SOME ASPECTS OF THE STRONG COUPLING THEORY OF
SUPERCONDUCTIVITY

By

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SOME ASPECTS OF STRONG COUPLING SUPERCONDUCTIVITY
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ABSTRACT

The formulation of the strong coupling theory of superconductivity on the imaginary axis has been used to investigate a wide variety of problems. First, $J_R$, the ratio of the jump in the quasiparticle current at the gap voltage, $\Delta_0$, in a superconducting tunneling junction, has been calculated for many materials to good accuracy. Correlations of $J_R$ with the strong coupling parameters $\lambda - \mu^* \pi$ and $T_c / \omega_\xi^c$ is confirmed, where $\lambda$ is the electron-phonon mass enhancement factor, $\mu^*$ the Coulomb repulsion pseudopotential, $T_c$ the critical temperature, and $\omega_\xi^c$ a frequency characteristic of the electron-phonon spectral density, $\alpha^2 F(\Omega)$. The functional derivative of $J_R$ is calculated for a selection of materials using a new faster method.

As well, the effect of the shape of $\alpha^2 F(\Omega)$ on $2\Delta_0 / k_B T_c$ and certain thermodynamic ratios is investigated. It is found that this ratio is largely determined by the parameters $T_c$ and $\omega_\xi^c$ for $2\Delta_0 / k_B T_c$ and by $T_c$, $\omega_\xi^c$, and the area, $A$, under $\alpha^2 F(\Omega)$ for the thermodynamics.

The effects of pressure on $\alpha^2 F(\Omega)$ are investigated using a simple model with a single adjustable parameter fitted to $T_c$. Model predictions of the behaviour of $\Delta_0$ and the thermodynamics under pressure compare well with experiment.

A simple model of alloying effects on $\alpha^2 F(\Omega)$ with a single free
parameter fitted to $T_c$ is investigated. Comparison to Nb-Ta alloys is made with good results.

Three procedures for extracting $2\Delta_0/k_B T_c$ from the electronic specific heat are examined for a selection of real and model spectra. One low temperature ($T < 0.5T_c$) method works well, but the other two high temperature ($T > 0.5T_c$) do not.

A recent tunneling measurement of $\alpha^2 F(\Omega)$ for NbN, displaying an unusually large value of $\mu^*$, has been studied. Computed results for thermodynamic and optical properties, using this spectra, are consistent with experiment.

Finally, inelastic scattering of electrons of paramagnetic impurities has been incorporated into strong coupling theory. Calculations show that this scattering can have measureable effect if the scattering potential is comparable to that of the host material.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER I:</th>
<th>INTRODUCTION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>The Elishaberg Equations</td>
<td>1</td>
</tr>
<tr>
<td>1-2</td>
<td>Scope of Thesis</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER II:</th>
<th>ON THE JUMP IN CURRENT AT THE GAP VOLTAGE OF A SUPERCONDUCTING JUNCTION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Tunneling</td>
<td>18</td>
</tr>
<tr>
<td>2-2</td>
<td>Numerical Calculation of the Jump</td>
<td>22</td>
</tr>
<tr>
<td>2-3</td>
<td>An Approximate Analytic Formula for the Jump</td>
<td>26</td>
</tr>
<tr>
<td>2-4</td>
<td>Conclusions</td>
<td>29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER III:</th>
<th>FUNCTIONAL DERIVATIVES OF THE CURRENT JUMP AT THE SUPERCONDUCTING GAP</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Functional Derivatives</td>
<td>38</td>
</tr>
<tr>
<td>3-2</td>
<td>Derivation of Basic Equations</td>
<td>40</td>
</tr>
<tr>
<td>3-3</td>
<td>The Analytic Continuation</td>
<td>46</td>
</tr>
<tr>
<td>3-4</td>
<td>Results</td>
<td>50</td>
</tr>
<tr>
<td>3-5</td>
<td>Conclusions</td>
<td>53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER IV:</th>
<th>DEPENDENCE OF $\frac{2\Delta_0}{k_B T_c}$ ON THE SHAPE OF THE ELECTRON-PHONON SPECTRAL DENSITY</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>Introduction</td>
<td>60</td>
</tr>
<tr>
<td>4-2</td>
<td>Scaling and Results for Realistic Shapes</td>
<td>62</td>
</tr>
<tr>
<td>4-3</td>
<td>The Two-Delta-Function Model</td>
<td>67</td>
</tr>
<tr>
<td>4-4</td>
<td>Conclusions</td>
<td>72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER V:</th>
<th>DEPENDENCE OF SUPERCONDUCTING THERMODYNAMIC RATIOS ON THE SHAPE OF THE ELECTRON-PHONON SPECTRAL DENSITY</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-1</td>
<td>Introduction</td>
<td>85</td>
</tr>
<tr>
<td>5-2</td>
<td>Effects of Scaling and Results for Realistic Shapes</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-3</td>
<td>A Less Restricted Model</td>
<td>90</td>
</tr>
<tr>
<td>5-4</td>
<td>Conclusions</td>
<td>94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER VI:</th>
<th>EFFECTS OF PRESSURE ON THE THERMODYNAMICS OF SUPERCONDUCTORS</th>
<th></th>
</tr>
</thead>
</table>
CHAPTER VII: ON THE THERMODYNAMICS OF SUPERCONDUCTING Pb UNDER HIGH PRESSURE

7-1 Introduction 142
7-2 Comparison to High Pressure Data 142
7-3 Conclusions 145

CHAPTER VIII: A SIMPLE MODEL OF ALLOYS

8-1 Alloys 149
8-2 Comparison to Experimental Results 152
8-3 Discussion and Conclusions 155

CHAPTER IX: ON THE RELATIONSHIP BETWEEN THE GAP EDGE AND THE SPECIFIC HEAT OF A SUPERCONDUCTOR

9-1 Empirical Relations 162
9-2 Methods for $\tilde{c} \epsilon \epsilon_s (T)$ 165
9-3 The Method of Padamsee et al. 170
9-4 Conclusions 172

CHAPTER X: SOME THERMODYNAMIC AND OPTICAL PROPERTIES OF NbN

10-1 Introduction 178
10-2 Results 180
10-3 Conclusions 186

CHAPTER XI: SUPERCONDUCTORS WITH FINITE MASS PARAMAGNETIC IMPURITIES

11-1 Effects of Paramagnetic Impurities 193
11-2 Formulation of the Basic Theory 194
11-3 The Free Energy Equation 208
11-4 Results 211
11-5 Discussion and Conclusions 216

CHAPTER XII: SUMMARY

APPENDIX A: DERIVATION OF AN APPROXIMATE ANALYTIC FORMULA FOR $J_R$ 226
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>$J_R$ Calculated for Various Materials</td>
<td>30 &amp; 31</td>
</tr>
<tr>
<td>4-1</td>
<td>$2\Delta_0/k_B T_c$ for Scaled Spectra</td>
<td>74</td>
</tr>
<tr>
<td>5-1</td>
<td>Thermodynamic Ratios for Scaled Spectra</td>
<td>96 &amp; 97</td>
</tr>
<tr>
<td>6-1</td>
<td>Characteristic Data for Various Materials</td>
<td>124 &amp; 125</td>
</tr>
<tr>
<td>6-2</td>
<td>Comparison of Trofimenkoff-Carbotte Model with Measured Spectra</td>
<td>125 &amp; 127</td>
</tr>
<tr>
<td>6-3</td>
<td>Model Predictions of Various Volume Derivatives</td>
<td>128 &amp; 129</td>
</tr>
<tr>
<td>6-4</td>
<td>Model and Actual Pressure Derivatives of $\Delta_0$, $\lambda$, and $\Lambda$</td>
<td>130</td>
</tr>
<tr>
<td>6-5</td>
<td>Model and Actual Pressure Derivatives of $H_c(0)$ and $H_c(T_c)$</td>
<td>131</td>
</tr>
<tr>
<td>6-6</td>
<td>Effects of Nonzero $d\mu/dnV$</td>
<td>132</td>
</tr>
<tr>
<td>6-7</td>
<td>Effects of Varied $\gamma_G$</td>
<td>133</td>
</tr>
<tr>
<td>7-1</td>
<td>Model and Actual Data for Pb Under High Pressure</td>
<td>147</td>
</tr>
<tr>
<td>9-1</td>
<td>Actual and Empirical Values of $2\Delta_0/k_B T_c$ for Various Real and Model Spectra</td>
<td>173</td>
</tr>
<tr>
<td>10-1</td>
<td>Calculated Data for NbN</td>
<td>188</td>
</tr>
<tr>
<td>10-2</td>
<td>$N_{bs}(0)$ and $\lambda$ for NbN</td>
<td>189</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>The Gap Function at ( T=0 )</td>
<td>14</td>
</tr>
<tr>
<td>1-2</td>
<td>The Renormalization Function at ( T=0 )</td>
<td>15</td>
</tr>
<tr>
<td>1-3</td>
<td>Temperature Dependence of the Gap Edge</td>
<td>16</td>
</tr>
<tr>
<td>1-4</td>
<td>Low Temperature Specific Heat Jump</td>
<td>17</td>
</tr>
<tr>
<td>2-1</td>
<td>( I-V ) Characteristic of a Tunneling Junction at ( T=0 )</td>
<td>32</td>
</tr>
<tr>
<td>2-2</td>
<td>Quasiparticle Density of States on Either Side of the Tunneling Junction at ( T=0 )</td>
<td>33</td>
</tr>
<tr>
<td>2-3</td>
<td>( J_R ) versus ( \lambda - \mu ) for Various Spectra</td>
<td>34</td>
</tr>
<tr>
<td>2-4</td>
<td>( J_R ) versus ( T_c/\omega_\xi n ) for Various Spectra</td>
<td>35</td>
</tr>
<tr>
<td>2-5</td>
<td>( (1+\lambda)/\lambda [d\Delta_1(\omega)/d\omega_0] ) versus ( T_c/\omega_\xi n ) for Various Spectra</td>
<td>36</td>
</tr>
<tr>
<td>2-6</td>
<td>( J_R ) versus ( \omega_\xi n ) for a ( \delta )-function Spectra</td>
<td>37</td>
</tr>
<tr>
<td>3-1</td>
<td>( \alpha^2 F(\Omega) ) Functional Derivative of ( \Delta_0 )</td>
<td>56</td>
</tr>
<tr>
<td>3-2</td>
<td>( \Omega P(\Omega) ) Functional Derivative of ( \Delta_0 )</td>
<td>57</td>
</tr>
<tr>
<td>3-3</td>
<td>( \delta \Omega J_R/\delta \alpha^2 F(\Omega) ) Versus ( \Omega/T_c ) for Various Spectra</td>
<td>58</td>
</tr>
<tr>
<td>3-4</td>
<td>( \delta \Omega J_R/\delta P(\Omega) ) Versus ( \Omega/T_c ) for Various Spectra</td>
<td>59</td>
</tr>
<tr>
<td>4-1</td>
<td>( 2\Delta_0/k_B T_c ) for Various Real and Scaled Spectra</td>
<td>75</td>
</tr>
<tr>
<td>4-2</td>
<td>Scaled and Pb ( \alpha^2 F(\Omega) )</td>
<td>76</td>
</tr>
<tr>
<td>4-3</td>
<td>( \lambda ) for Two-Delta-Function Spectra</td>
<td>80</td>
</tr>
</tbody>
</table>

\( \xi \)
4-4 a&b  $2\Delta_0/k_B T_c$ for Two-Delta-Function Spectra  82 & 83

4-5  $2\Delta_0/k_B T_c$ vs \(\lambda\) for Two-Delta-Function Spectra  84

5-1  \(\gamma_s[T_c/H_c(0)]^2\) for Various Real and Scaled Spectra  98

5-2  \(\Delta C_V/\gamma_s T_c\) for Various Real and Scaled Spectra  99

5-3  \(D(t)\) for Scaled Realistic Spectra  100

5-4 a&b  \(\gamma_s[T_c/H_c(0)]^2\) for Two-Delta-Function Spectra 101 & 102

5-5 a&b  \(\Delta C_V/\gamma_s T_c\) for Two-Delta-Function Spectra  103 & 104

5-6  \(D(t)\) for Two-Delta-Function Spectra  105

6-1 a-c  \(D(t)\) for Pressure Model and Measured \(\alpha^2 F(\Omega)\)  134 -136

6-2  Model Predictions of \(\frac{1}{H_c(0)} \left(\frac{dH_c(T)}{d\ln V}\right)\) for Various Materials  137

6-3  \(D(t)\) for Nonzero \(d\ln \mu /d\ln V\) at \(\nu=5.0\%\)  138

6-4  Predictions of \(\frac{1}{H_c(0)} \left(\frac{dH_c(T)}{d\ln V}\right)\) for Nonzero \(d\ln \mu /d\ln V\)  139

6-5  \(D(t)\) for Varied \(\tau_G\) at \(\nu=5.0\%\)  140

6-6  Predictions of \(\frac{1}{H_c(0)} \left(\frac{dH_c(T)}{d\ln V}\right)\) for Varied \(\tau_G\)  141

7-1  \(D(t)\) for Pb under High Pressure  148

8-1  \(\alpha^2 F(\Omega)\) of Nb and Ta  157

8-2  Predicted and Actual Values of \(\gamma_s[T_c/H_c(0)]^2\), \(\Delta C_V/\gamma_s T_c\), and \(2\Delta_0/k_B T_c\) Versus Concentration  158
8-3 
Predicted and Actual Values of Min(D(t))
Versus Concentration

8-4 
Predicted and Actual Values of H_c(0)
Versus Concentration

8-5 
Fitting Parameter, \( \lambda \), and \( N_{bs}(0) \) Versus
Concentration

9-1 
\( \tau n[C_{es}(T)/\tau_s(T_c)T_c] \) Versus \( T_c/T \) for
Various Materials

9-2 
\( [C_{es}(T)/\tau_s(T_c)T_c]x[T_c/T]^3 \) Versus \( T/T_c \)
for Scaled Realistic Spectra

9-3 
\( [C_{es}(T)/\tau_s(T_c)T_c]x[T_c/T]^3 \) Versus \( T/T_c \)
for Two-Delta-Function Spectra

9-4 
Padamsee \( [C_{es}(T)/\tau_s(T_c)T_c]x[T_c/T]^3 \) curves
for \( \alpha = 3.53, 4.0, 4.5, \) and 5.0

10-1 
Calculated and Actual D(t). Data for NbN

10-2 
\( \tau(T)/\tau(0) \) for NbN, Pb, and Pb_{0.6}T_{1.4}

10-3 
\( [\lambda_L(T)/\lambda_L(0)]^2/[1-t^4] \) for NbN, Pb, and Pb_{0.6}T_{1.4}

11-1 
Feynman Diagrammes for Inelastic Electron
Scattering Off Paramagnetic Impurities

11-2 
\( T_c^P/T_c^0 \) Versus Impurity Concentration for
Dynamic Paramagnetic Impurities

11-3 
\( \Delta C_v(T_c^P) \) Versus \( T_c^P/T_c^0 \) for Dynamic
Paramagnetic Impurities

11-4 
\( [H_c(0)/T_c]^2 \) Versus \( T_c^P/T_c^0 \) for Dynamic
Paramagnetic Impurities
\[
\frac{S(S+1) N_H}{4 N_I} \quad \text{R Versus Impurity Concentration for Various Values of B}
\]
CHAPTER I

INTRODUCTION

1-1 The Eliashberg Equations

The first thorough explanation of superconductivity was given by Bardeen, Cooper, and Schrieffer\(^{(1)}\) and is often referred to as BCS or weak coupling theory. In this theory there is a weak constant attractive interaction between the electrons near the Fermi surface of those metals which, at sufficiently low temperatures, become superconducting. At a certain characteristic critical temperature, \(T_c\), the system of electrons condenses into a new ground state of pairs of electrons having opposite spin and momentum states, \((k_f, -k_f)\), known as Cooper pairs. There is an energy difference, or gap, \(\Delta(T)\), between the superconducting and normal state which is temperature dependent. The physical possibility of such an attraction had been previously noted by Frolich\(^{(2)}\). He pointed out that the lattice could screen an electron's Coulomb charge in such a way that another electron would be attracted to it - the electron-phonon interaction. The BCS theory gave both qualitative understanding and quantitative predictions about the properties of superconductors. Despite the tremendous success of BCS theory, it was obvious that there was room for improvement. The theory predicted that such characteristic quantities of a superconductor as the ratio of the zero-temperature gap edge to the critical tem-
perature. $2\Delta_0/\kappa^{\infty}_c$, would be a constant independent of the superconductor being considered. This is only approximately true.

Soon a theory of superconductors, known as Eliashberg or strong-coupling theory, which treated the electron-phonon interaction fully by using Green function techniques was developed by Eliashberg\(^{(3)}\), and extended by Scalapino, Wilkins, and Schrieffer\(^{(4)}\), and others. The strong coupling equations are

$$\Delta(\omega)Z(\omega) = \int_{0}^{\infty} d\omega' \text{Re} \left\{ \frac{\Delta(\omega')}{\sqrt{\omega'^{2} - \Delta^{2}(\omega')}} \right\} \times$$

$$[\vec{K}_{-}(\omega,\omega') - \vec{K}_{-}(\omega,-\omega') - \mu(\omega)\tanh\left(\frac{\omega'}{2} \right)] \quad (1-1)$$

and

$$\omega Z(\omega) = 1 - \frac{1}{\omega} \int_{0}^{\infty} d\omega' \text{Re} \left\{ \frac{\omega'}{\sqrt{\omega'^{2} - \Delta^{2}(\omega')}} \right\} [\vec{K}_{-}(\omega,\omega') + \vec{K}_{-}(\omega,-\omega')] \quad (1-2)$$

where

$$\vec{K}_{\pm}(\omega,\omega') = \int_{0}^{\infty} d\Omega \alpha^{2} F(\Omega) \left\{ \left\{ N(\Omega) - f(\omega') \right\} \times \right.$$
and

\[ N(\Omega) = \frac{1}{[e^{\beta \Omega} - 1]^{-1}} \quad (1-4a) \]

\[ f(\omega) = \frac{1}{[e^{\beta \omega} + 1]^{-1}} \quad (1-4b) \]

give exact descriptions of superconducting properties. The main difference from BCS theory results is that the gap, \( \Delta(\omega, T) \), is now also frequency dependent. The temperature dependence of \( \Delta(\omega) \) and \( Z(\omega) \) in equations (1-1) and (1-2) has not been made explicit for economy of space. Peculiar to each superconductor, the interaction of the electrons with the lattice is described by an electron-phonon spectral density \( \alpha^2 F(\Omega) \); the interaction of the electrons with each other, by a repulsive pseudopotential \( \mu^* \) which takes into account the screened Coulomb interaction. \( Z(\omega) \) is a mass renormalization term for the phonon cloud which surrounds each of those electrons which are at or near the Fermi surface.

Strong coupling theory has proved to be an immensely powerful tool in the study of superconductivity. Given \( T_c \) and \( \alpha^2 F(\Omega) \), accurate calculations can be made for virtually every property of a superconductor. On the negative side, however, \( \alpha^2 F(\Omega) \) is often extremely difficult to measure accurately, and the equations, while exact, are so complicated that they obscure knowledge of which physical parameters, or combinations of parameters, are important to superconductivity is obscured.

For reasons of calculational ease, equations (1-1) and (1-2)
are dealt with in a different form in this thesis, one in which they are written, as follows, on the imaginary frequency axis:

\[ \Delta(i\omega_n)Z(i\omega_n) = \frac{\Delta(i\omega_m)}{\sqrt{\omega_m^2 + \Delta^2(i\omega_m)}} \]

(1-5)

and

\[ \omega_n Z(i\omega_n) = \omega_n + \frac{\lambda(n-m)}{\sqrt{\omega_m^2 + \Delta^2(i\omega_m)}} \]

(1-6)

where \( \Delta_n = \Delta(i\omega_n) \) and \( Z_n = Z(i\omega_n) \) are the Matsubara gap and renormalization functions, respectively, evaluated on the imaginary frequency axis at the discrete points

\[ i\omega_n = \pi k_B T(2n-1) \quad n = 0, \pm 1, \pm 2, \ldots \]

In equations (1-5) and (1-6), \( T \) is the temperature, \( k_B \) is Boltzmann's constant, \( \omega_c \) is a cutoff on the Coulomb repulsion needed to get a convergent sum over \( m \), and \( \mu^*(\omega_c) \) is the Coulomb pseudopotential appropriate to the cutoff. It should be pointed out that a sharp cutoff on the imaginary axis is not equivalent to one on the real axis.
Leavens and Fenton\(^{8}\) have shown how a sharp imaginary axis cutoff can be incorporated into a smoothly varying real axis \(\mu_c(\omega)\) but such complications are unnecessary here. The electron-phonon function is given by:

\[
\lambda(n-m) = 2 \int_0^\infty d\Omega \frac{\alpha^2 F(\Omega)}{\Omega^2 + (\omega_n - \omega_c)^2}.
\]

The electron-phonon spectral density is now known in a large number of cases from inversion of tunneling data. The measured \(\alpha^2 F(\Omega)\) spectra used in the calculations for this thesis are taken from references 9 to 22.

