$ is a Gaussian random variable with the first two moments being

$$\langle u_{\mathbf{Q}} \rangle = 0, \quad \langle |u_{\mathbf{Q}}|^2 \rangle = \frac{N\hbar}{2M\omega_{\mathbf{Q}}} \left(n_{\mathbf{Q}} + \frac{1}{2} \right). \quad (\text{W5.10})$$

Averages of products of Gaussian random variables are expressible in terms of the first two moments alone,

$$\langle u_{\mathbf{Q}_1} u_{\mathbf{Q}_2} u_{\mathbf{Q}_3} u_{\mathbf{Q}_4} \rangle = \langle u_{\mathbf{Q}_1} u_{\mathbf{Q}_2} \rangle \langle u_{\mathbf{Q}_3} u_{\mathbf{Q}_4} \rangle + \langle u_{\mathbf{Q}_1} u_{\mathbf{Q}_3} \rangle \langle u_{\mathbf{Q}_2} u_{\mathbf{Q}_4} \rangle + \langle u_{\mathbf{Q}_1} u_{\mathbf{Q}_4} \rangle \langle u_{\mathbf{Q}_2} u_{\mathbf{Q}_3} \rangle, \quad (\text{W5.11})$$

where the expansion includes all distinct permutations of the indices. Thus only even powers in the power series are nonvanishing. The series may then be resummed to give

$$\langle |S(\mathbf{G})|^2 \rangle = \sum_{\mathbf{R}\mathbf{R}'} \prod_{\mathbf{Q}} \exp\left\{ -\frac{2}{N} (\mathbf{G} \cdot \hat{\epsilon}_{\mathbf{Q}})^2 |u_{\mathbf{Q}}|^2 [1 - \cos \mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')] \right\}. \quad (\text{W5.12})$$

In a three-dimensional crystal the term $[1 - \cos(\cdot)]$ averages to $\frac{1}{2}$ and one obtains

$$\langle |S(\mathbf{G})|^2 \rangle = N^2 \exp\left[-\sum_{\mathbf{Q}} (\mathbf{G} \cdot \hat{\epsilon}_{\mathbf{Q}})^2 \frac{(n_{\mathbf{Q}} + \frac{1}{2}) \hbar}{M\omega_{\mathbf{Q}}} \right] = N^2 e^{-2W}. \quad (\text{W5.13})$$

This gives the desired expression for the Debye–Waller factor, $\exp(-2W)$. In the high-temperature limit, the Bose–Einstein distribution function may be replaced by $n_{\mathbf{Q}} \rightarrow k_B T / \hbar \omega_{\mathbf{Q}}$. It is also possible to use the Debye theory, used in Chapter 5 to evaluate the specific heat, to evaluate the Debye–Waller factor.

Appendix W5A: Quantization of Elastic Waves

In this appendix the classical elastic field will be *quantized*, that is, replaced by a set of phonons. It is a twofold procedure. First the elastic field is replaced by a set of independent harmonic oscillators, one for each normal mode. Then each of these is quantized in the same way that the simple harmonic oscillator is quantized. For the sake of simplicity, attention is restricted in this appendix to the one-dimensional monatomic lattice.

The starting point is the classical equation of motion for the particle displacements, given by Eq. (5.2):

$$M\ddot{u}_n = K(u_{n+1} - u_n) - K(u_n - u_{n-1}), \quad n = 1, 2, \dots, N. \quad (\text{W5A.1})$$

The energy of the system, or Hamiltonian, is the sum of the kinetic energy and the potential energy:

$$H = \frac{1}{2M} \sum_{n=1}^N p_n^2 + \frac{K}{2} \sum_{n=1}^N (u_{n+1} - u_n)^2. \quad (\text{W5A.2})$$

Here p_n represents the momentum conjugate to u_n . The equation of motion is obtained from Hamilton's equations of mechanics:

$$\dot{u}_n = \frac{\partial H}{\partial p_n} = \frac{p_n}{M}, \quad (\text{W5A.3})$$

$$\dot{p}_n = -\frac{\partial H}{\partial u_n} = K(u_{n+1} + u_{n-1} - 2u_n). \quad (\text{W5A.4})$$

Eliminating p_n from these equations gives Eq. (W5A.1).