Equations (1-5) and (1-6) are solved numerically for a given \(\alpha^2 F(\Omega)\) with \(\mu_c\) adjusted to give the measured \(T_c\). Next the equations are solved at a low temperature, usually 0.1 \(T_c\) and a set of \(\Delta_n\) and \(Z_n\) obtained. The real frequency functions \(\Delta(\omega,T)\) and \(Z(\omega,T)\) are obtained from \(\Delta_n\) and \(Z_n\) through Padé Approximant techniques as first used by Vidberg and Serene\(^{23}\) and implemented by Mitrovic et al.\(^{24}\). The N-point Padé approximant to a complex function \(u(z)\) of the complex variable \(z\), whose N values \(u_i(i=1,...,N)\) are given at N complex points \(z_i(i=1,...,N)\), is defined\(^{23,25}\) as a continued fraction:

\[
C(N;\omega,T) = \frac{a_1}{1 + a_2(\omega - z_1) / (1 + a_3(\omega - z_2) / \ldots / (1 + a_N(\omega - z_{N-1})})}
\]

such that
C(N; z_i) = u_i^i, \quad i = 1, \ldots, N \quad (1-8)

The coefficients $a_i$ are then given by the recursion

$$a_i = \zeta_i(z_i), \quad \zeta_i(z_i) = u_i^i, \quad i = 1, \ldots, N \quad (1-9)$$

$$\zeta_p(z) = \frac{\zeta_{p-1}(z_{p-1}) - \zeta_{p-1}(z)}{(z-z_{p-1})\zeta_{p-1}(z)}, \quad p \geq 2 \quad (1-10)$$

It can be shown that

$$C(N; \omega, T) = \frac{A_N(\omega)}{B_N(\omega)}$$

where $A_N$ and $B_N$ are polynomials given by the recursion

$$A_{n+1}(\omega) = A_n(\omega) + (\omega - z_n)A_{n+1}(\omega), \quad n = 1, 2, \ldots, N-1$$

$$B_{n+1}(\omega) = B_n(\omega) + (\omega - z_n)B_{n+1}(\omega), \quad n = 1, 2, \ldots, N-1 \quad (1-11)$$

and

$$A_0 = 0, \quad A_1 = a_1, \quad B_0 = B_1 = 1 \quad (1-12)$$

An assumption is made that $\Delta(\omega, 0, iT_c)$ is in the range of interest, practically identical to $\Delta(\omega, T-0)$. The gap edge, $\Delta_0$, is
In figures 1-1 and 1-2, the real and imaginary parts of $\Delta(\omega)$ and $Z(\omega)$, respectively, for Pb$_{0.9}$Bi$_{0.1}$ have been reproduced. While details vary from one superconductor to another, the general behaviour of $\Delta(\omega)$ and $Z(\omega)$ is the same for all known superconductors. At zero temperature and frequency, the real part of $\Delta(\omega)$, $\Delta_1(\omega)$, is positive definite. As $\omega$ increases structure related to the electron-phonon interaction appears forming a rough picture of $\sigma^2 F(\omega)$. At approximately the Debye frequency, $\omega_D$, the curve drops through zero and thereafter is negative with structure occurring at harmonics of the phonon modes and $\omega_D$. The imaginary part, $\Delta_2(\omega)$, is zero until the gap edge is reached, at which point it sharply increases and thereafter shows structure characteristic of the material. It passes through zero at approximately $2\omega_D$ and then remains negative, tending to zero for large $\omega$ as $1/\omega$. The main effect of increasing temperature, is to decrease the size of the curves but at low temperatures the change is negligible as can be seen in figure 1-3 of $\Delta_0(T)$ plotted against temperature. The renormalization function, $Z(\omega)$, in the normal (N) and superconducting (S) states is quite similar but differs greatly from $\Delta(\omega)$. At $\omega = 0$, $Z_{1N}(0) = 1 + \lambda$, where $\lambda$ is the electron mass enhancement parameter. At high frequencies, $Z_1(\omega)$ tends to unity as $1 + 1/\omega$. At $\omega = 0$, $Z_2(0)$ is zero until $\Delta_0$, then demonstrates phonon structure, and for large $\omega$ tends to zero as $1/\omega$. The structure in both the real and imaginary parts is material dependent. The normal state renormalization function, $Z_N(\omega)$, is found.
by setting $\Delta(\omega)$ to zero in equation (1-2).

Detailed knowledge of $\Delta(\omega)$, $Z(\omega)$, and $\alpha^2 F(\Omega)$ is obtained from tunneling data using the technique of tunneling inversion developed by McMillan and Rowell (26). It can be shown, from consideration of the standard quantum mechanical tunneling problem with the added complication that the materials are superconductors, that the $T \to 0$ tunneling density of states is

$$\frac{\sigma_s}{\sigma_n} = \frac{N(\omega)}{N(0)} = \text{Re} \left\{ \frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}} \right\} \quad (1-13)$$

where $\sigma$ is the conductance in the superconducting and normal states as indicated. The conductance and its derivative are the measured quantities in a tunneling experiment. Through an iterative technique, an $\alpha^2 F(\Omega)$ and a $\mu^*$ are found which give a $\Delta(\omega)$ from the Eliashberg equations such that a calculation of $N(\omega)/N(0)$ using this $\Delta(\omega)$ matches the measured conductance.

The thermodynamics of the material are, of course, also affected by the condensation into the superconducting state. There is a jump in the specific heat at $T_c$ as the material becomes superconducting at $T_c$. The specific heat of Al is plotted in figure 1-4. As well, a sufficiently strong magnetic field can break up the Cooper pairs and destroy the superconducting state. Both quantities can be calculated from the Bardeen-Stephen (27) equation for the free energy difference between the normal and superconducting states.
\[ \Delta F(T) = 2\pi N(0)T \sum_{n>0} \left[ 2 \left\{ \frac{\omega_n^2 + \delta_n^2}{2} - \frac{\Delta_n^2}{\sqrt{\omega_n^2 + \delta_n^2}} \right\} \right] \]

\[ - (\tilde{\omega}_n - \tilde{\omega}_n^0) \left\{ \frac{\omega_n}{\sqrt{\omega_n^2 - \delta_n^2}} - 1 \right\} \]  \hspace{1cm} (1-14)

where \( N(0) \) is the single spin electron density of states at the Fermi surface (not to be confused with the tunneling density). \( \tilde{\omega}_n \) and \( \tilde{\omega}_n^0 \) are \( \Delta_n\omega_n \) and \( \omega_n \), respectively, and \( \tilde{\omega}_n^0 \) is the solution of equation (1-6) with \( \Delta_n \) set to zero. Notice that the solutions of equations (1-5) and (1-6) and knowledge of \( N(0) \) are all that are needed to solve equation (1-14). The critical magnetic field \( H_C(T) \) is then given by the formula

\[ H_C(T) = \sqrt{8\pi \Delta F(T)} \]

while the difference in the specific heat is given by

\[ \Delta C_v(T) = T \frac{d^2 \Delta F(T)}{dT^2} \]

These quantities are commonly given in the dimensionless ratios:

\[ \gamma_s(T_C/H_C(0))^2 \], \( \Delta C_v(T)/\gamma_s T_C \), and \( D(T/T_C) = H_C(T)/H_C(0) - (1-(T/T_C)^2) \),

which like \( 2\Delta_0/k_B T_C \) are characteristic of the superconductor and the strength of the coupling. The parameter \( \gamma_s \) is the Sommerfeld constant defined
\[ \gamma_s = \frac{2}{3} \pi^2 k_B^2 N(0)(1+\lambda) \]

The normal state specific heat at \( T_c \) of the material is \( \gamma_s T_c \), thus \( \Delta C_v(T)/\gamma_s T_c \) is the ratio of the jump in the specific heat of a superconductor to its normal state value. In BCS theory, the ratio is 1.43. A plot of the low temperature specific heat of Al is given in figure 1-4. The critical magnetic field deviation function, \( D(t) \), where \( t = T/T_c \) is the reduced temperature, is normally plotted against \( t^2 \). In BCS theory, the curve is approximately parabolic with a minimum of \(-0.037\). Real superconductors show a broader range of behaviour, ranging from the BCS minimum to positive definite parabolas for strong coupling materials. Intermediate coupling materials show a sideways S shape. The form of \( D(t) \) is a remnant of early phenomenological theories in which a superconductor is assumed to be a composition of normal and super fluids. Such theories have a characteristic \( 1-t^2 \) shape for the critical field, and it became common to compare \( H_c(T) \) to this theory. It remains useful and convenient to do so.

1-2 Scope of thesis

The aim of this thesis is to show the wide range of applicability and uses of the Eliashberg equations; by using them in new ways and adapting them to new situations, by modelling \( \alpha^2 f(\Omega) \) to get a greater understanding of which parameters are important to superconductivity, by investigating the effects of pressure and alloying through simple models of the attendant changes in \( \alpha^2 f(\Omega) \), by
using the equations to check the accuracy of a new $\Delta^2(\Omega)$, and by testing of empirical relationships.

This thesis consists of twelve chapters, including the Introduction and a Summary, and 4 appendices. In all but chapter XI, the Eliashberg and free energy equations will be treated as given. In that specific chapter, a generalization of the equations will be made using Green function methods such that the basic steps of deriving and modifying equations (1-5), (1-6), and (1-14) should become clearer.

In chapter II, the ratio of the jump, at the gap voltage, in the quasiparticle (Cooper pair) current of a tunnel junction to its weak coupling value, which depends on $\frac{d\Delta(\omega)}{d\Omega}$, is examined. It is found that the calculation of this quantity from the Eliashberg equations agrees well with values calculated directly from tunneling data. The quantity, which is denoted $J_R$ in this thesis, is also calculated for a large number of materials and certain model spectra. An approximate formula, derived from the Eliashberg equations, is found which depends on a single dimensionless strong coupling parameter $T_c/\omega_{\text{en}}$, where $\omega_{\text{en}}$ is an average frequency of a given spectral density, and fitted to the available data. To examine the range of $J_R$ possible, the equations are solved for a delta-function spectra of constant weight at various frequencies.

In chapter III, the functional derivative of $J_R$ is calculated. The functional derivative of a quantity shows the relative contributions of the spectrum frequencies to the size of the quantity. In the calculations, a new method for calculating the functional
The derivative of the gap and functions of the gap such as \( J_R \) is derived and compared to the previous cruder method. The calculations are done for six materials representing the major sorts of superconductor.

In chapter IV, the effect of the shape of \( \alpha^2 F(\Omega) \) on the resultant values of \( 2a_0/k_B T_c \) is examined. First, measured material spectra are scaled on the horizontal and vertical axis to obtain the same value of \( T_c \) and \( \omega_{\text{en}} \) as Pb, which has been arbitrarily chosen as the standard to which the results are to be compared. Second, spectra consisting of two delta-functions of differing weights and frequency positions, but the same \( T_c \) and \( \omega_{\text{en}} \) as Pb, are used to see the extremes possible. This work provides important knowledge of which are the important parameters of a spectral density on the ratio.

In chapter V, similar to chapter IV, the effect of the shape of \( \alpha^2 F(\Omega) \) on the values of the thermodynamic ratios is examined.

In chapter VI, a simple model of how \( \alpha^2 F(\Omega) \) changes with low pressure is examined. The results for the pressure derivatives of many quantities are compared to the available experimental data. The aim of this chapter is to see if simple models can make up for the lack of detailed tunneling information on \( \alpha^2 F(\Omega) \) under pressure.

In chapter VII, the pressure model is used at much higher pressures for Pb and compared to experimental data to see if it will still give good results for the gap and thermodynamic ratios.

In chapter VIII, a rough model of how \( \alpha^2 F(\Omega) \) changes upon alloying is used to compare results on the gap and thermodynamic ratios with experimental data for Nb-Ta alloys.

In chapter IX, the accuracy of semi-empirical methods often
used to find $\Delta_0$ from specific heat data is examined on the basis of the results of chapters IV and V. Such an examination is useful since the reliability of the method is unknown, because corroboration of the tunneling measured gap with thermodynamic measurements is desirable, and because thermodynamic measurements are often easier to do.

In chapter X, the equations are solved for the newly measured spectra of NbN, as it represents a type of superconductor for which there are no other measured examples, and which has proved difficult to obtain good tunneling data. Solution of the Eliashberg equations and comparison to thermodynamic and optical data measurements of the material acts as a check on the accuracy of the spectrum.

In chapter XI, the Eliashberg and Bardeen-Stephen equations are derived for a superconductor containing paramagnetic impurities of finite mass. Previous calculations have been done for static impurities, that is impurities assumed to be of infinite mass. The effects of loosening that assumption will be examined. As well the steps in deriving the modified equations are basic to strong coupling theory and provide insight into the basic assumptions used.

Chapter XII is a brief summation of the thesis results. An attempt will be made to show how this work has contributed to a greater understanding of superconductivity.

The appendices contain mathematical derivations and details important to the results, but which would reduce the readability of the chapters to which they belong.
The real and imaginary parts of the gap function, $\Delta(\omega) = \Delta_1(\omega) + i\Delta_2(\omega)$, at zero temperature for $\text{Pb}_{0.9}\text{Bi}_{0.1}$.
Fig. 1-2  Top) The real and imaginary parts of the superconducting state renormalization function, \( Z_S(\omega) = Z_{1S}(\omega) + iZ_{2S}(\omega) \), at zero temperature for \( \text{Pb}_0.9\text{Bi}_{0.1} \).

Bottom) The real and imaginary parts of the normal state renormalization function, \( Z_N(\omega) = Z_{1N}(\omega) + iZ_{2N}(\omega) \), at zero temperature for \( \text{Pb}_0.9\text{Bi}_{0.1} \).
Fig. 1-3 Sketch of the temperature behaviour of the gap edge, $\Delta_0(\omega-\Delta_0(T),T)$, plotted against the reduced temperature $t=T/T_c$. 
Fig. 1-4 Sketch of the superconducting state (-----) and normal state (.....) specific heats $c_s$ and $c_n$. At $T_c$, $c_n = \gamma_s(T_c)T_c$. The jump in the specific heat, $\frac{\Delta C(T_c)}{\gamma_s(T_c)T_c} = \frac{C_s(T_c) - C_n(T_c)}{C_n(T_c)}$, has the BCS value 1.43. Often $\gamma_s(T_c)$ is approximated by $\gamma_s(T=0)$. 
CHAPTER II

ON THE JUMP IN CURRENT AT THE GAP VOLTAGE

OF A SUPERCONDUCTING JUNCTION

2-1 Tunneling

A tunneling junction consists of a sandwich of a metal layer, an oxide layer, and another metal layer. Electrons may flow through the oxide layer from one side to the other only if there are empty states of the proper energy in that layer for the electrons to occupy. The zero temperature behaviour of a junction where the metal is a superconductor differs from that of a normal (nonsuperconducting) metal. The I-V (current-voltage) characteristic of both types of junction is given in figure 2-1. The normal metal I-V characteristic is linear; the superconducting curve is much more complex. For a superconducting junction, no current will flow until a voltage of $2\Delta_0$ has been applied, at which point there is an abrupt sharp jump in the current. At high voltage, the curve approaches the normal metal result. Strong coupling corrections to figure 2-1 would be on the order of about 5%. It is the calculation of this jump from the Eliashberg equations that is the main interest of this chapter.

The strange shape of the superconductor's I-V characteristic can be understood from a consideration of the zero-temperature tunneling density of states on each side of the oxide barrier as is
shown in figure 2-2. The tunneling density of states is given by equation (1-13). At \( T = 0 \), all the states below \( E_F - \Delta_0 \) are filled and no more electrons can be added. The band of \( \Delta_0 \) around the Fermi surface is the gap in the excitation spectrum and there are no states or energy levels there to be occupied. Only above this gap are there empty states available. The effect of the voltage is to bias the Fermi surfaces of the sides as is shown in figure 2-2. Only when the biasing is \( 2\Delta_0 \) are there empty levels to which electrons from the higher side may tunnel. The current at voltage \( V \) is found from the formula

\[
I(V) = \frac{1}{R} \int_{\Delta_0}^{V - \Delta_0} \frac{N(\omega) N(V - \omega)}{N(0) N(0)} \, d\omega \quad (2-1)
\]

where \( N(\omega) \) is the tunneling density of states given in equation (1-13) and \( R \) is the normal state resistance of the junction. To find the jump in current at \( V = 2\Delta_0 \) it is useful to consider the Taylor expansion of \( N(\omega) \) at a frequency just greater than \( \Delta_0 \),

\[
N(\omega + \Delta_0) = \frac{|\omega|}{\sqrt{\omega^2 - \Delta_0^2}} \left( 1 + \frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega = \Delta_0} \right) \quad (2-2)
\]

Substituting (2-2) into (2-1), integrating, and taking the limit as \( V \to \Delta_0 \) yields

\[
I(2\Delta_0) = \frac{2\Delta_0}{R} \left( 1 + \frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega = \Delta_0} \right)^2 \quad (2-3)
\]
The BCS value is clearly

\[ I_{BCS}(2\Delta_0) = \frac{2\Delta_0 \pi}{R} \frac{\pi}{4} \]  

(2-4)

Thus the ratio of the jump in the current of a superconducting junction to its weak coupling value is given by

\[ J_R = \left(1 + \frac{\Delta_1(\omega)}{\Delta_0} \right)^2 \]  

(2-5)

where \( J_R \) is a convenient notation.

Harris, Dynes and Ginsberg\(^{(28)}\) showed that there exists a simple empirical relationship between the jump and the effective electron-electron coupling parameter \( \lambda - \mu^* \). For many cases \( \mu^* \) is small compared to \( \lambda \) so that an approximate correlation of \( J_R \) with \( \lambda \) is also implied.

In this chapter, the work of Harris, Dynes and Ginsberg\(^{(28)}\) is extended in several ways. First, \( J_R \) is calculated, within Eliashberg theory, for many materials previously unconsidered, including transition metals, A-15 compounds, and model systems with large values of \( \mu^* \) or a delta-function spectrum. These last systems make it possible to check on the validity of the empirical relationship in extreme situations.

In addition to the observed correlation of \( J_R \) with \( \lambda - \mu^* \), a possible correlation with the strong coupling parameter \( T_c/\omega_n \) is also
considered. The quantity $\omega_{\ell n}$ is a characteristic phonon frequency first introduced by Allen and Dynes (29) within the context of a discussion of approximate formulae for $T_c$. The definition of $\omega_{\ell n}$ is

$$\omega_{\ell n} = \exp \left[ \frac{2}{\lambda} \int \frac{dn}{n} \alpha^2 F(\Omega) \ell n(\Omega) \right]$$

Since a strong correlation between $J_R$ and $T_c/\omega_{\ell n}$ is indeed established, an approximate expression for $J_R$ which contains, in a crude way, strong coupling effects through a term of the form

$$b \left( \frac{T_c}{\omega_{\ell n}} \right)^2 \ell n \left( \frac{\omega_{\ell n}}{\omega T_c} \right)$$

with $a$ and $b$ constants is derived from the full Eliashberg equations on the real axis. It is found that $a$ and $b$ can be taken as material independent with the approximate formula for $J_R$ giving a good qualitative fit to the exact numerical data at the 11% accuracy level for most of the cases considered.

In the work described so far, the value of $\alpha^2 F(\Omega)$ has been restricted to observed shapes and strengths. To get some information on how widely $J_R$ might range when such restrictions on $\alpha^2 F(\Omega)$ are removed, model spectra consisting of a delta-function at the arbitrary frequency $\Omega_E$ are considered. In this case, the jump is completely independent of the area under $\alpha^2 F(\Omega)$, at least for $\mu^* = 0$, as is demonstrated in Chapter IV. In contrast, $J_R$ is found to range from a
value near 1. when $\Omega_E \gg T_c$ to 1.92 at $\Omega_E = 0.25$ meV. While the jump is still rising with decreasing $\Omega_E$ in this region, the calculations were nevertheless terminated because some numerical difficulties were becoming apparent. As well 0.25 meV is already unrealistically low, since most materials have spectra with weight spread out over tens of meV.

This chapter has 5 sections and, as well, some mathematical detail has been relegated to an appendix. Section 2-2 deals with the numerical work for observed as well as some model spectra. In section 2-3 the two parameters introduced during the derivation of an approximate analytic formula for the jump are fixed by comparison with the exact calculations. The derivation itself is outlined in Appendix A. Section 2-4 deals briefly with the delta-function results while conclusions are given in section 2-5.

2-2 Numerical calculation of the jump

The required derivative of the gap, $\frac{d\Delta_1(\omega)}{d\omega}_{\Delta_0}$, is obtained from a knowledge of $\Delta_1(\omega)$ at three frequencies near $\Delta_0$ through the fitting of a parabola. The method of finding $\Delta(\omega)$ is explained in the Introduction. The results for a large number of superconductors is presented in table 2-1. Along with $\frac{d\Delta_1(\omega)}{d\omega}_{\Delta_0}$, from which $J_R$ follows, additional useful physical data are given. These are $T_c$, $\omega_{\text{in}}$, the ratio $T_c/\omega_{\text{in}}$, the maximum phonon energy $\omega_D$ in $\sigma^2F(\Omega)$, the cutoff $\omega_c$ in units of $\omega_D$, the corresponding $\mu^*(\omega_c)$ chosen to get the measured $T_c$. 
and λ. Also given is the quantity \((1 + λ)/λ\) times \(d\Delta_1(\omega)/d\omega\biggr|_{\Delta_0}\), which will prove useful later on.

Four of the materials in table 2-1 have also been considered by Harris et al.\(^{28}\). They were chosen to check the analytic continuation technique at low, medium, and high values of \(T/T_c\). They are \(\ln_{0.9} T_{10.1}'\) Hg, \(\text{Pb}_{0.7} B_{10.3}'\) and Pb. With the exception of Pb, the agreement with that of Harris et al. is within 2% for the derivative \(d\Delta_1(\omega)/d\omega\biggr|_{\Delta_0}\). This is very satisfactory, since the method of calculation presented here is so very different from that of Harris et al. It should be noted in passing that perfect agreement cannot be expected since \(\mu^*\) is treated somewhat differently in the two approaches. In both cases a sharp cutoff is used on \(\omega\), but a sharp cutoff on the real axis does not correspond to a sharp cutoff on the imaginary axis and vice versa, as is described by Leavens and Fenton\(^{8}\).

For the case of Pb both the cutoff and the temperature for the analytic continuation has been varied. In table 2-1, there are entries for Pb with cutoffs of \(\omega_c = 10, 6, \) and \(3\omega_d\). As the cutoff is increased, there is a small reduction in \(J_R\) going from 1.0646 to 1.0631. These values are considerably larger than the 1.056 quoted by Harris et al.\(^{28}\). The calculation has also been done at the reduced temperature \(t = T/T_c = 0.05\), rather than the usual \(t = 0.1\), to make sure that the choice of temperature at which the analytic continuation is done is, indeed, not a factor. The results are entered as Pb\(^3\). It is clear that \(t = 0.1\) is low enough to get the normalized jump with sufficient
accuracy.

Other data entered in table 2-1 that should be mentioned explicitly are the results for NbN and for V₃Si. Note that the entry under V₃Si has a μ = 1.3, which is enormous, while the value for NbN is more modest but still large at 0.35 when compared with most other entries. These data can be used to reveal the effect of μ on the current jump as can the entries under Pb and Nb. In these last two cases, the electron-phonon spectrum \( \alpha^2 F(\Omega) \) for Pb and Nb were rescaled without changing their shape so as to retain the same \( T_c \) value with \( \mu = 0 \) and \( \mu = 0.75 \). It is seen that, under these circumstances, \( J_R \) increases quite substantially with increasing \( \mu \). For example, for a model having the spectrum of Pb, it can range from 1.051 to 1.082. To make further comparison, it is best to plot the data of table 2-1.

In view of the work of Harris et al., figure 2-3 shows a plot of \( J_R \) versus \( \lambda - \mu \). The dashed line is the empirical curve of Harris et al. for their data and which was read from their figure. It is seen that the new data confirms the established trend although only a few data fall at large values of \( \lambda - \mu \). Some deviations from the general trend which are worth mentioning have been labeled explicitly in the figure. It is seen, in the case of the scaled spectra Nb and Pb with the unusual values of \( \mu \), that the trend given by the dashed line is violated. This is also true for the V₃Si data labeled V₃Si. This spectrum was derived from tunneling data by Bangert et al. (17) but has an unreasonably large Coulomb pseudopotential value \( \mu = 1.3 \). It has been shown that it does not lead to a good fit to the observed thermodynamics or to some optical properties. On the other hand, the
more conventional spectra for similar samples of $V_3$Si by Kihlstrom\(^{(18)}\) do fall close to the dashed line. From all this, it can be concluded that the relationship between $J_R$ and $\lambda - \mu^*$ is more complicated when $\mu^*$ is unusually large, but, that for most of the real material cases known at present, the empirical relationship of Harris et al. is reasonably valid and can be used with confidence.

For the gap edge and for thermodynamic properties, there exist in the literature approximate analytic formulae \(^{(24,30-33)}\) derived from the full Eliashberg theory, which contain a rough correction for strong coupling of the form

$$c \left( \frac{T}{\omega} \right)^2 \ln \left( \frac{\omega}{T_c d} \right),$$

(2-6)

where $c$ and $d$ are constants, and $\omega$ is some appropriate phonon frequency. In the original literature\(^{(31-33)}\) $c$ and $d$ are found to take on definite values fixed during the course of the approximations, but the precise nature of $\omega$ remains ambiguous, and several suggestions have been made in the past as to the most appropriate choice for this parameter. Very recently, complete numerical solutions of the Eliashberg equations have been generated for many materials\(^{(34-39)}\) which have $\alpha^2 F(\Omega)$ and $\mu^*$ are known from tunneling. It has been found that, if $\omega$ appearing in the form 2-6 is chosen to be $\omega_{kn}$, the exact numerical data for the gap edge and for several thermodynamic coefficients can be fit sufficiently by an expression of the form 2-6 with $c$ and $d$ taken to be material independent and adjusted to give the
best overall agreement to the many cases considered. These works on the gap edge and the thermodynamics suggests that the data on \( J_R \) be plotted as a function of \( T_c/\omega_c \) to see if a new empirical correlation holds between these two quantities. This is shown in figure 2-4, where it is seen that the correlation of \( J_R \) with \( T_c/\omega_c \) is as good as with \( \lambda-\mu^* \) in most cases and can be better, as in the case of \( V_3Si \). The dashed curve through the points was adjusted by eye to give a reasonable fit to the data but does not imply any theory.

2-3 An approximate analytic formula for the jump

To better understand the approximate correlations found in figure 2-4, an approximate formula for \( J_R \) based on Eliashberg theory is now derived. It is most convenient for this work to begin with the Eliashberg equations on the real axis. The derivation, as outlined in Appendix A, follows the method used by Mitrović, Zarate and Carbotte (24) in deriving an approximate result for \( 2\Delta_0/k_B T_c \). The result is

\[
\frac{1+\lambda}{\lambda} \frac{d\Delta(\omega)}{d\omega} \bigg|_{\omega=\Delta_0} = a \left( \frac{T_c}{\omega_c} \right)^2 \frac{\omega_c}{\omega_c} \frac{\ln(\omega_c/bT_c)}{bT_c}, \tag{A-10}
\]

where \( a \) and \( b \) are the fitting parameters.

Recall, in figure 2-4, that \( J_R \) was plotted against \( T_c/\omega_c \) to see how good a correlation exists between these two quantities. Formula (A-10) suggests that, instead,
$$\frac{1+\lambda}{\lambda} \frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega=\Delta_0}$$

versus $T_c/\omega_{fn}$ should be plotted. This is done in figure 2-5. Note that the scatter of data points is much less than in figure 2-4. The dashed curve was chosen to conform with (A-10) with parameters $a$ and $b$ chosen to give the best visual fit to the overall set of points. No single curve of course can reproduce the entire data set exactly but that is not the point here. Some precision has been sacrificed in order to get material independent values for $a$ and $b$. It can be seen that in most cases

$$\frac{1+\lambda}{\lambda} \frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega=\Delta_0} = 4.6 \left( \frac{T_c}{\omega_{fn}} \right) \ln \left( \frac{\omega_{fn}}{2T_c} \right)$$

(2-7)

will give a good first estimate of the slope of the gap at the gap edge and, therefore, of the current voltage characteristics. To get more precision, it is necessary to go to numerical work which can be quite tedious. For most applications, formula (2-7) should be sufficient.

2-4 A delta-function spectrum

So far, mainly realistic forms of $\alpha^2 F(\alpha)$ and values of $\mu^*$ that fall within the conventional range (0.0 to 0.2) have been considered. A few cases with large values for $\mu^*$ were also discussed. At this point, a related question will be studied, namely: what range of values
for $J_R$ can be found when the shape of $\alpha^2 F(\Omega)$ is not constrained to be
that observed in tunneling experiment? A complete answer to such a
question cannot be obtained, since not all possible shapes can be
tried. Trying all shapes, however, is not necessary for the main
purpose here. A delta-function

$$\alpha^2 F(\Omega) = A\delta(\Omega - \Omega_E)$$ (2-8)

positioned at $\Omega = \Omega_E$ with area under $\alpha^2 F(\Omega)$ given by $A$, can serve the
purpose. Such an $\alpha^2 F(\Omega)$ ranges from weak to very strong coupling as
the frequency $\Omega_E$ ranges from large to small values. It is to be noted
that such a spectrum, that $\Delta(\omega)$ scales like $A$ and $\Omega_E$, as is shown
in chapter IV, so that $\Delta(\omega)/A$ is independent of $A$. This implies that
all properties dependent only on the gap will also scale like $A$. This
scaling is exact for $\mu^* = 0$, and very nearly so for finite $\mu^*$. The
three delta-function entries at the end of table 2-1 show that this is
indeed true. It can be seen that as $A$ changes from 2.0 to 6.0, the
correction to $J_R$ due to strong coupling varies by only 1/2%. It is
sufficient, therefore, to choose a single value for $A$ and change $\Omega_E$.
Results for the current jump $J_R$, as a function of $\Omega_E$, are presented in
figure 2-6. It is seen that as $\omega_{in} = \Omega_E$ is decreased $J_R$ increases
radically from its weak coupling limit ($J_R = 1$) to 1.92 at $\Omega_E = 0.25$ meV.
The calculations were stopped at this point for two reasons. The
numerical work was showing signs of breaking down, and, second, $\Omega_E$ is
already unreasonably small. No real spectrum could be close to a delta
function with all its weight around 0.25 meV. Figure 2-6, however,
does show clearly that $J_R$ can get very large if the shape of $\alpha^2 F(\Omega)$ is allowed to vary beyond the expected physical region.

2-5 Conclusions

The jump, $J_R$, in the quasiparticle current at the gap voltage has been calculated numerically from $\alpha^2 F(\Omega)$ data for many materials not previously considered. A correlation previously found between $J_R$ and the coupling parameter $\lambda - \mu^*$ is confirmed. An additional correlation with the much used strong coupling parameter $T_c/\omega_n$ is noted, and an approximate analytic formula has been derived that fits well the numerical data at the 11% level. Using a delta-function for $\alpha^2 F(\Omega)$ with all the weight at a single frequency, it is found that $J_R$ can become very large for such an unconstrained spectrum compared with the values found for real spectra.
Table 2-1 Various parameters characterizing the electron-phonon spectral densities \( [\alpha^2 F(\alpha)] \) used in this chapter, as well as the results of the Eliashberg calculations based on those spectra. The specific quantities considered are the derivative of the real part of the gap at the gap edge \( [d\Delta_1(\omega)/d\omega|_{\Delta_0}] \) and the derived quantities \( J_R \) and \( (1-\lambda)/\lambda[d\Delta_1(\omega)/d\omega|_{\Delta_0}] \). \( J_R \) is the ratio of the jump, at the gap voltage, in the quasiparticle current of a tunnel junction compared to the BCS value. \( \lambda \) is the electron-phonon coupling parameter.
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Fig. 2-1. The current-voltage (I-V) characteristic of a tunneling junction in both the normal (...) and superconducting (...) states at zero temperature. The normal state result is simply Ohm's Law.
$T = 0$

Current ($I$)

Electron Volts

$0$ $\Delta_0$ $2\Delta_0$ $3\Delta_0$ $4\Delta_0$ $5\Delta_0$
Fig. 2-2 Schematic diagram of the quasiparticle energy levels on both sides of a tunneling junction at zero temperature. There is a gap of size $\Delta_0$ about the Fermi energy, $E_F$, with no energy levels. All the states below $E_F - \Delta_0$ are occupied and all states above $E_F + \Delta_0$ are unoccupied. The number of states, above and below $E_F$ on either side, is given by equation (1-13). The applied voltage biases the Fermi surfaces of the two sides.
Fig. 2-3  Plot of the calculated values of $J_R$, the jump ratio at the gap voltage in the quasi particle current of a tunnel junction, versus the effective electron-phonon coupling $\lambda-\mu^*$. The dashed line is the empirical curve of Harris et al.
Fig. 2-4  Plot of the calculated values of $J_R$ (dots) and the data of Harris et al. (crosses) plotted versus the strong coupling parameter $T_c/\omega_\epsilon n$. The dashed line is empirical and does not represent any theory.
Fig. 2-5  Plot of the calculated values of \((1+\lambda)/\lambda[d\Delta_i'(\omega)/d\omega|^\Delta_0]\) (dots) and the values derived from the data of Harris et al. plotted versus the strong coupling parameter \(T_c/\omega_n\). The dashed line is that of the approximate formula given in Eq. (2-7).
Fig. 2-6  Plot of $J_R$, calculated for δ function spectra of constant area, versus the frequency.
CHAPTER III
FUNCTIONAL DERIVATIVES OF THE CURRENT JUMP
AT THE SUPERCONDUCTING GAP

3-1 Functional Derivatives

The functional derivative was introduced into the study of superconductivity for the critical temperature by Bergmann and Rainer (5, 6). The critical temperature, $T_c$, is a functional of $\alpha^2F(\Omega)$, that is, it is a function of a parameter, $\alpha^2F(\Omega)$, which is, in turn, a function of the frequency $\Omega$. Bergmann and Rainer were interested in how infinitesimal changes in $\alpha^2F(\Omega)$ as a function of $\Omega$ affected $T_c$ to see which frequencies contribute most to its size. From the Eliashberg equations, Bergmann and Rainer were able to derive an equation for the functional derivative of $T_c$ which relied only on the solutions of the Eliashberg equations at $T_c$. They found a universal shape for $\delta T_c/\delta \alpha^2F(\Omega)$ versus $\Omega/T_c$ for all the materials studied. The curves start from zero — indicating that zero frequency phonons do not contribute to $T_c$, then rise to a maximum at an approximately universal value of $\Omega/T_c$, and then drop off to zero at infinity roughly as $1/\Omega$. The major difference between superconductors was the height of these curves which varied more or less inversely with the coupling strength. The usefulness of functional derivatives is the knowledge provided of which phonons are important to a quantity, such as $T_c$. Thus, for
example, an approximate equation for $T_c$ which properly treats those phonon energies found to be important would be physically more correct. As well, this work indicates why superconductors of the A-15 structure have such high critical temperatures; they have a great deal of spectral weight about the most important frequencies.

Thus it is clear that one would also wish to find the functional derivatives of the gap edge, as has been done by Mitrovic et al. (40), and of the thermodynamic ratios as has been done by Marsiglio et al. (41). In each case the shape of the functional derivative is similar to that for $T_c$, although the most important frequency depends on the quantity being considered.

This being so, this chapter complements the work of the last by determining the functional dependence of $J_R$ on small changes in the electron-phonon spectral density, $\alpha^2F(\Omega)$, and in the paramagnon spectral density, $P(\Omega)$. The functional derivative shows which phonon or paramagnon frequencies in the spectral density influence the size of $J_R$ the most. To do this, a new method for calculating functional derivatives of functions of the gap is introduced in section 3-2. A new equation for the infinitesimal part of the perturbed Matsubara gaps is derived which is basically their functional derivative. A set of inhomogeneous linear algebraic equations is obtained with a kernel and an inhomogeneous term dependent only in the unperturbed gaps and $\alpha^2F(\Omega)$ and $P(\Omega)$. As well, a brief discussion of paramagnons is given. In section 3-3, the analytic continuation from the functional derivatives of the Matsubara gaps to the real frequency axis is discussed and is based on Padé approximants (23-25). In section 3-4, the new method is
tested against the previous results of Mitrovčič et al.\((40)\) for the gap edge, although this is not the quantity of primary interest here. These authors carry out two separate calculations, one for the pure spectral density and another with its weight augmented by a small delta-function around some specific frequency. The comparison is successful, and so the functional derivative of the normalized jump for Pb, Nb\(_3\)Sn, V, Nb, V\(_3\)Si and Nb\(_3\)Ge are calculated. As a further test, the brute force method of Mitrovčič et al.\((40)\) is extended to the current jump and compared with the results for Pb and Nb\(_3\)Sn. In a final section (3-5), the results are summarized and conclusions drawn.

3-2 Derivation of Basic Equations

In this section, a new method for calculating the functional derivative of functions of \(\Delta(\omega)\) is derived. To begin, a form of the imaginary axis Eliashberg equations, modified to account for electron-paramagnon interactions, is used which combines the usual two equations into one with the summation ranging from 1 to a cutoff \(N_c\) determined by the Coulomb repulsion pseudopotential \(\mu^*\).

\[
\Phi = \sum_{m=1}^{N_c} \left\{ \frac{1}{\sqrt{1-\Delta^2_m}} \left[ n(n-m)+\lambda^*(n+m-1) \right] \left[ \lambda^*(n-m)-\lambda^*(n+m-1) \right] \right\}
\]

\[
\Delta_m = \sum_{m=1}^{N_c} \left[ \lambda^*(n-m)+\lambda^*(n+m-1)-2\mu^* \right] \frac{\Delta_m}{\sqrt{1-\Delta^2_m}}
\]  

(3-1)
The imaginary axis gap function $\Delta_n = \Delta(\omega_n)$ is related to $\tilde{\Delta}_n$ by

$$\tilde{\Delta}_n = \Delta_n / |\omega_n|.$$

(3-2)

For convenience units are used in which $k_B = \hbar = 1$.

The paramagnon spectral density arises because of strong electron-electron interactions. Electron-electron interactions cause spin fluctuations, so that regions, in time and space, of net nonzero spin are formed. An electron in a Cooper pair scattering off such an area would undergo a spin flip breaking up the pair (if the electron-electron interaction is very strong, of course, the conduction electrons could line up into domains forming a ferromagnet). By breaking up Cooper pairs the critical temperature is reduced. $P(\Omega)$ is the spectral density of the electron-paramagnon interactions. Since the paramagnons involve all the conduction electrons, whereas superconductivity involves only those within a few $\omega_D$ of the Fermi surface, $P(\Omega)$ has weight up to frequencies on the order of the Fermi energy, $\epsilon_F$. Paramagnon effects, however, are rare and very small compared to the electron-phonon effects, especially for $\omega < \omega_D$; in most materials, solutions of the Eliashberg equations with $P(\Omega)$ set to zero match the measured results quite well. For this reason, $P(\Omega)$ will be set to zero in the solutions of the equations used in this chapter. Despite this, the functional derivatives with respect to $P(\Omega)$ are done so that one can see which are the important paramagnon frequencies in superconductors.

The electron-phonon and paramagnon spectral densities enter via
the parameters

\[ \lambda^\pm(n-m) = \int_0^\infty \frac{d\Omega}{2\Omega} \frac{[\alpha^2 F(\Omega) + F(\Omega)]}{\Omega^2 + (2\pi)^2 (n-m)^2} \] (3-3)

Note that, for the electron-phonon part alone of \( \lambda^\pm(n-m) \), the \( n=m \) term drops out of equation (3-1) because it appears once on each side of the equation with the same sign. In contrast, for the paramagnon part, \( \lambda^+(n-m) \) appears on one side and \( \lambda^-(n-m) \) on the other resulting in opposing signs so that no cancellation can occur for the term \( n=m \).

This is very important because it implies that if an infinitesimal part \( \epsilon \delta(\Omega - \Omega_0) \) is added at frequency \( \Omega_0 \) with \( \epsilon \to 0 \) to the electron-phonon part, nothing happens to the gap functions as \( \Omega_0 \to 0 \) because the change in \( \lambda^\pm(n-m) \) for \( n=m \) does not appear and for \( n \neq m \) it is

\[ \epsilon \frac{2\Omega_0}{\Omega_0^2 + (2\pi)^2 (n-m)^2}, \quad n \neq m \]

which goes to zero as \( \Omega_0 \to 0 \). This means that adding phonons at \( \Omega_0 = 0 \) does not affect the superconductivity in any way. On the other hand, a very different result arises when an infinitesimal term is added to the paramagnon spectral density. It leads to a \( \frac{1}{\Omega_0} \) divergence in equation (3-1) from the term \( \lambda^\pm(n-m) \) with \( n=m \).