Introduce a new set of coordinates $\{Q_j\}$ and momenta $\{P_j\}$, which we call *normal-mode coordinates* and *momenta*, defined by

$$u_n = \frac{1}{\sqrt{N}} \sum_{j=1}^N Q_j e^{inak_j}, \quad (\text{W5A.5})$$

$$p_n = \frac{1}{\sqrt{N}} \sum_{j=1}^N P_j e^{inak_j}, \quad (\text{W5A.6})$$

where a is the lattice constant and k_j is defined in Eq. (5.4). It is convenient to impose periodicity and define $Q_{N+j} = Q_j$ and $P_{N+j} = P_j$. Two powerful identities may be proved. The first involves a sum over lattice positions:

$$\sum_{n=1}^N \exp[ina(k_j - k_l)] = N\delta_{j,l}, \quad (\text{W5A.7})$$

and the second involves a sum over modes:

$$\sum_{j=1}^N \exp[ik_j a(n - m)] = N\delta_{n,m}. \quad (\text{W5A.8})$$

As Figs. W5A.1 and W5A.2 show, the sums will be zero when summed either over lattice positions with a given wave vector or summed over modes with a given lattice position. The one exception to both cases is when the lattice position is zero or when the wave vector is zero. For u_n and p_n to be real numbers, one can show from Eqs. (W5A.5) and (W5A.6) that

$$Q_{N-j}^* = Q_{-j}^* = Q_j, \quad P_{N-j}^* = P_{-j}^* = P_j. \quad (\text{W5A.9})$$

By making use of the identities (W5A.7) and (W5A.8), the Hamiltonian may be rewritten in terms of the P 's and Q 's:

$$H = \sum_{j=1}^N \left(\frac{P_j^* P_j}{2M} + \frac{M\omega_j^2}{2} Q_j^* Q_j \right). \quad (\text{W5A.10})$$

In this form, the Hamiltonian is expressed as the sum of N independent harmonic oscillators, each representing one of the normal modes of the lattice. The P_j and Q_j

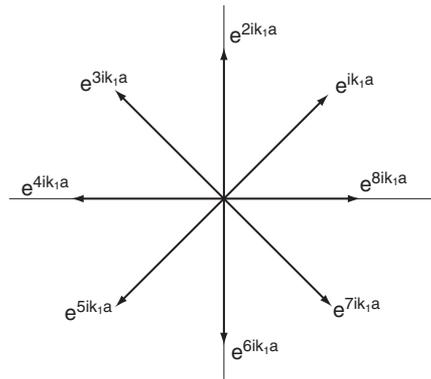


Figure W5A.1. Representation of the sum over lattice positions given in Eq. (W5A.7). Note that the vector sum is zero. In this diagram $N = 8$ and $j - l = 1$.

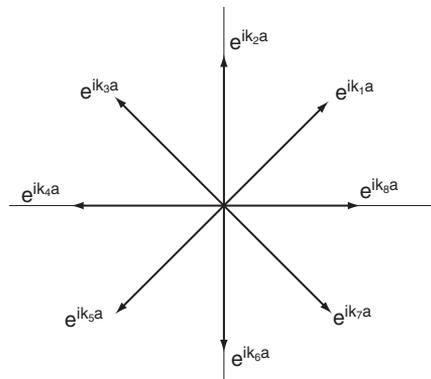


Figure W5A.2. Representation of the sum over modes given in Eq. (W5A.8). Note that the vector sum is zero. In this diagram $N = 8$ and $n - m = 1$.

coordinates are also expressible in terms of p_n and u_n :

$$Q_j = \frac{1}{\sqrt{N}} \sum_{n=1}^N u_n e^{-inak_j}, \quad (\text{W5A.11})$$

$$P_j = \frac{1}{\sqrt{N}} \sum_{n=1}^N p_n e^{-inak_j}. \quad (\text{W5A.12})$$

The quantization procedure is straightforward. One regards $\{u_n\}$ and $\{p_n\}$ as sets of quantum-mechanical operators obeying the usual equal-time commutation relations (see Appendix WC):

$$[u_n, u_m] = 0, \quad [p_n, p_m] = 0, \quad [p_n, u_m] = -i\hbar\delta_{m,n}. \quad (\text{W5A.13})$$

Hamilton's equations of motion are regarded as equations governing the time evolution of these operators. The Hamiltonian H , given above, is now an operator. Using the commutation rules, it can be shown that

$$[P_j, Q_l] = -i\hbar\delta_{j,l}, \quad [P_j, P_l] = 0, \quad [Q_j, Q_l] = 0. \quad (\text{W5A.14})$$

A further simplification of the problem results from introducing specific linear combinations of the P 's and Q 's,

$$a_j = \frac{1}{\sqrt{2M\omega_j\hbar}}(M\omega_j Q_j + iP_j), \quad a_j^+ = \frac{1}{\sqrt{2M\omega_j\hbar}}(M\omega_j Q_{N-j} - iP_{N-j}). \quad (\text{W5A.15})$$

These operators are referred to as *ladder operators*. They obey the commutation rules

$$[a_j, a_l] = 0, \quad [a_j^+, a_l^+] = 0, \quad [a_j, a_l^+] = \delta_{j,l}. \quad (\text{W5A.16})$$