The functional derivative of a functional \( F \) of \( G(\Omega) \) at some frequency \( \Omega_0 \) is defined
\[
\frac{\delta F}{\delta G(\Omega)} = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \left\{ F(G(\Omega) + \varepsilon \delta(\Omega - \Omega_0)) - F(G(\Omega)) \right\} - \frac{1}{t} (3-4)
\]

where \(G(\Omega)\) is the spectrum, \(\Delta F(G)\) or \(F(G)\), in which one is interested, and \(t = T/T_c\) is the fraction of the critical temperature, \(T_c\), at which one is working. Ordinarily, for \(F = \Delta(\omega)\), one wants the \(t = 0\) results, however these are impossible to attain with the imaginary axis equation. Instead, temperatures such that \(t \ll 1\) (usually \(t = .1\)) are worked with, and it is assumed that \(\Delta(\omega, T = tT_c)\) is very similar to \(\Delta(\omega, T = 0)\) for the frequency range \(\omega\) of interest.

Note, from equation (3-1), that \(\Delta_n\) is an explicit function of \(G(\Omega)\) through the factors \(\lambda^\pm\), as well as being a function of temperature \(T\). When the temperature is kept fixed, the variation in \(\Delta_n\) will be denoted by \(\frac{\delta \Delta_n}{\delta G(\Omega)}\). It satisfies the equation

\[
\sum_{m} \frac{\delta \Delta_n}{m} \frac{H_{n,m}}{S(G(\Omega))} = h_n \quad (3-5)
\]

with

\[
H_{n,m} = \delta_{n,m} \left( \frac{n}{nT} + \sum_{m'} [\lambda^+(n-m') - \lambda^+(n+m'-1)] \frac{1}{\sqrt{1+\Delta_m^2}} \right)
- \Delta_n \left[ \lambda^+(n-m) - \lambda^+(n+m-1) \right] \frac{\Delta_m}{(1+\Delta_m^2)^{3/2}}
\]
\[
- \left[ \lambda^-(n-m) + \lambda^-(n+m-1) - 2\mu^2 \right] \frac{1}{(1 + \Delta_m^{2/3})^{3/2}}.
\]

(3-6)

Note that this quantity can be constructed explicitly from the solution of the Eliashberg equation (2) and a knowledge of \(\alpha^2F(\Omega)\) and \(P(\Omega)\).

In equation (3-5),

\[
h_n = \sum_m \frac{2\Omega_0}{\sqrt{n_m^2 + (2\pi T)^2 (n-m)^2}} \left( \Delta_n \pm \Delta_m \right) \frac{-\Delta_n \pm \Delta_m}{\sqrt{1 + \Delta_m^2}}
\]

\[
+ \sum_m \frac{2\Omega_0}{\sqrt{n_m^2 + (2\pi T)^2 (n+m-1)^2}} \left( \Delta_n \pm \Delta_m \right) \frac{-\Delta_n \pm \Delta_m}{\sqrt{1 + \Delta_m^2}}
\]

(3-7)

which is also known from the solutions to Equation (3-1). Thus equation (3-5) is completely determined and yields \(\delta \tilde{\Delta}_m / \delta G(\Omega)\).

On the other hand, \(\tilde{\Delta}_n\) can be thought of as an explicit function of \(G(\Omega)\) and of \(T = tT_c\), and one can consider keeping \(t\) constant rather than \(T\). In this case, the complete variation can be written as

\[
\frac{\delta \tilde{\Delta}_n}{\delta G(\Omega)} = \frac{\delta \tilde{\Delta}_n}{\delta G(\Omega)} + \frac{\delta \tilde{\Delta}_n}{\delta T} t \frac{\delta T_c}{\delta G(\Omega)}
\]

(3-8)

where \(T \frac{\delta \tilde{\Delta}_n}{\delta T}\) satisfies the equation

\[
\sum_{n,m} \Sigma_{n,m} T \frac{\delta \tilde{\Delta}_m}{\delta T} - \tilde{\Sigma}_n = 0
\]

(3-9)
with

\[ \xi_n = \sum \frac{\Delta_n}{\sqrt{1 + \Delta_m^2}} \frac{\Delta_n}{\sqrt{1 + \Delta_m^2}} \]

\[ \sum \frac{\Delta_n}{\sqrt{1 + \Delta_m^2}} \frac{\Delta_n}{\sqrt{1 + \Delta_m^2}} \]

(3-10)

where, by definition,

\[ \Delta_\pm(n-m) = 4 \int_0^\infty d\Omega \frac{[\alpha^2 P(\Omega) + P(\Omega)] \Omega}{[\alpha^2 + (2\pi T)^2 (n-m)^2]^2} (2\pi T)^2 (n-m)^2 \]  

(3-11)

As with \( h_n \), the new quantities \( \xi_n \) are known from solutions to equation (3-1) for the spectral densities for the material of interest. Note, finally, that the equation for \( \delta \Delta_n / \delta G(\Omega) \) is

\[ \sum \frac{\delta \Delta_n}{\delta G(\Omega)} = h_n + \xi_n \frac{1}{T_c} \frac{\delta T_c}{\delta G(\Omega)} \]  

(3-12)

which involves explicitly the functional derivative of the critical temperature. This is a well known quantity since the pioneering work of Bergmann and Rainer\(^{5,6}\) whose work gives the appropriate formula. The formal solution to equation (3-12) is given by
\[
\frac{\delta A_n}{\delta G(\Omega)} = \sum_m n_{nm}^{-1} \left( h_m + \sum_m \frac{1}{T_c} \frac{\delta T_c}{\delta G(\Omega)} \right)
\] (3-13)

The Eliashberg programmes have been generalized to compute
\[
\frac{\delta A_n}{\delta G(\Omega)}
\] in addition to \( A_n \), and it is now necessary to construct, from
this information, the functional derivative of the gap function \( \Delta(\omega,T) \)
for real frequencies, namely \( \frac{\delta \Delta(\omega,T)}{\delta G(\Omega)} \). This is the subject of the next
section.

3-3 The Analytic Continuation

It is now necessary to analytically continue to the real
frequency axis. First, note that the \( \tilde{A}_n \)'s used in the numerical work
are related to the \( A_n \)'s by \( \tilde{A}_n \omega_n = A_n \) for positive \( n \) with the analytic
continuation of \( A_n \) being \( \Delta(\omega,T) \). Thus

\[
\frac{\delta A_n}{\delta G(\Omega)} = \omega_n \frac{\delta \tilde{A}_n}{\delta G(\Omega)} + \frac{\Delta_n}{T_c} \frac{\delta T_c}{\delta G(\Omega)}
\] (3-14)

The Matsubara gaps for the system with the added piece \( \epsilon \delta(\Omega-\Omega_0) \) are
denoted by \( \Delta'(i\omega_n') \) and related to those with \( \epsilon = 0 \) by the equation

\[
\Delta'(i\omega_n') - \Delta(i\omega_n) + \epsilon \frac{\delta \Delta(i\omega_n)}{\delta G(\Omega)}
\] (3-15)

For \( t \) constant, \( T' \) and \( T \) are related by the ratio \( (\delta T_c + T_c)/T_c = 1 + \frac{\delta T_c}{T_c} \)
with \( \delta T_c = \epsilon \frac{\delta T_c}{\delta G(\Omega)} \), so one can write:

\[
\Delta'(\omega_n') = \Delta(\omega_n'(1 + \frac{\delta T_c}{T_c})) + \epsilon \frac{\delta A(\omega_n)}{\delta G(\Omega)} .
\] (3-18)

Both sides can now be analytically continued to get

\[
\Delta'(\omega, T) = \Delta(\omega[1 - \frac{\delta T_c}{T_c}], T) + \epsilon \frac{\delta A(\omega_n)}{\delta G(\Omega)} .
\] (3-17)

where the last term stands for analytical continuation using, in this case, Padé approximants. On expanding (3-17), one finds

\[
\Delta'(\omega, T) = \Delta(\omega, T) - \omega \frac{\delta A(\omega, T)}{\delta \omega} \frac{\delta T_c}{T_c} + \epsilon \frac{\delta A(\omega_n)}{\delta G(\Omega)} .
\] (3-18)

For a fixed value of \( \omega \), this last equation reveals, on rearranging terms, that

\[
\frac{\delta A(\omega, T)}{\delta G(\Omega)} = \lambda(\frac{\delta A(\omega_n)}{\delta G(\Omega)}) - \omega \frac{\delta A(\omega, T)}{\delta \omega} \frac{1}{T_c} \frac{\delta T_c}{\delta G(\Omega)} .
\] (3-19)

Also, the gap \( \Delta_0' = \Delta_0' \Delta_0 \frac{\delta A_0}{\delta G(\Omega)} \) is obtained from the equation

\[
\Delta_0' = \text{Re} \Delta'(\omega = \Delta_0', T) \equiv \Delta_1'(\omega = \Delta_0', T)
\] (3-20)

which leads to
\[
\frac{\delta A_0}{\delta G(\Omega)} = \frac{\lambda_1 \left( \frac{\delta A(\omega_n)}{\delta G(\Omega)} \right) \left| \Delta_0 \right| - \left| \Delta_0 \frac{\partial \Delta_1(\omega,T)}{\partial \omega} \right| \left| \Delta_0 \frac{1}{T_c} \frac{\delta T_c}{\delta G(\Omega)} \right|}{\left[ 1 - \frac{\partial \Delta_1(\omega,T)}{\partial \omega} \left| \Delta_0 \right| \right]}
\] (3-21)

where \( \lambda_1 \) is the real part of the analytic continuation \( \lambda \). This last formula can be evaluated directly, using computer programmes, to give \( \lambda(\frac{\delta A(\omega_n)}{\delta G(\Omega)}) \) and \( \Delta(\omega,T) \) through Padé approximants techniques, as illustrated in the Introduction, Chapter I.

While formula (3-21) is the most useful in this work, it can be rewritten in another way which is sometimes good for the purpose of discussion. Substituting (3-19) into (3-21) leads to

\[
\frac{\delta A_0}{\delta G(\Omega)} = \frac{\delta A_1(\omega,T)}{\delta G(\Omega)} \left| \Delta_0 \right| - \left| \Delta_0 \frac{\partial \Delta_1(\omega,T)}{\partial \omega} \right| \left| \Delta_0 \frac{1}{T_c} \frac{\delta T_c}{\delta G(\Omega)} \right| \left[ 1 - \frac{\partial \Delta_1(\omega,T)}{\partial \omega} \left| \Delta_0 \right| \right]
\] (3-22)

but at constant \( t \) this can be rewritten

\[
\frac{\delta A_1(\omega,T)}{\delta G(\Omega)} = \frac{\delta A_1(\omega,T)}{\delta G(\Omega)} + \frac{\partial \Delta_1}{\partial T} t \frac{\delta T_c}{\delta G(\Omega)}
\] (3-23)

leading to
\[ \frac{\delta \Delta_0}{\delta G(\Omega)} = - \frac{\delta \Delta_1(\omega,T) \left[ \Delta_0 + T \frac{\delta \Delta_1(\omega,T)}{\delta T} \Delta_0 \right]}{\delta G(\Omega)} \frac{1}{\delta G(\Omega)} \frac{\delta T}{\delta G(\Omega)} \left[ 1 - \frac{\delta \Delta_1(\omega,T)}{\delta \omega} \right] \Delta_0 \] (3-24)

This last formula involves the temperature derivative of the real gap \( \frac{\partial \Delta_1(\omega,T)}{\partial T} \) which is not evaluated directly here. If it is assumed that it is finite, however, it can be seen from (3-24) that the second term drops out as \( T \to 0 \) because it contains an explicit factor of temperature leaving the formula

\[ \frac{\delta \Delta_0}{\delta G(\Omega)} = \frac{\delta \Delta_1(\omega,T)}{\delta G(\Omega)} \left[ \Delta_0 \right] \left[ 1 - \frac{\delta \Delta_1(\omega,T)}{\delta \omega} \right] \Delta_0 \quad (3-25) \]

This reveals that, at low temperature it does not matter whether \( T \) or \( t \) is kept constant, as would be expected. Numerical work confirms this as well and suggests that working with \( t = .1 \) is good enough.

To obtain the functional derivative of \( J_R \) first note that

\[ \frac{\delta J_R}{\delta G(\Omega)} = J_R \left[ \frac{\delta}{\delta G(\Omega)} \left[ \frac{\delta \Delta_1(\omega,T)}{\delta \omega} \right] \Delta_0 \right] \quad (3-26) \]

To find the functional derivative of \( \frac{\delta \Delta_1(\omega,T)}{\delta \omega} \) the derivative with respect to \( \omega \) of both sides of the real part of (3-18) is taken, evaluated at \( \Delta'_0 \), and expanded to first order in \( \epsilon \). This gives
\[
\frac{\delta}{\delta g(\Omega)} \left[ \frac{dA_1(\omega)}{d\omega} \right]_{\Delta_0} = \left[ \frac{d}{d\omega} A_1 \left( \frac{\delta A_1(\omega, \Omega)}{\delta g(\Omega)} \right) \right]_{\Delta_0} + \frac{d^2A_1(\omega, T)}{d\omega^2} \left[ \frac{\delta A_1}{\delta g(\Omega)} \right]_{\Omega_0} \]

\[
- \left[ \frac{dA_1(\omega, T)}{d\omega} \right]_{\Delta_0} + \Delta_0 \left[ \frac{d^2A_1}{d\omega^2} \right]_{\Delta_0} \frac{1}{T} \frac{\delta T_c}{\delta g(\Omega)} \right]_{\Omega_0} \tag{3-27}
\]

3-4 Results

In this section, results for Pb, Nb\textsubscript{3}Sn, V, Nb, V\textsubscript{3}Si, and Nb\textsubscript{3}Ge are presented. As a check, the results for Pb and Nb\textsubscript{3}Sn are compared to those found using the method of Mitrovic et al.\textsuperscript{(40)} In that method the Eliashberg equations are solved for a given material spectrum and $\Delta(\omega)$ determined. Next, the equations are again solved, but with a delta-function of finite weight $A$ added to either $\alpha^2F(\Omega)$ or $P(\Omega)$, as desired, at some frequency $\Omega$. The critical temperature is found by keeping $\mu^*$ unchanged. At the same reduced temperature $t$, the new $\Delta'(\omega)$ is determined. The difference between the gap edges, or between the derivatives at the gap edge, divided by $A$ gives the approximate functional derivative of each of those quantities. Of course $A$ must be small enough that there is an approximately linear dependence on $A$. To check the linearity, two or more values of $A$ must be used for each frequency $\Omega$. The main advantage of the method proposed in sections 3-2 and 3-3 is that only one calculation need be done for each value of $\Omega$. As well, decisions on a choice of $A$ and on how constan...
derivative is with varying $\Delta$ are no longer present. Results for $\frac{\delta a_0}{\delta G(\Omega)}$ will not be presented as it was found that the results from the two methods agreed to within approximately 2% and because the Mitrović et al.\textsuperscript{(7)} paper thoroughly discusses that functional derivative. The same level of agreement, 2%, is obtained when the direct ("brute force") method of Mitrović et al.\textsuperscript{(40)} is applied to the calculation of the functional derivative of the critical temperature and compared with the results for the same quantity based on the analytic formulas given in Bergmann and Rainer\textsuperscript{(5,6)}.

The comparison for $\delta \tau J_R / \delta a^2 P(\Omega)$ as a function of $\Omega / T_c$ is given in figure 3-1; for $\delta \tau J_R / \delta P(\Omega)$ in figure 3-2. The solid and dashed curves in each figure were obtained using formulas (3-26) and (3-27) of section 3-3 while the $x$'s represent results of direct calculations ("brute force"). That is, $J_R$ is calculated twice, once for the desired spectrum and again for an augmented spectrum by a delta-function of small weight $\Delta$. As might be expected, since the derivative is much smaller than for the gap edge and, by the nature of the analytic continuation, less accurate, the difference between the two methods is greater, roughly 5%. In Nb$_3$Sn, for the $P(\Omega)$ functional derivative, the difference at the low frequencies is actually worse, about 10%, but at these frequencies the linear dependence on $\Delta$ was not as consistent as at higher frequencies or as in Pb. In fact, the figure of 5% also describes the consistency of the values of $\frac{\delta J_R}{\delta G(\Omega)}$ found by the method of Mitrović et al.\textsuperscript{(40)} due to a lack of linearity in results as a function of the weight $\Delta$. 
In figures $3-3$ and $3-4$, results for $\frac{\delta \ln J_R}{\delta \alpha^2 F(\Omega)}$ and $\frac{\delta \ln J_R}{\delta \delta(\Omega)}$ respectively, are shown for V, Nb, V$_3$Si, and Nb$_3$Ge. For reasons of numerical accuracy, it was not possible to calculate values at the very lowest values of $\Omega/T_C$. The method of Mitrović et al. (40) also has this problem but at even higher frequencies. This deficiency is unfortunate, for as can be seen, it is the phonons of frequency about $\Omega = .25 T_C$ that influences $J_R$ the most. On the other hand, the very low $\omega$ region corresponds to the sound regime where the phonon frequency distribution is very small for any physical situation. It is therefore of little physical interest. From the previous discussion, it is known that the functional derivatives of the Matsubara gaps, and consequently $\frac{\delta \ln J_R}{\delta \alpha^2 F(\Omega)}$, will go to zero as $\Omega \to 0$; hence it is expected that the curve will peak somewhere below $0.25$ of $T_C$ and then drop towards zero. The peak is resolved only in the case of V. While an attempt to increase accuracy at low $\omega$ was possible, it is felt that it is of no physical interest to do so.

On comparing various materials, the magnitude of the curves obtained correlates well with the strength of the material's electron-phonon coupling - the weaker this coupling, the larger the functional derivative. This is similar to what was found for $\frac{\delta \ln T_C}{\delta \alpha^2 F(\Omega)}$, $\frac{\delta \ln \Delta_0}{\delta \alpha^2 F(\Omega)}$. The major difference of $\frac{\delta \ln J_R}{\delta \alpha^2 F(\Omega)}$ compared to $\frac{\delta \ln T_C}{\delta \alpha^2 F(\Omega)}$ and $\frac{\delta \ln \Delta_0}{\delta \alpha^2 F(\Omega)}$ is that the peaks occur at considerably smaller frequencies. The heights of the peaks are also several times larger than those of
\[
\frac{\delta \ln T_c}{\delta \alpha^2 f(\Omega)} \quad \text{or} \quad \frac{\delta \ln \Delta_0}{\delta \alpha^2 f(\Omega)}.
\]
The curves for \(\frac{\delta \ln T}{\delta P(\Omega)}\) differ little from \(\frac{\delta \ln T_c}{\delta P(\Omega)}\) and \(\frac{\delta \ln \Delta_0}{\delta P(\Omega)}\). The curves start from zero at \(\Omega/T_c = \infty\) and smoothly approach \(-\infty\) at \(\Omega/T_c = 0\). This corroborates taking \(P(\Omega) = 0\) since structure would appear only at high frequencies (> \(\omega_D\)), frequencies which contribute very little to the functional derivative. In general, the weaker the coupling of the material, the faster it falls to infinity, at least in the range shown. This is the same behaviour as \(\frac{\delta \ln T_c}{\delta P(\Omega)}\) and \(\frac{\delta \ln \Delta_0}{\delta P(\Omega)}\). The only difference is again in the sensitivity: at a given \(\Omega/T_c\), the absolute value of \(\frac{\delta \ln T}{\delta P(\Omega)}\) is several times larger than \(\frac{\delta \ln T_c}{\delta P(\Omega)}\) or \(\frac{\delta \ln \Delta_0}{\delta P(\Omega)}\).

3.5 Conclusions

A new method for calculating the functional derivative of the gap \(\Delta(\omega)\) on the real frequency axis and of its derivative with respect to frequency \(\omega\) has been derived. The method is based on imaginary axis equations that deal directly with the change in the Matsubara gaps \(\Delta(\omega_n)\) with spectral weight \(G(\Omega)\), namely \(\delta \Delta(\omega_n)/\delta G(\Omega)\). Here \(G(\Omega)\) can be the electron-phonon \((\alpha^2 f(\Omega))\) or the paramagnon spectral density \((P(\Omega))\). The coefficients in the equations, which are a set of linear inhomogeneous algebraic equations, require only the material parameters of the particular superconductor under consideration and the solutions of the Eliashberg equations at the Matsubara energies. The functional derivative of the gap edge on the real axis \(\delta \Delta_0/\delta G(\Omega)\) then follows on analytical continuation of the \(\delta \Delta(\omega_n)/\delta G(\Omega)\) and \(\Delta(\omega_n)\) which is
accomplished by the method of Pade approximates. Comparison with results obtained by the brute force method of Mitrovic et al. (40) shows that this new method is accurate in all cases considered but much faster and more direct.

The new methods have been used to calculate $\delta t n J_R / \delta \alpha^2 F(\Omega)$ and $\delta t n J_R / \delta P(\Omega)$ as a function of $\Omega / T_c$ for Pb, Nb, Sn, V, Nb, V, Si and Nb, Ge, where $J_R$ is the normalized jump in the current at the gap edge ($\Delta_0$) in a tunneling junction. This quantity has, apparently, never before been calculated. Although, for reasons of numerical accuracy, it was not possible to continue the calculations beyond $\Omega / T_c = .25$, at which point $\delta t n J_R / \delta \alpha^2 F(\Omega)$ is still rising as $\Omega$ is lowered (except for V), it can be argued that the curve starts from zero at $\Omega / T_c = 0$, increases to a maximum at some approximately universal value of $\Omega / T_c$, and then decreases to zero at infinity. This shape for $\delta t n J_R / \delta \alpha^2 F(\Omega)$ is similar to that previously found for $\delta t n T_c / \delta \alpha^2 F(\Omega)$ and $\delta t n \Delta_0 / \delta \alpha^2 F(\Omega)$, but the magnitude is greater and the peak is at much lower frequencies, $\Omega < .25 T_c$. In general, weaker coupling materials have higher values of $\delta t n J_R / \delta \alpha^2 F(\Omega)$ indicating that $J_R$ is more sensitive to a given small change in $\alpha^2 F(\Omega)$ in weak coupling materials than in strong coupling materials.

The results for the functional derivative of the current jump at the gap edge with electron-paramagnon spectral density $P(\Omega)$ are even more similar to its $\delta t n T_c / \delta P(\Omega)$ and $\delta t n \Delta_0 / \delta P(\Omega)$ counterparts. The curves start at zero at infinite frequency and are negative for all finite frequencies. They decrease steadily as $\Omega \to 0$ and diverge as $1/\Omega$. This indicates that paramagnons of any frequency reduce the jump
$J_R$ with the lowest frequencies having proportionally the largest effect.
Fig. 3-1  The functional derivative, with respect to $\alpha^2 F(\omega)$, the electron-phonon spectral density, of the ratio of the jump at the gap edge $\Delta_0$, in the quasiparticle current of a superconducting tunneling junction to its weak coupling limit, $\frac{\delta \ln J_R}{\delta \alpha^2 F(\omega)}$, plotted against $\omega/T_C$ for Pb (---) and Nb$_3$Sn (----) using the method of sections 3-2 and 3-3 of this chapter. For comparison, values of $\frac{\delta \ln J_R}{\delta \alpha^2 F(\omega)}$ determined by an extension of the method of Hitrovic et al. (40) are also given (x).
Fig. 3-2 Same as Fig. 3-1, but for the functional derivative with respect to $P(n)$, the paramagnon spectral density.
Fig. 3-3  Plots of $\frac{\delta \ln J_R}{\delta \alpha^2 F(\alpha)}$ vs $\Omega/T_c$ for $V$ (-----), $Nb$ (-----), $V_3Si$ (-----), and $Nb_3Ge$ (-----).
Fig. 3-4  Same as Fig. 3-3, but for $\frac{\delta \ln J}{\delta P(\Omega)}$. 
CHAPTER IV

DEPENDENCE OF $2\Delta_0/k_B T_c$ ON THE SHAPE OF

THE ELECTRON-PHONON SPECTRAL DENSITY

4-1 Introduction

Mitrovic, Zareta and Carbotte\(^{(24)}\) have given theoretical results for the ratio of the gap edge $\Delta_0$ to the critical temperature $T_c$, that is $2\Delta_0/k_B T_c$, for a large number of superconductors. The results were obtained by numerical solutions of the Eliashberg equations represented on the imaginary frequency axis with electron-phonon spectral density $\alpha^2 F(\Omega)$ determined, in each case considered, from inversion of tunneling data. If the ratio $2\Delta_0/k_B T_c$ is plotted against the dimensionless parameter $T_c/\omega_{\ell n}$, with $\omega_{\ell n}$ a characteristic phonon energy, it is found that no single smooth curve can pass through the points. The overall qualitative behaviour, however, is well represented by the formula

$$
\frac{2\Delta_0}{k_B T_c} = 3.54 \left[ 1 + 12.5 \left( \frac{T_c}{\omega_{\ell n}} \right)^2 \frac{\omega_{\ell n}}{2 T_c} \right]^2 (4-1)
$$

Expression (4-1), established in reference (24), is of the same general functional form as first derived by Geilikman and Kresin\(^{(31)}\). The derivation of the equation (A-10) is modeled on this derivation.
In this chapter, the nature of the fluctuations off the general trend expressed in the relationship (4-1) is studied. To accomplish this, it will be sufficient to consider a particular case - to be definite. Pb will be considered - and ask how the ratio $2\Delta_0/k_B T_c$ changes as $\alpha^2 F(\Omega)$ is altered while both $T_c$ and $\omega_{\epsilon n}$ are left fixed. The Coulomb pseudopotential $\mu$ is also kept fixed, being adjusted only for changing cutoff frequency. Since it is not practical to consider all possible arbitrary distortions of $\alpha^2 F(\Omega)$ consistent with the above constraints, the study will be restricted to a selection of known forms for $\alpha^2 F(\Omega)$ representative of the shapes revealed by tunneling inversion in real materials (9-19). To be more specific, consider a known spectral density other than that of Pb. Say Hg is chosen. Denote its $\alpha^2 F(\Omega)$ by $\alpha^2_{\text{Hg}} F(\Omega)$. It will be shown that it is possible to get the same $T_c$ and $\omega_{\epsilon n}$ as for Pb through an appropriate adjustment of the vertical and horizontal scales of the Hg spectral density, namely for $\alpha^2 F(\Omega) = B \alpha^2_{\text{Hg}} F(\gamma \Omega)$ with $B$ and $\gamma$ constant factors. In this way how the different observed shapes for electron-phonon spectral densities lead to variations in $2\Delta_0/k_B T_c$ while $T_c$ and $\omega_{\epsilon n}$ are kept fixed, can be studied.

Besides studying the influence on the ratio $2\Delta_0/k_B T_c$ of various physically realized shapes for the electron-phonon spectral density, a two-delta-function model, chosen with a view at gaining some insights into the full range of variations that are possible when odd shapes are allowed, is also considered. The model calculations begin with both delta-functions placed at $\omega_{\epsilon n}$. This serves as a reference case. Next, one of the delta-functions is positioned below $\omega_{\epsilon n}$ with the other
needling to be placed above in order to preserve the value of $\omega_{\text{fn}}$. This constraint fixes the relative amount of spectral weight in each delta-function while the requirement that $T_c$ remains that of Pb determines the overall strength of the entire distribution. A sufficient number of cases are considered so that a clear pattern emerges.

In section 4-2, a problem is posed and a theorem proved which is helpful in developing a procedure to determine specific values for the two scaling parameters $\beta$ and $\gamma$. Results for $2\Delta_0/k_B T_c$, based on several scaled spectra, are tabulated and also displayed on a graph of formula (4-1). In section 4-3, the two-delta-function model is introduced, some calculational details given, and results presented and discussed. In a final section, 4-4, conclusions are drawn.

4-2 Scaling and results for realistic shapes

Figure 4-1 reproduces some of the results obtained in reference (24), as well as others (35,36,38) for the ratio $2\Delta_0/k_B T_c$ plotted as a function of $T_c/\omega_{\text{fn}}$, where $\omega_{\text{fn}}$ is the characteristic phonon energy introduced by Allen and Dynes (29). Note, in many cases, that the ratio falls close to the dashed curve which represents equation (4-1). Some points, however, do fall off the curve. It is desirable to understand better what feature of the spectral density $\alpha^2 F(\Omega)$ causes these deviations.

One can now pose the question which is to be addressed in this section. For a given material, how does the value of the ratio $2\Delta_0/k_B T_c$ vary as $\alpha^2 F(\Omega)$ is changed, though still retaining the same
value of $T_c$ and of the strong coupling parameter $T_c/\xi n$. To gain insight into this problem, it will be sufficient to consider a specific case. For definiteness, Pb is chosen as it falls about half way on the curve of figure 4-1 between Al at one extreme and Pb 69 Bi 35 at the other. It also falls close to the curve given by equation (4-1).

It is, of course, quite impossible to consider arbitrary changes to the spectral density of Pb. Therefore, to start, only realistic shapes, that is shapes which have to be observed from tunneling measurements of $\alpha^2 F(\Omega)$, will be considered. At present, tunneling measurements of $\alpha^2 F(\Omega)$ have been carried out on many different materials, as previously described, and a variety of shapes are observed. It will, of course, be necessary to introduce some change in a given $\alpha^2 F(\Omega)$, for a material other than Pb, in order to satisfy the constraint on $T_c$ and $\xi n$. This can be accomplished by a simple scaling of the vertical and horizontal axes. The new $\alpha^2 F(\Omega)$ is related to the original by

$$\alpha^2 F(\Omega) = B\alpha^2_0 F(\gamma \Omega)$$

(4-2)

with $B$ and $\gamma$ constants. To see how the constants $B$ and $\gamma$ are to be determined, a scaling theorem will be proven.

How are the gap edge and the critical temperature for a system with spectral density $B\alpha^2_0 F(\gamma \Omega)$ related to their values in the system characterized by $\alpha^2_0 F(\Omega)$? To answer this question, first consider the electron-phonon function $\lambda_\tau(n-m)$ appearing in equations (1-5) and (1-6). For the scaled spectrum,
\[
\lambda_T(n-m) = B \int \frac{2\Omega^2_0 F (\Omega) d\Omega}{\Omega^2 + (\omega_n(T) - \omega_m(T))^2} \tag{4-3}
\]

Multiplying top and bottom on the right hand side of (4-3) by \( \tau^2 \), and changing variables to \( \nu = \tau \Omega \) and to \( T' = \tau T \), gives

\[
\lambda_T(n-m) = B \int \frac{2\nu \omega_0^2 F (\nu) d\nu}{\nu^2 + (\omega_n(T') - \omega_m(T'))^2} \equiv B \lambda_{T'}^0(n-m) \tag{4-4}
\]

Substituting equation (4-4) into equations (1-5) and (1-6), multiplying each side by \( \tau \), and introducing an additional factor of \( \tau \) in the numerator and denominator of the right hand side gives

\[
\tau \Delta_n(T) = \pi T' \sum_m \left[ B \lambda_{T'}^0(n-m) \right] \frac{\tau \Delta_m(T)}{\sqrt{(\tau \Delta_m(T))^2 + (\tau \omega_m(T))^2}} \tag{4-5}
\]

\[
\tau \omega_n Z_n(T) = \omega_n(T') + \pi T' \sum_m \left[ B \lambda_{T'}^0(n-m) \right] \frac{\tau \omega_m(T)}{\sqrt{(\tau \Delta_m(T))^2 + (\tau \omega_m(T))^2}} \tag{4-6}
\]

For \( B = 1 \), note that these two equations have the same form as (1-5) and (1-6) with the spectral density replaced by \( \omega_0^2 F (\Omega) \) and temperature \( T \) replaced by \( T' \). It can therefore be concluded that

\[
\tau \Delta_n(T) Z_n(T) \equiv \Delta_n^0(T') Z_n^0(T') \tag{4-7a}
\]
and

\[ \tau \omega_n(T) z_n(T) = \omega_n^0(T') z_n^0(T') \]  \hspace{1cm} (4-7b)

where the superscript zero applies to the case of the spectrum \( \alpha_0^2 f(\Omega) \).

By definition, \( \omega_n(T') = \tau \omega_n^0(T) \); therefore, on reference to (4-7), one obtains

\[ \Delta_n(T) = \frac{1}{\gamma} \Delta_n^0(T') \]  \hspace{1cm} (4-8)

This last equation reveals that \( T_C \) and \( T_C^0 \) are related by \( T_C \gamma = T_C^0 / \gamma \) and that \( \Delta_0^0 = \gamma \Delta_0 \). Thus the ratio \( 2\Delta_0 / k_B T_C \) is unchanged by scaling along the frequency axis while the critical temperature is changed by a factor of \( \gamma \).

Another important fact is that the scaling (4-2), when applied to the characteristic phonon energy \( \omega_{\text{ch}} \) defined by

\[ \omega_{\text{ch}} = \exp \left( \frac{2}{\lambda} \int \frac{\alpha_0^2 f(\Omega)}{\Omega} \ln(\Omega) d\Omega \right) \]  \hspace{1cm} (4-9)

leads to the simple result \( \omega_{\text{ch}} = \frac{1}{\gamma} \omega_{\text{ch}}^0 \), independent of the vertical axis scaling factor \( B \). This is obvious on noting that the mass enhancement parameter \( \lambda \), defined as \( \lambda = 2 \int \frac{\alpha_0^2 f(\Omega)}{\Omega} d\Omega \), is proportional to \( B \), so this factor drops out of the right hand side of equation (4-9).

The procedure adopted to test the effect of different shapes
for $\alpha^2 F(\Omega)$ on the ratio $2\Delta_0/k_B T_c$ can now be described. The Coulomb repulsion parameter $\mu^*$ is fixed to that of Pb and never changed. A new realistic spectrum $\alpha^2 F(\Omega)$, say that for Hg, is considered. It is then scaled by a factor $\gamma$ chosen to change the $\omega_{\text{en}}$ for Hg into that for Pb. Having done this, the scaling factor $B$ is adjusted to yield the $T_c$ value of Pb. This last adjustment leaves $\omega_{\text{en}}$ unchanged; in this way both $\omega_{\text{en}}$ and $T_c$ are those of Pb, but the electron-phonon spectral density now has the same shape as that for the Hg spectrum. In figure 4-2, the rescaled spectra (denoted by an asterisk) based on a variety of materials (9-19) are shown on the same graph as Pb. The scaling parameters, $B$ and $\gamma$, are entered in columns 1 and 2 of table 4-1. Note the considerable variations in $\alpha^2 F(\Omega)$ from spectrum to spectrum, especially the considerable differences in height and in maximum phonon energy $\omega_0^*$. These variations lead to variations in the mass enhancement parameter $\lambda^*$ (twice the first inverse moment of $\alpha^2 F(\Omega)$) and $\lambda^*$ (the area under $\alpha^2 F(\Omega)$). These quantities are entered in columns 3 and 4 of table 4-1. Although, as noted, the spectra themselves vary greatly, the characteristic numbers $\lambda^*$ and $\lambda^*$ clearly show much less variation.

For the convenience of the reader, the values of $\omega_0^*$, as well as the results for the ratio $2\Delta_0/k_B T_c$, are entered in the same table in columns 5 and 6 respectively. It is clear that the ratio $2\Delta_0/k_B T_c$ is not very sensitive to the differences in chosen shapes, ranging from 4.362 to 4.525. This variation is also shown in figure 4-1 where the insert shows more clearly the variation obtained. It is clear now why formula (4-1) is so successful as a semi-phenomenological formula for $2\Delta_0/k_B T_c$ in strong coupling systems. As long as the shape chosen for
the $\alpha^2 F(\Omega)$ of Pb is kept within the bounds of those observed in real superconductors, $2\Delta_0/k_B T_c$ is not significantly affected by the shape. It would seem then that, while formula (4-1) is not an exact relationship, it can probably be used with confidence in cases for which the shape of $\alpha^2 F(\Omega)$ is not too unusual. An estimate of the possible error involved is provided by the limiting values 4.525 to 4.362 derived for Pb. If the BCS value of 3.54 is subtracted from these two extremes in order to extract the strong coupling correction, one gets 0.98 and 0.82 which represents a 16% variation.

4-3 The two-delta-function model

In order to gain more insight into the question of how the shape of the electron-phonon spectral density affects the ratio $2\Delta_0/k_B T_c$, a two-delta-function model is considered next. Results for a single delta-function placed at $\omega_{\xi n}$ for Pb have already been presented in the previous section and found not to differ very much from the case of real Pb. These results will serve as a reference in what follows. Now consider moving the delta-function to higher energies $\omega_G$ with $\omega_G > \omega_{\xi n}$. If $\omega_{\xi n}$ is to remain invariant, this cannot be accomplished without, at the same time, shifting part of the spectral weight to some lower energy $\omega_L$ with $\omega_L < \omega_{\xi n}$. Of necessity then, a delta-function model of the form

$$\alpha^2 F(\Omega) = C[\delta(\Omega-\omega_L) + \delta(\Omega-\omega_G)]$$

(4-10)
must be considered with $\omega_L$ and $\omega_G$ varied at will within a physically reasonable range. The constants $C$ and $\bar{B}$ are determined by the constraints for the relative admixture of $\omega_L$ and $\omega_G$ in $\alpha^2 F(\Omega)$. $\bar{B}$ can immediately be obtained from the formula

$$\bar{B} = \frac{\omega_G \ell n(\omega_{\ell n}/\omega_L)}{\omega_L \ell n(\omega_G/\omega_{\ell n})}.$$  \hspace{1cm} (4-11)

Once $B$ is fixed by a given choice of $\omega_L$ and $\omega_G$, the constant $C$ is determined from a calculation of the critical temperature.

Before presenting results for $2\Delta_0/k_B T_C$ based on spectrum (4-10), it must be stressed that the electron-phonon mass renormalizing parameter $\lambda$ is not fixed in this model but varies according to the formula

$$\lambda = \frac{2C}{\omega_L} \left[1 + \frac{\ell n(\omega_{\ell n}/\omega_L)}{\ell n(\omega_G/\omega_{\ell n})}\right].$$  \hspace{1cm} (4-12)

In figure 4-3a, $\lambda$ has been plotted as a function of $\omega_{\ell n}/\omega_L$ in the range 1 to 5 for 6 different values of $\omega_G/\omega_{\ell n}$, namely 1.1, 1.5, 2.0, 4.0, 8.0, and 12.0. In this range of values for $\omega_L$ and $\omega_G$, $\lambda$ ranges from approximately 1.9 (which occurs for $\omega_{\ell n}/\omega_L = 1.7$ and $\omega_G/\omega_{\ell n} = 12.0$) to minimum value of about 1.3 (for $\omega_{\ell n}/\omega_L = 5.0$ and $\omega_G/\omega_{\ell n} = 4.0$). Note that, as $\lambda$ varies over this considerable range, $T_C$ remains unchanged while McMillan equation (42.29) in the form
\[ T_c \approx \frac{\omega_{\ell n}}{1.2} \exp \left( -\frac{1.04(1+\lambda)}{\lambda-\mu \left(1+0.62\lambda\right)} \right). \] (4-13)

would predict changes in critical temperature or alternatively, for fixed \( T_c \), \( \omega_{\ell n} \) and \( \mu \), imply a unique value of \( \lambda \). It is clear that equation (4-13) is quite inadequate for the kind of work described here for which it is essential to solve numerically the complete Eliashberg equations (1-5) and (1-6) in their linearized form. While this is not at all a main aim of the present work, please note that figure 4-3 can be taken as a clear indication of the failure of the McMillan equation (4-13) in certain cases.

Returning to the main concern, it is clear from figure 4-3a, that the range of possible \( \lambda \) values considered could be increased even further, by going to yet larger values of \( \omega_{\ell n}/\omega_L \) and of \( \omega_G/\omega_{\ell n} \). This ought to be unnecessary since the limiting values of \( \omega_{\ell n}/\omega_L = 5.0 \) and \( \omega_G/\omega_{\ell n} = 12.0 \) are already very extreme. It is very unlikely that an \( \alpha^2 F(\Omega) \), in a real material, could exhibit significant spectral weight at \( \omega_L = 1 \text{ meV} \) and at \( \omega_G = 58 \text{ meV} \). To be more specific, for \( \omega_{\ell n}/\omega_L = 1.5 \) and \( \omega_G/\omega_{\ell n} = 12.0 \), the contribution to \( \lambda \) coming from the low energy peak is 1.60, while for the case \( \omega_{\ell n}/\omega_L = 2.0 \) and \( \omega_G/\omega_{\ell n} = 12.0 \), it is 1.43. These very large values for \( \lambda \) are just not realistic for such low phonon energies. Even around the minimum for \( \lambda (\lambda \approx 1.3) \), which corresponds to the case \( \omega_{\ell n}/\omega_L = 5.0 \) and \( \omega_G/\omega_{\ell n} = 4.0 \), the contribution of the low energy peak to \( \lambda \), while reduced to .6, is still much too large to be realistic.

The very large variations in \( \lambda \) possible in the delta-function
model are in sharp contrast to the much smaller variations from 1.50 to 1.67 obtained in the previous section (table 4-1) when only realistic spectra were considered. Finally, for the convenience of the reader, and for further reference, the same results for $\lambda$ are shown in figure 4-3b, as just presented and discussed, but now plotted as a function of $\omega_c/\omega_e$, namely 1.1, 1.5, 2.0, 3.0, and 5.0. In contrast to the curves in figure 4-3a which displayed maxima, these new curves display well defined minima.