The P and Q operators become

$$Q_j = \sqrt{\frac{\hbar}{2M\omega_j}}(a_j + a_{-j}^+), \quad (\text{W5A.17})$$

$$P_j = -i\sqrt{\frac{M\hbar\omega_j}{2}}(a_j - a_{-j}^+). \quad (\text{W5A.18})$$

The Hamiltonian finally becomes

$$H = \sum_{j=1}^N \hbar\omega_j (a_j^+ a_j + \frac{1}{2}). \quad (\text{W5A.19})$$

The quantity $n_j = a_j^+ a_j$ is the number operator for phonons in mode j . Its eigenvalues are the non negative integers $0, 1, 2, \dots$. Its eigenfunctions are states with a definite

number of phonons of mode j . Thus a given phonon mode may be unoccupied, have one phonon, two phonons, and so on. The corresponding energy is

$$E_j = \left(n_j + \frac{1}{2}\right) \hbar \omega_j. \quad (\text{W5A.20})$$

The problem has thus been reduced to a system of noninteracting harmonic oscillators, each corresponding to a different mode, j . Note the presence of energy even in the absence of phonons ($n_j = 0$). This is called *zero-point energy*.

Appendix W5B: Dispersion Relations in the General Case

Consider a crystal structure and select any point O in the crystal to serve as an origin. Translate it through the Bravais lattice, thereby replicating O through the set of translation vectors $\{\mathbf{R}\}$. Denote the replicated points by $\{O_R\}$. The set of points in space which are closer to O than any other O_R is called the *Wigner–Seitz (WS) cell* and has a polyhedral shape. (Note that this definition is slightly more general than the previous definition of the WS cell in Chapter 3. In that point O need not be on an atom). Due to the periodicity of the lattice, the WS cell contains exactly s atoms. Around each of the origins $\{O_R\}$ one may similarly construct a WS cell, thereby filling all of space.

In a phonon excitation the amplitude of vibration of atoms in a neighboring cell $\{O_R\}$ is simply related to the excitations of atoms in the base cell O :

$$\mathbf{u}^\sigma(\mathbf{R}) = \mathbf{u}^\sigma \exp(i\mathbf{k} \cdot \mathbf{R}), \quad \sigma = 1, 2, \dots, s. \quad (\text{W5B.1})$$

Rather than using the spring constants directly, note that the expression for the elastic energy [see Eq. (5A.2)] is written as a quadratic form. This permits the introduction of an alternative set of elastic coefficients and expressing the energy in a simpler form. Let the α th component of the displacement of the σ th atom of cell \mathbf{R} be denoted by $u_\alpha^\sigma(\mathbf{R})$. Expand the elastic energy of the crystal in terms of the atomic displacements and truncate the expansion at second order, a procedure known as the *harmonic approximation*. The zeroth-order term is just a constant added to the energy and may be neglected. The first-order term vanishes because the elastic energy has a minimum at the equilibrium state. The second-order term is thus

$$U = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{\alpha, \alpha'} \sum_{\mathbf{R}, \mathbf{R}'} u_\alpha^\sigma(\mathbf{R}) L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R} - \mathbf{R}') u_{\alpha'}^{\sigma'}(\mathbf{R}'), \quad (\text{W5B.2})$$

where the set of elastic coefficients is defined in terms of the second derivatives:

$$L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R} - \mathbf{R}') = \frac{\partial^2 U}{\partial u_\alpha^\sigma(\mathbf{R}) \partial u_{\alpha'}^{\sigma'}(\mathbf{R}')}. \quad (\text{W5B.3})$$

The indices σ and σ' range over $\{1, 2, \dots, s\}$, and the indices α and α' over $\{1, 2, 3\}$. Note that invariance of the crystal under Bravais lattice translations dictates that L depends only on $\mathbf{R} - \mathbf{R}'$. One sees from the definition that L is symmetric, that is,

$$L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R} - \mathbf{R}') = L_{\alpha', \alpha}^{\sigma', \sigma}(\mathbf{R}' - \mathbf{R}). \quad (\text{W5B.4})$$

The dynamical equations become

$$M_\sigma \ddot{u}_\alpha^\sigma(\mathbf{R}, t) = - \sum_{\sigma'} \sum_{\alpha'} \sum_{\mathbf{R}'} L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R} - \mathbf{R}') u_{\alpha'}^{\sigma'}(\mathbf{R}', t). \quad (\text{W5B.5})$$

This represents a set of $3Ns$ coupled second-order differential equations for the amplitudes.