It is now possible to present results for $2\Delta_0/n_{B_c}$ based on the two-degta-function model (4-10). In figure 4-4a, results as a function of $\omega_e/\omega_L$ for the same six values of $\omega_c/\omega_e$: 1.1, 1.5, 2.0, 4.0, 8.0, and 12.0 as previously considered are shown. It is seen from the figure that $2\Delta_0/n_{B_c}$ can range from approximately 4.88 to 4.06. Again it is clear, disregarding what may be physically realistic as opposed to mathematically possible, that arbitrarily shaped electron-phonon spectral densities could generate an even larger range of values for $2\Delta_0/n_{B_c}$. As stressed previously in the discussion of $\lambda$, this would be pushing the model just too far and add little to an understanding of the problem. As it stands, the range (4.88 to 4.06) for $2\Delta_0/n_{B_c}$ is already significant. As done previously, the BCS value of 3.54 is subtracted from each of these two numbers to extract the strong coupling effects which are 1.33 and 0.51 respectively. These numbers differ by nearly a factor of three.

In figure 4-4b, the same results as just presented are shown again, but now $2\Delta_0/n_{B_c}$ is plotted against $\omega_c/\omega_e$ for five values of $\omega_e/\omega_L$, namely 1.1, 1.5, 2.0, 3.0, and 5.0. It is to be noted that
both figures 4-4a and 4-4b correlate well with figures 4-3a and 4-3b for the electron-phonon mass renormalization factor λ. Certainly, it is clear that as λ increases so does $2\Delta_0/k_B T_c$. The correlation between these two quantities is seen more clearly in figure 4-5 where $2\Delta_0/k_B T_c$ as a function of λ is shown, and where it can be seen that fluctuations off the general trend, while significant, are not really large.

The correlation between λ and $2\Delta_0/k_B T_c$ just noted is really not very surprising. It could have been expected on the basis of the work of Mitrović, Leavens and Carbotte\(^{(40)}\) who have calculated the functional derivative of this ratio with the spectral density. The functional derivative

$$\frac{2\Delta_0}{k_B T_c} \frac{\delta(2\Delta_0/k_B T_c)}{\delta \Delta^2 F(\omega)}$$

gives the response of $2\Delta_0/k_B T_c$ to an infinitesimal change in $\Delta^2 F(\Omega)$ at frequency $\omega_0$. It is found to be positive for all $\omega_0$ with a peak near $\omega_0 = \frac{2}{3} \Delta_0$ and to approach zero for both $\omega_0 \to 0$ and $\omega_0 \to \infty$. In this latter region, it follows reasonably well a $1/\omega_0$ dependence, and this is the region of most relevance to the present work. In this case, any infinitesimal shift in spectral weight will lead to a change $\delta[2\Delta_0/k_B T_c]$ related to the change $\delta[\Delta^2 F(\omega_0)]$ by

$$\delta[2\Delta_0/k_B T_c] = \int_0^\infty [\frac{\delta(2\Delta_0/k_B T_c)}{\delta \Delta^2 F(\omega_0)}] \delta[\Delta^2 F(\omega_0)] \, d\omega_0 \quad \text{(4-16)}$$
which depends only on the change in $\lambda$. If $\delta(2\Delta_0/k_B T_C)/\delta$ has a behavior like $1/\omega_0$.

4-4 Conclusions

The change in the ratio $2\Delta_0/k_B T_C$ for the case of Pb, when the shape of its electron-phonon spectral density $\alpha^2 F(\Omega)$ is varied at fixed value of the Coulomb repulsion pseudopotential $\mu$ as well as fixed $T_C$ and characteristic phonon energy $\omega_{\text{en}}$ has been studied. If the analysis is restricted to shapes that are known to occur in nature, that having the same shape as for some other superconductor A with $\alpha^2_A F(\Omega)$ accurately measured by tunneling spectroscopy, the resultant variation of $2\Delta_0/k_B T_C$ is found not to be very large. To be specific, the range of variation found for the materials examined was 4.363 for a Ga shape to 4.525 for a delta-function at $\omega_{\text{en}}$ - very nearly the same for Pb itself. Such variations are less than 3%.

By realistic shape (seen to occur in nature) what is meant is any $\alpha^2 F(\Omega)$ related to a measured spectral density $\alpha^2_A F(\Omega)$ by a simple scale change on the horizontal and vertical axes, namely $\alpha^2 F(\Omega) = B \alpha^2_A F(\gamma \Omega)$ with $B$ and $\gamma$ constants. If less restrictive shapes are allowed, a much greater variation in $2\Delta_0/k_B T_C$ is possible. Results for a two-delta-function model centered respectively at $\omega_L$ and $\omega_G$ with $\omega_L < \omega_{\text{en}} < \omega_G$ have been examined in some detail. Values of $\omega_{\text{en}}/\omega_L$ and $\omega_G/\omega_{\text{en}}$ as large as 5 and 12 respectively were considered. For such parameters, the electron-phonon mass renormalization $\lambda$ ranged from
approximately 1.9 to approximately 1.3, with $2\Delta_0/k_B T_C$ ranging from 4.87 to 4.06. This is a considerable range of variation if one considers that the BCS value is 3.54 and no superconductor falls below this value (ignoring anisotropy, etc.). An even larger range of variation in $2\Delta_0/k_B T_C$ is possible within the same model should one be willing to consider even more extreme values for $\omega_G$ and $\omega_L$. Already, however, the values considered are at the limits quite unphysical.
Table 4-1  Details of the scaled spectra, each with the same values of $T_c$ and $\omega_\text{cm}$ as Pb, used in this chapter based on the known values of $\alpha^2\beta(\Omega)$ for Al, In, Tl, Ga, Nb, V, Sn, Pb$_{0.5}$Bi$_{0.5}$, Nb$_3$Sn, Nb$_3$Ge, and Hg and for $\alpha^2\beta(\Omega)$ a $\delta$-function. Entered are the values of the scaling parameters $B$ and $\tau$, the electron-phonon mass enhancement factor $\lambda$*, the area $A^*$ under $\alpha^2\beta(\Omega)$, the maximum phonon energy $\omega_0^*$, and the ratio $(2\Delta_0/k_BT_c)^*$ and its percentage variation from the Pb value, i.e., \[
(2\Delta_0/k_BT_c)^* = \frac{(2\Delta_0/k_BT_c)^*_{\text{Pb}} - (2\Delta_0/k_BT_c)^{\text{Pb}}}{(2\Delta_0/k_BT_c)^{\text{Pb}}}\]
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<th>B</th>
<th>γ</th>
<th>λ</th>
<th>A</th>
<th>$\theta_D$</th>
<th>$2\Delta_0/k_B T_c$</th>
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<td>3.78</td>
<td>11.0</td>
<td>4.525</td>
<td>0.63</td>
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Fig. 4-1 The ratio of the gap $\Delta_0$ to the critical temperature $T_c$ for several superconductors. The horizontal axis gives the strong-coupling parameter $T_c/\omega_n$ with $\omega_n$ a characteristic phonon energy first introduced within the context of approximate equations for $T_c$ by Allen and Dynes. The dashed line represents formula (4-1) for $2\Delta_0/k_B T_c$ established in ref. 24 from which this figure is largely taken. The entries (dots) in the insert are for the scaled realistic spectra described in the text and in Table 4-1. The insert shows the appropriate region on an expanded scale so that the different scaled systems can be individually identified.
Scaled model spectra for Pb compared with that of Pb itself. The models are based on the electron-phonon spectral densities $\alpha_A^2 F(\Omega)$ for various materials $A$, namely Al, In, Tl, Ga, Nb, V, Sn, Pb$_{0.5}$Bi$_{0.5}$, Nb$_3$Sn, Nb$_3$Ge, and Hg. The scaling procedure involves $\alpha_B^2 F(\Omega)$ with $B$ and $\gamma$ chosen to give the same value of $T_c$ and $\omega_\xi$ as for Pb. Note the considerable differences from one system to another.
Figure b)

Graph showing $\alpha^2 F(\omega)$ vs $\omega$ (meV) for different materials:
- Pb
- Sn
- In
- Nb$_3$Ge
Fig. 4-3  The electron-phonon mass renormalization parameter $\lambda$ for the two-\(\delta\)-function model as a function of the choice of $\omega_L$ and $\omega_G$, the positions of the two $\delta$-functions. Here $\omega_L < \omega_n \text{ and } \omega_G > \omega_n \text{ with } \omega_n \text{ fixed.} \text{ (a) Curves labelled according to } \omega_G/\omega_n = 1.1, 1.5, 2.0, 4.0, 8.0, \text{and } 12.0 \text{ as a function of } \omega_n/\omega_L. \text{ (b) The same data with curves labelled by } \omega_n/\omega_L = 1.1, 1.5, 2.0, 3.0, \text{and } 5.0 \text{ as a function of } \omega_G/\omega_n.$
Fig. 4-4  The ratio $2\Delta_0/k_BT_c$ resulting from the two-$\delta$-function model for the electron-phonon spectral density (4-10) for the various choices of $\omega_L$ and $\omega_G$, the positions of the two $\delta$-functions. Here $\omega_L<\omega_{\epsilon_n}$ and $\omega_G>\omega_{\epsilon_n}$ with $\omega_{\epsilon_n}$ fixed. (a) Curves labelled according to $\omega_G/\omega_{\epsilon_n} = 1.1$, 1.5, 2.0, 4.0, 8.0, and 12.0 as a function of $\omega_{\epsilon_n}/\omega_L$. (b) The same data, with curves labelled by $\omega_{\epsilon_n}/\omega_L = 1.1$, 1.5, 2.0, 3.0, and 5.0 as a function of $\omega_G/\omega_{\epsilon_n}$. 
$\frac{2\Delta_0}{k_B T_c}$

$\frac{\omega_G}{\omega_{in}}$

$\frac{\omega_{in}}{\omega_L}$
Fig. 4-5 The ratio \( \frac{2\Delta_0}{k_B T_c} \) resulting from the two-\( \delta \)-function model for the electron-phonon spectral density (4-10) plotted against the electron-phonon mass enhancement factor, \( \lambda \). The figure illustrates the close correlation that exists between these two quantities.
CHAPTER V

DEPENDENCE OF SUPERCONDUCTING THERMODYNAMIC RATIOS ON THE SHAPE OF THE ELECTRON-PHONON SPECTRAL DENSITY

5-1 Introduction

To complement the work of the last chapter, the effect of how the shape of $\alpha^2F(\Omega)$, as a function of phonon energy $\Omega$, affects certain thermodynamic properties is examined. The effects on the ratio $\gamma_s(T_c/H_c(0))^2$, where $\gamma_s$ is the Sommerfeld constant and $H_c(0)$ the critical magnetic field at zero temperature, on the normalized jump in the specific heat at $T_c$, $\Delta C_v(T_c)/\gamma_s T_c^3$, and on the critical field deviation function, $D(t)$, where $t = T/T_c$ is the reduced temperature, will be considered.

Such a study clearly cannot be carried out without imposing some constraint on the allowed $\alpha^2F(\Omega)$. This is somewhat arbitrary, and several choices are possible. Here, chapter IV is followed, and only "realistic" shapes, and a more widely varying two-delta-function model, are considered. The point is the following. A single system, Pb to be definite, is considered. Its spectral density is well established from tunneling inversion, as are those of many other metals and alloys, including some A-15 compounds (9-19). The implied thermodynamics follow from solution of the Eliashberg equations and the agreement with
experiment is good\(^{(34, 24, 38)}\). Next, consider by how much will the
calculated thermodynamic properties be changed as the shape of \(\alpha^2 F(\Omega)\)
is changed in an arbitrary way. As stated, it is necessary to impose
some constraints, and, to begin, to restrict the analysis to other
known shapes. At the same time, the same value of Coulomb
pseudopotential \(\mu^*\) and \(T_c\) as Pb is kept. Further, one could, for
example, insist that the electron-phonon mass renormalization
\[
\lambda = 2 \int \frac{\alpha^2 F(\Omega)^2}{\Omega} d\Omega
\]
remain fixed, and conceivably some other moments as
well. Here, instead, the characteristic phonon energy \(\omega_{\ell n}\), introduced
by Allen and Dynes\(^{(29)}\) in their analysis of the critical temperature,
is fixed. The motivation for this is found in the recent work of
Marsiglio and Carbotte\(^{(30)}\), where they were able to establish
approximate formulae, which include a strong coupling correction of the
form \((T_c/\omega_{\ell n})^2 \omega_{\ell n}^b \exp(-\omega_{\ell n}/\omega_{\ell n})\) with \(b\) some fixed number, for the thermodynamic
ratios of many superconductors. This indicates that \(\omega_{\ell n}\) is a
significant parameter for characterizing a spectrum. Other moments of
\(\alpha^2 F(\Omega)\) may of course be involved, as is made clear from the fact that
the approximate formulas of Marsiglio and Carbotte\(^{(30)}\) can, at best,
represent only the overall trend in the actual numerical data. In some
cases, a particular material can fall considerably off the curve.
These deviations are the matters of interest here.

In a first set of calculations, various measured spectra,
rescaled by a linear change on the vertical and horizontal axes, are
considered. As described in the last chapter, this procedure is unique
if \(T_c\) and \(\omega_{\ell n}\) are chosen to be those for Pb. Such scaled spectra will
lead to changes in the thermodynamics which can be taken as a representative measure of how other details of $\alpha^2 F(2)$ (other than $T_c$ and $\omega_{en}$) can enter the theory. Besides these scaled "realistic" spectra, a two-delta-function model is investigated which ranges over much more of parameter space, including quite extreme unphysical possibilities, so that the variation in thermodynamics that occurs can be recorded.

In section 5-2, some of the basic theory needed is reviewed, the scaled "realistic" spectra are introduced, and results are presented for $\gamma_s(T_c/H_c(0))^2$, $\Delta C(T_c)/\gamma_s T_c$, and $H_c(0)$ in both tabular and graphical form. The critical magnetic field deviation function, $D(t)$, is also discussed. Section 5-3 deals with the two-delta-function model. Many results are presented and discussed. In a final section, 5-4, conclusions are drawn.

5-2 Effects of Scaling and Results for Realistic Shapes

To start, figures 5-1 and 5-2, reproducing the previous results of reference (30), give the ratios $\gamma_s(T_c/H_c(0))^2$ and $\Delta C_v/\gamma_s T_c$, respectively, for a very large number of superconductors identified in the caption. The plots are as a function of $T_c/\omega_{en}$. This quantity gives some measure of a characteristic phonon energy in the system. In many cases, the points fall close to the solid curves represented by

$$\gamma_s(T_c/H_c(0))^2 = \frac{T}{\omega_{en}} \left[ 1 - \frac{12.1}{\omega_{en} \ln(\frac{T_c}{3\omega_{en}})} \right]$$

(5-1)
and

$$\Delta C_v / \gamma_s T_c = 1.43 \left[ 1 + 53 \left( \frac{\omega_c}{\omega_{\ell n}} \right) \ln \left( \frac{T_c}{3 \omega_{\ell n}} \right) \right]$$

respectively. It is clear that $\omega_{\ell n}$ is a useful parameter in characterizing some of the properties of a superconductor. Some aspects go beyond this, however, since some of the points fall off the general trend. This is the topic of this chapter.

Next, the specific case of Pb is considered, and the effects on the thermodynamics of a change in shape of $\alpha^2 F(\Omega)$ away from that measured for Pb is explored. Following Chapter IV, several other measured spectra for the spectral density are considered. Denote the measured spectra in some other material by $\alpha^2_0 F(\Omega)$. Next consider a simple scaling of the vertical and horizontal axes such that the new $\alpha^2 F(\Omega)$ related to the original by

$$\alpha^2 F(\Omega) = B \alpha^2_0 F(\eta \Omega)$$

with $B$ and $\gamma$ constants. For such a spectrum, it was shown in Chapter IV that $\omega_{\ell n} = \frac{1}{\gamma} \omega_0$, independent of the vertical axis scaling factor $B$. Thus $\gamma$ can be adjusted to get the desired $\omega_{\ell n}$ and then $B$ fixed to get the $T_c$ of Pb. The procedure is clear and now results are presented.

In Table 5-1, the material spectra, and the results of calculations using these spectra, are listed. As well, as the scaling
parameters \( B \) and \( \gamma \) are entered in columns 1 and 2. These scaled spectra (which are shown in Chapter IV) vary considerably with large differences in height and in maximum phonon energy \( \omega_D^* \). These variations lead to variations in the electron-phonon mass enhancement factor \( \lambda^* \) (twice the first inverse moment of \( \alpha^2 F(\Omega) \)) and \( A^* \) (the area under \( \alpha^2 F(\Omega) \)). The quantities are entered in columns 3 and 4 of table 5-1. Although, as noted, the spectra themselves vary greatly, the characteristic numbers \( \lambda^* \) and \( A^* \) clearly show much less variations. In column 5, values of \( \omega_D^* \) are entered. In the next six columns, the values for the thermodynamics \( H_c(0), \gamma_s'(T_c/H_c(0))^2, \) and \( \Delta C / \gamma_s T_c \) are given, as well as the percent difference of the quantities from the values for Pb. In determining \( H_c(0),\ N(0) = 0.823 \times 10^{19} \) states/meV-cm\(^3\) has been used. The thermodynamic ratios, including \( D(t) \), are, of course, independent of \( N(0) \). In the last two columns, for comparison, the previous results for \( 2\Delta_0 / k_B T_c \) are entered. Also, in figure 5-3, \( D(t) \) curves for these scaled spectra are shown. It is clear from these results, compared to \( 2\Delta_0 / k_B T_c \), that the thermodynamics are much more sensitive to the differences in the chosen shapes. This is consistent with the work of Marsiglio and Carbotte\(^{(30)} \) on a variety of superconductors. There, it is stated that the visual fit of thermodynamic data to equations of the form (5-1) and (5-2) is worse than for \( 2\Delta_0 / k_B T_c \). The values of the thermodynamics range from 759.0 Oe to 809.5 Oe for \( H_c(0), \) from 0.1299 to 0.1485 for \( \gamma_s'(T_c/H_c(0))^2, \) and from 2.0110 to 3.0289 for \( \Delta C / \gamma_s T_c, \) while \( 2\Delta_0 / k_B T_c \) ranges from 4.3623 to 4.5246. The variation of \( \gamma_s'(T_c/H_c(0))^2 \) and \( \Delta C / \gamma_s T_c \) are shown more clearly in the inserts of figures 5-1 and 5-2 respectively. Variations
in. $D(t)$ range from the positive definite function characteristic of Pb to an S-shaped function when Ga and Pb(Bi) are considered. This may not be a completely fair comparison in that both these spectra have considerable weight at low phonon energies, a characteristic of amorphous metals. This would not be the case for crystalline materials. If the comparison is restricted to these, then the amount of variation found for $D(t)$ is greatly reduced, but still quite significant. Thus $D(t)$ does reflect some of the details of $\chi^2_F(\Omega)$ beyond $\omega_m$ and a strength sufficient to give the Pb value for $T_c$.

Returning now to table 5-1, it is seen that those spectra with $A^*$ (the area under $\chi^2_F(\Omega)$) close to that of Pb have much closer thermodynamic values as well. This indicates that the observed variations can be reduced if $A^*$ is additionally constrained to be close to that of Pb. This also applies to the critical field deviation functions of figure 5-3.

5-3 A Less Restricted Model

In order to understand better how the shape of the electron-phonon spectral density affects the thermodynamic ratios: $\tau_c(T_c/H_c(0))^2$, $\Delta_c/\tau_s T_c$, and $D(t)$, model spectra are considered next. A single delta-function at the $\omega_m$ of Pb is the starting point. Results for this case have already been presented in the previous section and found to be close to Pb, although the $D(t)$ obtained in this case showed the largest positive deviation of all other cases considered. Suppose moving part of the delta-function weight to higher
energy $\omega_G$ with $\omega_G > \omega_{\ell n}$ is desired. To keep $\omega_{\ell n}$ invariant, it is necessary to also shift part of the spectral weight to some lower energy $\omega_L < \omega_{\ell n}$. Therefore a two-delta-function model, of the form

$$\alpha^2 F(\Omega) = C[\delta(\Omega - \omega_L) + \tilde{B}\delta(\Omega - \omega_G)]$$

(5-4)

with $\omega_L$ and $\omega_G$ varied at will within a physically reasonable range. must be considered. The constants $C$ and $\tilde{B}$ are to be determined by the constraints on $\omega_{\ell n}$ and $T_c$. The constant $\tilde{B}$ gives the relative admixtures of $\omega_L$ and $\omega_G$ in $\alpha^2 F(\Omega)$ and is

$$\tilde{B} = \frac{\omega_G}{\omega_L} \frac{\ell n(\omega_{\ell n}/\omega_L)}{\ell n(\omega_G/\omega_{\ell n})}$$

(5-5)

Once $\tilde{B}$ is fixed by a given choice of $\omega_L$ and $\omega_G$, the constant $C$ is determined from a calculation of the critical temperature.

In figure 5-4a, $\tau_s(T_c/H_c(0))^2$ has been plotted as a function of $\omega_{\ell n}/\omega_L$ in the range 1 to 5 for 6 different values of $\omega_G/\omega_{\ell n}$, namely 1.1, 1.5, 2.0, 4.0, 8.0, and 12.0. In this range of values for $\omega_L$ and $\omega_G$, it can be seen that $\tau_s(T_c/H_c(0))^2$ ranges from approximately 0.125 (for $\omega_{\ell n}/\omega_L = 1.5$ and $\omega_G/\omega_{\ell n} = 12.0$) to a maximum value of about 0.176 (for $\omega_G/\omega_{\ell n} = 5.0$ and $\omega_G/\omega_{\ell n} = 12.0$). Note that the maximum value obtained is larger than the BCS limiting value of 0.168. The two-delta-function model can give larger values than this, but only when there is considerable spectral weight in $\alpha^2 F(\Omega)$ at low energies, namely around 1 meV. When this is so, the BCS limit does not apply.
The BCS limit applies only when all phonon energies are much greater than the critical temperature. Also, for the cases with significant low-energy spectral weight, the normal state specific heat at \( T_c \) can be quite different from \( \gamma_s T_c \) because of an important temperature dependence of the electron-phonon renormalization as described by Grimvall (77,78). Such effects are neglected here, and the zero temperature Sommerfeld constant has been used rather than the temperature dependent true value which can be smaller. Note that the range of \( \gamma_s [T_c^2 / H_c(0)]^2 \) could be increased even further by extending the range of values of \( \omega_n / \omega_L \) and \( \omega_G / \omega_n \). This is unnecessary, since it is very unlikely that a real material \( \alpha^2 F(\Omega) \) would exhibit significant spectral weight outside the range considered. For the convenience of the reader, the same results as just presented and discussed, are now plotted, in figure 5-4b, as a function of \( \omega_G / \omega_n \), namely 1.1, 1.5, 2.0, 3.0, 5.0. In contrast to the curves in figure 5-4a which displayed minima, these new curves display maxima.

In figure 5-5a, results for \( \Delta C / \gamma_s T_c \) are shown as a function of \( \omega_n / \omega_L \) for the same six values of \( \omega_G / \omega_L = 1.1, 1.5, 2.0, 4.0, 8.0 \), and 12.0 as previously considered. Again it is clear that, if one were willing to go to arbitrarily shaped electron-phonon spectral densities of the two-delta-function type, an even larger range of values for \( \Delta C / \gamma_s T_c \) could be generated. It is seen from the figure that \( \Delta C / \gamma_s T_c \) can range from approximately 3.10 to 1.19. Again, the zero temperature Sommerfeld constant has been used rather than the temperature dependent value, and, for this reason, there are values of \( \Delta C / \gamma_s T_c \) less than the BCS limit of 1.43. The behaviour shown by \( \Delta C / \gamma_s T_c \) is quite similar
to the behaviour of $\gamma_s(T_c/H_c(0))^2$ shown in figure 5-4a, provided one realizes that large values of $\Delta C_T/\gamma_s$ are an indication of strong coupling while the converse is true for $\gamma_s(T_c/H_c(0))^2$. There are no peaks in $\Delta C_T/\gamma_s$ however, corresponding to the troughs in $\gamma_s(T_c/H_c(0))^2$ shown in figure 5-4a. This is a further indication that these two thermodynamic ratios do not always react to changes in $\alpha^2F(\Omega)$ in the same way. In figure 5-5b, the same results as just presented are again shown but now $\Delta C_T/\gamma_s$ is plotted against $\omega_c/\omega_{\ell n}$ for five values for $\omega_{\ell n}/\omega_L$, namely 1.1, 1.5, 2.0, 3.0 and 5.0.

It should be noted that the electron-phonon mass renormalization parameter $\lambda$ varies in the model according to the formula:

$$\lambda = \frac{2C}{\omega_L} \left[ 1 + \frac{\ell n(\omega_{\ell n}/\omega_L)}{\ell n(\omega_c/\omega_{\ell n})} \right]$$

Thus the results for $\gamma_s(T_c/H_c(0))^2$ and $\Delta C_T/\gamma_s$ are affected twice by the model, once for the effects on the free energy difference, and then again in the $1+\lambda$ dependence of $\gamma_s$. The variations in $\lambda$ possible in the two-delta-function models are much larger than the variations obtained in the previous section (table 5-1) when only realistic spectra were considered.

In figure 5-6, $D(t)$ curves for the two-delta-function model are presented to show the range of variation possible under this model, along with, for comparison, $D(t)$ for the single delta-function and for real Pb. The numbers in brackets refer to the value of $\omega_{\ell n}/\omega_L$ and $\omega_c/\omega_{\ell n}$ respectively, for the particular $D(t)$ curve. The variation is
again large, with large negative values of \( D(t) \) possible when there is an unphysical amount of spectral weight at 1 meV. That these \( D(t) \) curves are possible, can be seen from the functional derivative of \( D(t) \)\(^{(112)} \). It starts at zero, is negative until a small frequency, and is positive thereafter. The trough can be quite deep compared to the height of the positive region. Recalling that the BCS limit applies only for systems with all spectral weight at high frequencies while the two-delta-function model can have significant weight in the trough, it becomes clear why these large negative \( D(t) \) curves appear.

To study the effects of area \( A \) as a further constraint on the model, lines have been plotted in figures 5-4b and 5-5b illustrating how \( A \) changes along the curves. Clearly, as a constraint \( A \) is effective. With \( A = 4.03 \), the Pb value, the range possible for the thermodynamics is reduced; in fact, reduced to a range smaller than the scaled real spectra with unconstrained area. The parameter \( \lambda \) is also constrained, to a range of 1.4 to 1.6, by fixing \( A \) to that of Pb.

5-4 Conclusions

The thermodynamic ratios \( \tau_s (T_c / H_c(0))^2 \), \( \Delta c / \gamma_s T_c \) and the critical field deviation function \( D(t) \) change when the shape of the electron-phonon spectral density \( \alpha^2 \phi(\Omega) \) of Pb is varied while keeping fixed the value of Coulomb repulsion pseudopotential \( \mu \), the critical temperature \( T_c \), and the characteristic phonon energy \( \omega_{\text{eh}} \). Considering first known shapes characteristic of other superconductors, considerable variations are found that are much larger than for \( 2\Delta_0 / k_B T_c \).
If, however, the value of the area under $\alpha^2 F(\Omega)$ (A) is further constrained to be near that of Pb, the variation is greatly reduced.

To investigate the range of variation in $\gamma_s (T_c/H_c(0))^2$, $\Delta C_V/\gamma_s T_c$, and $D(t)$ that can be expected if less restricted shapes are considered, the case of a model consisting of two delta-functions, centered respectively at $\omega_L < \omega_{\epsilon n}$ and $\omega_G > \omega_{\epsilon n}$ with relative weights chosen to preserve the value of $\omega_{\epsilon n}$ has been studied. For the range of parameters considered, $\gamma_s (T_c/H_c(0))^2$ varied from 0.125 to 0.176, $\Delta C_V/\gamma_s T_c$ varied from 1.19 to 3.10, and $D(t)$ varied in shape and size from positive definite, through S-shaped, to negative definite. This indicates clearly that the shape of $\alpha^2 F(\Omega)$ is an important ingredient in determining the details of the thermodynamics. On the other hand, it was found that if the area under $\alpha^2 F(\Omega)$ is also constrained to a value close to that for Pb, the range of values of $\omega_L$ and $\omega_G$ is reduced and variations in the thermodynamics becomes, for $\gamma_s (T_c/H_c(0))^2$, 0.130 to 0.142, and, for $\Delta C_V/\gamma_s T_c$, 2.43 to 3.10. Thus $T_c$, $\omega_{\epsilon n}$, $\mu$ and area A play an important role in defining the thermodynamic ratios of superconductors, although other moments of the spectral density must also enter in some cases.
Table 5-1. Details of the various scaled spectra, each giving the same $T_c$ and $\omega_\phi$ as for Pb, used in section 6-2. They are based on the known values of $\alpha^2 F(\Omega)$ for Al, In, Tl, Ga, Nb, V, Sn, Pb$_{0.5}$Bi$_{0.5}$, Nb$_3$Sn, Nb$_3$Ge and Hg and for $\alpha^2 F(\Omega)$ a $\delta$-function. Entered are values of the scaling parameters $B$ and $\gamma$, the electron-phonon mass enhancement factor $\lambda^*$, the area under $\alpha^2 F(\Omega)$ ($A^*$), the maximum phonon energy $\omega_\phi^*$, the values of $H_c(0)^*$ (using $N(0) = 0.823 \times 10^{19}$ states/meV-cm$^2$), $\gamma_s (T_c/H_c(0))^{2*}$, and $(\Delta C_v/\gamma_s T_c)^*$ and its percent variation off the Pb value, i.e. $(V^* - V_{PB}^*)/V_{PB}^*$. For comparison, also included are the previously published values of $2\Delta_0/k_B T_c$ and its variation.
### Table 5-1

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<tr>
<td>$\delta$-function</td>
<td>0.1299</td>
<td>1.89</td>
<td>3.0289</td>
<td>9.48</td>
<td>4.5246</td>
<td>0.63</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5-1  The ratio $\gamma_s (T_c/H_c(0))^2$ for a number of superconductors plotted against $T_c/\omega_{en}$. The solid dots represent real material results obtained in reference (30). In decreasing order of $\gamma (T_c/H_c(0))^2$, they correspond to the following systems: Al, Tl, Ta, V, Sn, In, Tl.9Bi.1, Nb (Butler), Nb (Arnold), Nb (Robinson), V$_3$Si, Pb.4Tl.6, Nb.75Zr.25, V$_3$Ge, Nb$_3$Al (2), Pb.7Tl.4, Nb$_3$Ge (2), Pb.7In.3, Nb$_3$Al (3), Nb$_3$Sn, Hg, Nb$_3$Ge (1), Pb.8Tl.2, Pb, Nb$_3$Al (1), Pb.8Bi.1, Pb.8Bi.2, Pb.7Bi.3, Pb.65Bi.35. The solid curve corresponds to $\gamma_s (T_c/H_c(0))^2 = 0.168 [1 - 12.1(T_c/\omega_{en})^2 \ln(T_c/3\omega_{en})]\,$ which is formula (5-1). The entries (solid dots) shown in the insert are the scaled realistic spectra results described in the chapter and Table 5-1.
Fig. 5-2

The ratio $\Delta C / \gamma T_C$ for a number of superconductors plotted against $T_C / \omega_{\text{fn}}$. The solid dots represent results for real materials obtained in reference (30). In increasing order of $\Delta C(T_C) / \gamma T_C$, they correspond to the following systems:

Al, Ta, V, Sn, Tl, In, Tl, Bi, Nb (Butler), Nb (Arnold), Nb (Robinson), V, Si, Nb-75Zr.25, Pb-4Tl.6, Nb-Al (2), V-Ga, Hg, Nb-Al (3), Nb-Ge (2), Nb-Ge (1), Pb-6Tl.4, Nb-Sn, Nb-Al (1), Pb, Pb-8Tl.2, Pb-9Bi.1, Pb-8Bi.2, Pb-65Bi.35, Pb-7Bi.3. The solid curve corresponds to $\Delta C(T_C) / \gamma T_C = 1.43(1 + 53(T_C / \omega_{\text{fn}})^2 \ln(\omega_{\text{fn}} / 3T_C))$ which is formula (5-2) in the text. The entries (solid dots) shown in the insert are the scaled realistic spectra results described in the chapter and Table 5-1.
Fig. 5-3 Plots of the critical magnetic field deviation function $D(t)$ versus the reduced temperature $t = T/T_c$ for the scaled materials listed in Table 5-1. All have the same $T_c$, $\mu^*$, and $\omega_{\varepsilon n}^*$. The differences come entirely from differences in shape of the spectral density where $\alpha^2 F(\Omega) = B_0^2 F(\gamma \Omega)$ with $\alpha_0^2 F(\Omega)$ the spectral density of the materials described in Table 5-1 and $B, \gamma$ the scaling parameters.
The thermodynamic ratio $\gamma_s (T_c / H_c(0))^2$ for the two delta function model as a function of choice of $\omega_L$ and $\omega_G$, the positions of the two delta functions. Here $\omega_L < \omega_G$ and $\omega_G > \omega_{\ell n}$ with $\omega_{\ell n}$ fixed. Figure 5-4a gives 6 curves labelled according to $\omega_G / \omega_{\ell n} = 1.1, 1.5, 2.0, 4.0, 8.0$ and $12.0$ as a function of $\omega_{\ell n} / \omega_{\ell n}$. Figure 5-4b gives the same data and involves 5 curves labelled by $\omega_{\ell n} / \omega_L = 1.1, 1.5, 2.0, 3.0,$ and $5.0$ as a function of $\omega_G / \omega_{\ell n}$. The dashed lines join points on the curves which have the same combined delta function weight, $A^*$ for $A^* = 4.03$ (the Pb value), 4.5, and 5.0.
\[ \frac{\gamma S T_c^2}{H_c(0)^2} \]

\[ \omega \ln / \omega_L \]

Values of \( \omega_G / \omega_L \):

- 1.1
- 1.5
- 2.0
- 4.0
- 8.0
- 12.0
Fig. 5-5  The same as Fig. 5-4, but for the specific heat jump ratio
\[ \Delta C_v / \gamma_s T_c \]
Fig. 5-6  Plots of the critical magnetic field deviation $D(t)$ versus reduced temperature $t = T/T_C$ for a selection of the two-delta-function models along with Pb and a delta-function. The values of $\omega_L/\omega_{\epsilon n}$ and $\omega_G/\omega_{\epsilon n}$ and $A$ are given respectively by the numbers in the brackets.
CHAPTER VI

EFFECTS OF PRESSURE ON
THE THERMODYNAMICS OF SUPERCONDUCTORS

6-1 Introduction

The Eliashberg equations, along with the Bardeen-Stephen free energy formula, determine completely the gap and thermodynamics of a superconductor. Provided one knows the superconducting critical temperature, $T_c$, and the electron-phonon spectral density, $\alpha^2 F(\Omega)$, these equations may be solved to determine these quantities exactly. The spectrum $\alpha^2 F(\Omega)$ is determined from tunneling inversion methods as first derived by McMillan and Rowell\(^{(26)}\) and carried out by them and by others for many materials. However this method is difficult, and, for superconductors under pressure, only a restricted number of spectra are known. A common way to avoid the gaps in our knowledge is to make do with simplified equations\(^{(42,29-33,24,43)}\) that depend only on broad characteristics of $\alpha^2 F(\Omega)$ such as the area $A$, the electron-phonon mass renormalization parameter $\lambda$, or $\omega_{\text{en}}$, a characteristic phonon energy first introduced by Allen and Dynes\(^{(29)}\). In this work, though, a slightly different approach is taken. How $\alpha^2 F(\Omega)$ changes with changing pressure will be investigated. If the model of these changes is good, then, along with a knowledge of $dT_c/dP$ which is used to fit a parameter in the model, the exact equations may be solved and, hopefully good
results for other properties of the material under pressure may be obtained.

The model used is a simple modification of that introduced by Trofimenkoff and Carbotte (44). That model has shown itself to be reliable for simple metals and alloys under low pressure, where by low pressure a volume change of approximately 5% at most is meant. Trofimenkoff and Carbotte (44) suggest, as a reasonable first approximation to the electron-phonon spectral density, \( \alpha^2_F(\Omega) \), under pressure, that

\[
\alpha^2_F(\Omega) = \frac{B}{\beta^2} \alpha^2_{F_0}(\Omega),
\]

(6-1)

where the subscript zero on the right hand side denotes zero pressure. By denoting the fractional volume decrease, \(-\Delta V/V\), by \(\nu\), the \(\beta\) in equation (6-1) may be written as

\[
\beta(\nu) = 1 + \nu \gamma_G,
\]

where \(\gamma_G\) is a low temperature average Grüneisen constant which is taken to be the same for all phonons on the assumption that only the gross behaviour of phonons under pressure is critical. The model gives a rough account of the observed changes in the \(\alpha^2_F(\Omega)\) of simple metals with pressure; the height decreases and the phonon modes generally move upwards in frequency. Grüneisen constants give the shift of the phonon modes with pressure.

From equation (6-1), it can be seen that the factor \(B\) is given
\[
B = \frac{\int \omega \alpha^2 F(\omega) \, d\omega}{\int \omega \alpha^2 F_0(\omega) \, d\omega}
\tag{6-2}
\]

Both the numerator and denominator, respectively, in (6-2) are related to the finite and zero pressure (P) McMillan - Hopfield\(^{(45)}\) parameters \(\eta_j\) so that

\[
B = \frac{\sum_j \eta_j(P)/M_j}{\sum_j \eta_j(0)/M_j}
\tag{6-3}
\]

with

\[
\eta_j = \frac{1}{N(0)} \sum_{kk'} \left| \left\langle k' \delta V \frac{\partial \phi}{\partial \bar{R}} \mid k \right\rangle \right|^2 \delta(E_k - E_F) \delta(E_k' - E_F)
\tag{6-4}
\]

In equation (6-3), the sum over \(j\) goes over all the atoms (mass \(M_j\)) in the unit cell. In equation (6-4), \(E_k\) is the energy of the \(k\)'th state with \(k\) momentum and branch index. \(E_F\) is the Fermi energy. \(V\) the electron-ion potential, and \(R_j\) the position of the \(j\)'th atom in the cell. The factor \(N(0)\) is the single spin density of states at the Fermi energy.

While in the original work of Trofinenko and Carbotte\(^{(44)}\) on simple metals the \(\eta\)'s were calculated from pseudopotential theory, here \(B\) will be fitted such that the solution of the Eliashberg
equations matches the experimental critical temperature under pressure to 0.05% or better. By this adjustment, it is hoped that all effects not already included in the model will be accounted for at least approximately.

How well this model will work for superconductors for which \( \frac{d\epsilon_n T_c}{d\epsilon n V} \) is a constant, and which do not undergo structural phase transitions at the pressures considered, will be explored quantitatively in this chapter. In section 6-2, the model results will be compared with the results obtained from tunneling derived spectral densities at nonzero pressures for Pb, Pb\( _{0.7} \)Bi\( _{0.3} \), and In. In section 6-3, for a varied selection of superconductors: Pb, Pb\( _{0.7} \)Bi\( _{0.3} \), In, Nb, Ta, Sn, Nb\( _3 \)Sn, and Nb\( _3 \)Al, the model will be used to determine \( \frac{d\epsilon_n X}{d\epsilon n V} \), where \( X \) is a quantity such as the gap edge, \( \Delta_0 \), the zero temperature critical magnetic field \( H_c(0) \), the reduced thermodynamic ratio \( \gamma_s(T_c/H_c(0))^2 \) with \( \gamma_s \) the Sommerfeld constant, or \( \Delta C_v(T_c)/\gamma_s T_c^3 \), the normalized specific heat jump at the critical temperature. As well, the critical field deviation function \( D(t) \) will be examined. In section 6-4, the effects of assumptions used in the calculation in the previous sections will be investigated. In section 6-5, conclusions will be drawn.