If the atomic displacements were all made equal [i.e., $u_\alpha^\sigma(\mathbf{R}) = d_\alpha$ (for all σ and \mathbf{R})], there would be no restoring force and both sides of the equation would be zero. Thus

$$0 = - \sum_{\sigma'} \sum_{\alpha'} \sum_{\mathbf{R}'} L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R} - \mathbf{R}') d_{\alpha'}. \quad (\text{W5B.6})$$

This is true for any vector \mathbf{d} . Also note that as \mathbf{R}' sweeps over the Bravais lattice, so does the vector $\mathbf{R} - \mathbf{R}'$. Thus one obtains the sum rule:

$$\sum_{\sigma', \mathbf{R}'} L_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{R}') = 0. \quad (\text{W5B.7})$$

Using the symmetry of the L matrix [Eq. (W5B.4)] this may also be written as

$$\sum_{\sigma, \mathbf{R}'} L_{\alpha', \alpha}^{\sigma', \sigma}(\mathbf{R}') = 0. \quad (\text{W5B.8})$$

For a mode with frequency ω and wave vector \mathbf{k} the dynamical equations become

$$M_\sigma \omega^2 u_\alpha^\sigma = \sum_{\sigma'} \sum_{\alpha'} D_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{k}) u_{\alpha'}^{\sigma'}, \quad (\text{W5B.9})$$

where the *dynamical matrix* is defined as

$$D_{\alpha, \alpha'}^{\sigma, \sigma'}(\mathbf{k}) = \sum_{\mathbf{R}'} L_{\alpha, \alpha'}^{\sigma, \sigma'}(-\mathbf{R}') \exp(i\mathbf{k} \cdot \mathbf{R}'). \quad (\text{W5B.10})$$

Equation (W5B.9) is a set of only $3s$ coupled algebraic equations, so considerable simplification has been achieved. A solution to these equations determines the phonon frequencies as the eigenvalues and the polarizations of the phonons as the eigenvectors. This procedure usually involves the numerical diagonalization of a matrix with $3s$ rows and $3s$ columns.

Appendix W5C: Van Hove Singularities

In this appendix an analysis is made of the density of states in the neighborhood of a van Hove singularity at position \mathbf{k}_0 . The first-order term in the expansion of the frequency vanishes so, to second order

$$\omega_\mu(\mathbf{k}) = \omega_\mu(\mathbf{k}_0) + \frac{1}{2} \sum_{\alpha, \beta} (k - k_0)_\alpha (k - k_0)_\beta \frac{\partial^2 \omega_\mu}{\partial k_\alpha \partial k_\beta} + \dots \quad (\text{W5C.1})$$

Introduce a new coordinate system which is both translated, so that the new origin is \mathbf{k}_0 , and rotated, so that the matrix

$$h_{\alpha\beta} = \frac{1}{2} \frac{\partial^2 \omega_\mu(\mathbf{k})}{\partial k_\alpha \partial k_\beta} \quad (\text{W5C.2})$$

is diagonalized. In this new $\{\mathbf{k}'\}$ coordinate system

$$\omega_\mu(\mathbf{k}) = \omega_\mu(\mathbf{k}_0) + \sum_\alpha h_\alpha k_\alpha'^2, \quad (\text{W5C.3})$$

where h_α are the eigenvalues of $h_{\alpha\beta}$. Assuming that none of the h_α vanishes, one may further rescale the coordinates by defining

$$k_\alpha'' = |h_\alpha|^{1/2} k_\alpha'. \quad (\text{W5C.4})$$

Note that translating or rotating a vector does not alter the size or shape of a volume element in \mathbf{k} space, but the scale transformation does, so $d\mathbf{k}'' = |h_1 h_2 h_3|^{1/2} d\mathbf{k}$. Let

$$\omega_\mu(\mathbf{k}) = \omega_\mu(\mathbf{k}_0) + \Delta\omega, \quad (\text{W5C.5})$$

so

$$\rho(\omega) = \sum_\mu \frac{V}{(2\pi)^3 |h_1 h_2 h_3|^{1/2}} \int d\mathbf{k}'' \delta \left[\sum_\alpha k_\alpha''^2 \text{sgn}(h_\alpha) - \Delta\omega \right]. \quad (\text{W5C.6})$$

The $\{\text{sgn}(h_\alpha)\}$ numbers are ± 1 , depending on the nature of the extremum. For an absolute minimum the signature is $\{+1, +1, +1\}$. For an absolute maximum it is $\{-1, -1, -1\}$. Saddle points are characterized by having mixed signs [e.g., $\{+1, +1, -1\}$, $\{+1, -1, +1\}$, etc.]. Thresholds occur at the van Hove singularities. On one side of the threshold there is an added (or subtracted) density which varies as $|\Delta\omega|^{1/2}$. Depending on the type of extremum, it could rise, fall, lie to the left, or lie to the right of the critical point.