6-2 Comparison to Results for Real Spectra

In this section, the model spectra are compared to the tunneling derived spectra of superconductors under pressure. This is done by taking the measured and model spectra and solving the
Eliashberg and Bardeen-Stephen equations. The systems investigated are Pb, Pb$_{0.7}$Bi$_{0.3}$, and In. The measured spectrum for Pb at $P = 12.2$ GPa ($\nu = 2.70\%$) was read from Sviystunov et al.$^{(20)}$, for Pb$_{0.7}$Bi$_{0.3}$ at 9.5 GPa ($2.40\%$) from Borodai and Sviystunov$^{(21)}$, and for In at 10 GPa ($2.42\%$) from Revenko et al.$^{(22)}$. The $P = 0$ spectra used in the model come from Rowell et al.$^{(9)}$. In calculating volume changes from pressures for Pb and In, the equations of Gschneidner$^{(46)}$ have been used; for Pb$_{0.7}$Bi$_{0.3}$ the tables of Bridgman$^{(47)}$ for Pb$_{0.6914}$Bi$_{0.3086}$ have been used. In table 6-1, $P = 0$ data is presented for the materials examined in this paper, including those to appear in the next section. In column 1 are the values of the Sommerfeld constant. For Pb, the value found by Culbert et al.$^{(48)}$ has been used, and for In, the value given by Gschneidner$^{(46)}$. The value for Pb$_{0.7}$Bi$_{0.3}$ is calculated from an extrapolation of the data for $N(0)$ of Pb-Bi compounds given in Hermann et al.$^{(49)}$. In column 2 are the densities of atoms (or molecules for compounds) used to derive $N(0)$, shown in column 3, from $\gamma_S$. It has been assumed that $N_{\text{Pb}_{0.7}\text{Bi}_{0.3}} = N_{\text{Pb}}$. It is also assumed that $N(0)$ varies with volume according to the free electron theory $\frac{d\ln N(0)}{d\ln V} = -\frac{1}{3}$, an assumption which is not likely to be valid for transition metals and A-15 compounds, but which can be compensated for if desired. To determine the critical temperature at the appropriate volume changes, the values of $T_c(P=0)$ and $\frac{d\ln T_c}{d\ln V}$ given in columns 4 and 5 have been used. The values of $\frac{d\ln T_c}{d\ln V}$ for Pb and In are those of Smith and Chu$^{(50)}$. The value of $\frac{d\ln T_c}{d\ln V}$ for Pb$_{0.7}$Bi$_{0.3}$ is calculated from the value of $\frac{dT_c}{dP}$ given by Borodai and Sviystunov$^{(21)}$. 
and the pressure/volume data of Bridgman (47). In column 12 are the values of the average Gruneisen $\tilde{\gamma}_G$ used in the model. The values given for Pb and In are the best estimates of Garland and Bennemann (51). It has been assumed $\tilde{\gamma}_G(Pb_{0.7}Bi_{0.3}) = \tilde{\gamma}_G(Pb)$, since data on $\tilde{\gamma}_G$ is sparse. Since these values may be rough, the importance of the choice of $\tilde{\gamma}_G$ in this model will be examined for a specific case in section 6-4. Columns 6 to 9 give details of the spectra used. The value of $\mu^*$ is found by solving the Eliashberg equations for $T_C$ with a cutoff of NW times the Debye frequency, $\omega_D$.

In table 6-2, the results of the calculations for the measured spectra, for the model spectra, and, for comparison, the $P = 0$ spectra are presented. Also given are the quantities $B$ and $\beta$ used in forming the model spectra. In addition, a number of quantities are included that are often used in describing superconductors in a general way: $\lambda$, the area $A$ of the spectrum, the Debye frequency $\omega_D$ and the characteristic phonon frequency $\omega_{cn}$ first introduced by Allen and Dynes (29) and defined

$$\omega_{cn} = \exp\left(\frac{2}{\lambda} \int \frac{d\Omega}{\Omega} \alpha^2 P(\Omega) \Omega n \right)$$

There are a few oddities here: $\omega_{cn}$ for the tunneling derived $\alpha^2 P(\Omega)$ of Pb at $P = 12.2$ GPa is smaller than the $P = 0$ value, and the areas of the spectra for Pb$_{0.7}$Bi$_{0.3}$ and Pb increase with pressure. This is contrary to the behaviour assumed by the Trofimenkoff-Carbotte model. Of course these differences are of only a few percent and could reflect uncertainties introduced in reading the spectra from the references, or
in the tunneling derived spectra themselves. It will be seen later
that these spectra are not always consistent from one experiment to the
other, and this raises concerns about the accuracies.

In general, the model gives lower values of $2 \Delta_0 / k_B T_C$, $H_c(0)$,
$\Delta C_v / T_c$, $\gamma_s (T_c / H_c(0))^2$, and $-dH_c(T)/dT|_{T_c}$ than does the measured
spectra. Considering the difference of these values for the model and
measured spectra from the $P = 0$ results, the model and measured
spectrum differences differ by up to 41% in the case of $2 \Delta_0 / k_B T_C$ for
Pb. Of these five properties, only $-dH_c(T)/dT|_{T_C}$ is uniformly
different (at about 30%): the other four fluctuate in no obvious
pattern. If one considers an average of the ratio of the differences
for each material for these five properties, one finds a difference of
18%, 19%, and 15% for Pb, Pb$_{0.7}$Bi$_{0.3}$, and In respectively. Averaging,
instead, the ratios for each property the range is from 10% for
$\gamma_s (T_c / H_c(0))^2$ to 30% for $-dH_c(T)/dT|_{T_C}$. In figure 6-1, the comparison
of the D(t) curves for the model and measured $\alpha^2 P(\Omega)$, and the $P = 0$
$\alpha^2 P(\Omega)$ are given. In the worst case, in the difference in the maximum
values of D(t) from the $P = 0$ value is 9% which is remarkably good
agreement.

In comparing the model and measured spectra results, it must be
borne in mind that the changes in $2 \Delta_0 / k_B T_C$, $H_c(0)$, $\Delta C_v / T_c$,
$\gamma_s (T_c / H_c(0))^2$, and $-dH_c(T)/dT|_{T_C}$ caused by these pressures are less
than 10%. Therefore uncertainties in the measured pressure $\alpha^2 P(\Omega)$,
relative to the zero pressure $\alpha^2 P(\Omega)$, are quite probably significant.
A 1.0% uncertainty in the values of the five properties under pressure,
relative to zero pressure, could account for almost all the variation with the model predictions. Accurate measurement of the volume dependence of the reduced thermodynamic ratios calculated in this chapter, which, by the way, would not change at all in a BCS theory, would be helpful in choosing between the model spectra and the tunneling derived ones. While the agreement between the two approaches is not always good, indicating the need for more accurate tunneling data and more thermodynamic measurements, it is still useful to proceed with the model in the more complicated case such as transition metals and A-15 compounds for which no tunneling data under pressure is available. Such calculations represent the state of the art at the present time, and it is hoped that they will encourage further experiments.

6-3 Volume Derivatives of $A_0$ and $H_c(T)$

On the strength of the comparison between the model and actual spectra results, this section will investigate the behaviour of the gap edge and thermodynamic quantities as a function of volume change for a varied selection of materials: Pb, Pb$_{0.7}$Bi$_{0.3}$, In, Sn, Nb, Ta, Nb$_3$Sn, and Nb$_3$Al. To determine the volume change dependence, the Eliashberg and Bardeen-Stephen equations have been solved for the model at $\nu = 2.5\%$ and $\nu = 5.0\%$, as well as at zero pressure. Again $B$ has been fitted to give the correct $T_c$ as determined from the $d\ln T_c/d\ln V$ data. In calculating thermodynamic quantities, $d\ln N(0)/d\ln V = -\frac{1}{3}$, the free electron value, has been used. It will be shown how this may be
compensated for in the next section. Then from a quadratic fit to the
data the appropriate derivatives are found.

The references for the $\alpha^2 F(\Omega)$ used for Pb, Pb$^{0.7}$Bi$^{0.3}$, and In
have already been cited. The Sn and Ta spectra are those of Rowell and
Dynes (9). The Nb$_3$Sn spectrum is taken from Wolf et al. (14) The spectrum
for Nb was measured by Arnold et al. (11). The $\alpha^2 F(\Omega)$ for Nb$_3$Al was of a
thin film measured by Kwo and Geballe (12). It had a $T_c$ of 16.4 K
rather than the bulk value of 18 K, nevertheless this spectra has been
used with the bulk value of $\partial\delta n_T / \partial \delta n_V$. In section 6-4, the effect of
using an incorrect $\partial\delta n_T / \partial \delta n_V$ will be discussed.

In table 6-1, as previously mentioned, are listed some of the
characteristics of those spectra: $T_c$, $A$, $\lambda$, $\omega_n$, $\omega_D$, and $\mu$ (NWX,L,D).
The values of $\gamma_s$ given by Gschneidner (46) for Nb, Ta, and Sn, and the
values of Stewart (52) for Nb$_3$Sn and Nb$_3$Al have been used. The values
of $\gamma_s$, $N$, and N(0) given refer to molecules for Nb$_3$Sn and Nb$_3$Al. Also
given are the constants used with the model: $\partial\delta n_T / \partial \delta n_V$, $\gamma_G$, and the
compressibility $\kappa$. The value of $\partial\delta n_T / \partial \delta n_V$ for Sn is that of Smith and
Chu (50). For Nb, Ta, Nb$_3$Sn, and Nb$_3$Al the values of Garland and
Bennemann (51) have been used. Also given are the values listed by
Garland and Bennemann (51) of $\gamma_G$ for Sn, Nb$_3$Sn, and Nb$_3$Al and of $\kappa$ for
Nb$_3$Sn and Nb$_3$Al. The values of $\kappa$ for Nb, Ta, and Sn are from
Gschneidner (46). For Nb and Ta $\gamma_G$ as given by Smith (53) is used. The
importance of $\gamma_G$ will be examined in section 6-4. It should be noted
that the values of $\kappa$ were determined at room temperature, and, though
these values should be good approximations to those at low temperature,
this has introduced some error into the conversions from volume change
to pressure.

In table 6-2, the values of the gap edge $A_0$ and the thermodynamic quantities: $H_c(0)$, $dH_c(T)/dT|_{T_c}$, $\Delta C_v/\gamma_s T_c$, and $\gamma_s(T_c/H_c(0))^2$, which come from the solution of the Eliashberg and Bardeen-Stephen equations are listed. These values agree well with the experimental results cited in this chapter. Also given are $d\ln X/d\ln V$, where $X = A$, $\lambda$, $A_0$, $H_c(0)$, $\Delta C_v/\gamma_s T_c$, and $\gamma_s(T_c/H_c(0))^2$. These values were calculated by fitting a parabola to the zero pressure values and to the values of these parameters calculated from the model spectra at $\nu = 2.5\%$ and $5.0\%$. The values of $B(\nu)$ needed to fit $T_c$ determined from $d\ln T_c/d\ln V$ and $\nu$ are also given. The values of $A$ and $\lambda$ can be found using the relations

$$A(\nu) = \frac{B(\nu)}{\beta(\nu)} A_0$$  \hspace{1cm} (6-5)$$

and

$$\lambda(\nu) = \frac{B(\nu)}{\beta(\nu)} \lambda_0$$  \hspace{1cm} (6-6)$$

and the values of $\gamma_s$ given in table 6-1. Notice that the model predicts that $A$ increases with pressure for Nb and Ta. Although $T_c$ varies linearly with small volume changes, the quantities examined here are not so clearly linear. The slope of a linear fit to the data could differ by about 10% from that of the parabola, though the exact amount varied with the quantity and the material in question.
In table 6-4, the results for Pb, Pb_{0.7}Bi_{0.3}, and In for d\mu_0/dP, d\mu/\mu, and d\sigma/\sigma are compared with the little experimental data that is available. The values of \kappa given in table 6-1 were used to convert the results to pressure derivatives. The values of Pb are in good agreement with the work of Borodai and Svistunov\textsuperscript{(54)} and of Svistunov et al.\textsuperscript{(20)}, and indicate that the values of Franck and Keeler\textsuperscript{(55)} and of Franck, Keeler and Wu\textsuperscript{(56)}, especially for d\mu/\mu, are somewhat suspect. The inconsistency found between tunneling data emphasizes the need for more measurements. The simple model should not be discarded. For Pb_{0.7}Bi_{0.3} the agreement is much poorer, the values of -d\mu_0/dP, -d\mu/\mu, and -d\sigma/\sigma need to be 10%, 35%, and 22% larger to agree with the experiments of Borodai and Svistunov\textsuperscript{(21,54)}. The values for In are also a little lower than the experimental results of Revenko et al.\textsuperscript{(22)} and Mostovoi and Revenko\textsuperscript{(57)}, however the values of d\sigma/dP do not quite agree. This could be because of the value of \kappa used, in which case a simple scaling to match the experimental d\sigma/dP is in order. This would give very good results. The value of \kappa need not be wrong, however, since measurements of d\sigma/dP are not always consistent. In section 6-4, it will be argued that the results scale with d\sigma/dP so that the data should be scaled for comparison anyway.

A much broader selection of experimental work exists for dH_c(T)/dP at T = 0 and at T = T_c. Unfortunately not all the experiments agree, as is mentioned in the reviews by Olsen and Rohrer\textsuperscript{(58)} and Swenson\textsuperscript{(59)}. In table 6-5, the values of dH_c/dP,
$dH_c(0)/dP_c$ and $dH_c(T)/dP|_{T_c}$ are presented as well as the experimental values $(60-69)$. The quantity $dH_c(T)/dP|_{T_c}$ is calculated from the thermodynamic relation

$$
\frac{dH_c(T)}{dT} \bigg|_{T_c} = \frac{dH_c(T)}{dP} \bigg|_{T_c} \frac{dT_c}{dP}
$$

and, as mentioned, the values of $dH_c(T)/dT|_{T_c}$ agree to within 2\% of experiment. The results are quite consistent within the experimental error of at least some of the experiments on Pb, Sn, In, and Ta. For Nb, there seems to be only one set of experimental data available, that by White $(69)$, and, even after scaling for differences in $dT_c/dP$, the calculated result is at least 10\% too low. This may not be too worrying in view of the data scatter between experiments for Ta and the other materials listed, and since the free electron approximation of $d \eta N(0)/d \eta V$ is suspect for other than simple or transition metals. A method for compensating for $d \eta N(0)/d \eta V \neq -\frac{1}{3}$ will be shown in section 6-4.

It is generally found in experiments that $dH_c(T)/dP|_{T}$ is linear in $T^2$ within experimental error. In figure 6-2, $\frac{1}{H_c(0)} \frac{dH_c(T)}{d \eta V}$ versus $T^2$ has been plotted for the eight spectra being investigated. All the curves are approximately linear, with some more so than others. Schirber and Swenson $(67)$ find a sharp change in the slope of the curve for Sn near $T^2 = 0.2$ and suggest anisotropy, or a strange $dT_c/dP$ dependence at low pressures, as a possible cause. The model gives no
evidence of such a large change in slope, although there is a small one, and would not, since complicated behaviour has been explicitly ignored in the model. Above $t^2 = 0.2$, however, the curve is qualitatively the same.

This general agreement implies that the model is accurately giving the general behaviour of changes in $D(t)$ with pressure.

6-4 Effects of $d\rho / d\sigma$, $\Gamma$, $d\rho T / d\rho T$, and $d\rho N(0) / d\rho N$

In this section, the effect of how some of the assumptions used in the model on the model's predictions are examined. Specifically, the effects of a $\mu^*$ that changes with pressure, of uncertainties in $\Gamma$ and in $d\rho T / d\rho T$, and how a $d\rho N(0) / d\rho N \neq -\frac{1}{3}$ may be incorporated into the results will be investigated.

It has been assumed in the calculations in the previous sections that the strength of the repulsive interaction, given by

$$\mu^* = \frac{\mu}{1 + \mu \ln(E_F/\omega_0)}$$

where $\mu$ is the screened Coulomb interaction, varies little, if at all, with volume change. To examine the effects of a $\mu^*$ varying with pressure, the Eliashberg and Bardeen-Stephen equations are again solved for the model at $\nu = 2.5\%$ and $5.0\%$ for Pb, but letting $d\rho T / d\rho T = +d\rho T / d\rho N$ and $+2d\rho T / d\rho N$ (i.e. $\pm 2.31$ and $\pm 4.62$). In table 6-6, the values of $B$, $\Delta_0$, $H^2_c(0)$, and $\Delta C / \tau s^3 T$ at $\nu = 2.5\%$ and $5.0\%$ for nonzero
values of \( \frac{d\mu}{d\nu} \) and the associated volume derivatives \( \frac{d\Delta}{d\nu} \), \( \frac{d\lambda}{d\nu} \), \( \frac{d\Delta \rho}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \), and \( \frac{d\Delta \eta}{d\nu} \) are given. In figure 6-4, the effect on \( \frac{1}{\frac{\rho_c}{d\nu}} \) versus \( t^2 \) curves is shown, and in figure 6-5, the effect on \( D(t) \) at \( \nu = 5.0\% \) is illustrated. Smith (53) points out that, in the Thomas-Fermi approximation, \( \frac{d\mu}{d\nu} = \frac{d\mu(N)}{d\nu} \), the free electron theory value of which is \( -\frac{1}{3} \). Since the numbers in table 6-5 for \( \frac{d\mu}{d\nu} \) are up to fourteen times larger, the effect of keeping \( \mu \) constant would be a great deal smaller than exhibited, and thus should be negligible. Only for a material like Nb, where \( \frac{d\Delta \rho}{d\nu} \) is small, should a varying \( \mu \) have an appreciable effect.

The values of \( \tau \) used in the model have estimated errors of up to 15% (51,53). However since \( \tau \) is multiplied by \( \nu \), which is \( \leq 5.0\% \), the uncertainty in \( \beta \) is much smaller, and consequently, the overall effect of \( \tau \) should be small. Nonetheless, to see exactly how varying \( \tau \) affects the results, the model has again been solved for Pb at \( \nu = 2.5\% \) and 5.0%, but for \( \tau = 0, 2, 3, \) and 5. The results for B, \( \Delta \rho \), \( \rho_c \), \( \Delta \rho \), \( \Delta \rho \), the maximum of \( D(t) \) at 2.5% and 5.0%, and the volume derivatives \( \frac{d\Delta}{d\nu} \), \( \frac{d\Delta \rho}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \) are given in table 6-7. As well, the effect on \( \frac{1}{\frac{\rho_c}{d\nu}} \) and on \( D(t) \) at \( \nu = 5.0\% \), are shown in figure 6-5 and 6-6 respectively. The values of \( \frac{d\Delta \rho}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \), \( \frac{d\Delta \eta}{d\nu} \), and \( \frac{d\Delta \eta}{d\nu} \) for \( \tau = 3.0 \), which is almost 30% bigger than \( \tau = 2.35 \), differ from those \( \tau = 2.35 \) results by 5%, 5%, 13%, and 6% respectively. Clearly the uncertainty in \( \tau \) is not a major problem. Only in
$^{208}$Pb $^{207}$Bi $^{207}$Bi where the error in $\gamma_c$ is unknown, is there a possible problem with the results, but the agreement with experiment in section 6-3, and the measured spectra results in section 6-2, indicate that the choice of $\gamma_c$ is reasonable.

Since it is $\nu_c$ that occurs in the definition of $\beta$, these comments have equal validity for uncertainties in $\nu$ originating from an incorrect value of $\delta n T_c / \delta n V$. It is the value of $T_c$ at which the model is used that is most important - uncertainties in $\nu$ or $\nu_c$ affect the absolute values of $H_c(0)$ and $\Delta_0$ minimally. Of course, the derivatives would change, since the fit to the data points has used the incorrect values of $\nu$. But the correct values $\nu'$ are related to the old values by the simple relation $\nu' = R \nu$, where $R$ is the ratio of the values of $\delta n T_c / \delta n V$, thus the slope is then $1/R$ times the calculated value.

While exact numbers would vary for the $\alpha^2 F(\Omega)$ used and the parameter examined, it is expected that the behaviour for other materials would be similar to Pb. Thus one could expect that the model will typically give correct values of $\Delta_0$ and the thermodynamics to within approximately 2%, and that the volume derivatives will have a rough uncertainty of 10%.

The assumption that $\delta n N(0) / \delta n V = - \frac{1}{3}$, the free electron theory value, cannot be confidently applied to other than simple, non-transition metals. If $\delta n N(0) / \delta n V$ is a constant, not necessarily the free electron value, this would not affect the results for the thermodynamic ratios: $\Delta C / \pi^2 T_c$, $\gamma_c (T_c / H_c(0))^2$, and $D(t)$, or their volume derivatives since these are independent of $N(0)$. On the other
hand, the results for \( \frac{1}{H_c(0)} \frac{dH_c(T)}{dnN} \bigg|_T \) as given in figure 6-2 would change, but this can be compensated for in the following manner. First of all, at \( T = T_c \), the thermodynamic relation equation (6-7) holds, and, since neither \( \frac{dH_c(T)}{dT} \bigg|_{T_c} \) nor \( d{\bar{n}}_{T_c}/dnN \) are dependent on \( d{\bar{n}}N(0)/dnN \), this indicates that the \( t = 1 \) points are also independent of \( d{\bar{n}}N(0)/dnN \). This is not the true for \( t < 1 \). If one writes

\[
H_c(T) = \sqrt{N(0)} \ h_c(T),
\]

then

\[
\left. \frac{1}{H_c(0)} \frac{dH_c(T)}{dnN} \bigg|_T = \frac{1}{h_c(0)} \frac{dh_c(T)}{dnN} \bigg|_T + \frac{1}{2} \frac{h_c(T)}{h_c(0)} \frac{d{\bar{n}}N(0)}{dnN} \right. \quad (6-8)
\]

At \( T = 0 \), for the free electron value, this is

\[
d{\bar{n}}h_c(0)/dnN = d{\bar{n}}h_c(0)/dnN - \frac{1}{6} \quad (6-9)
\]

Thus the \( T = 0 \) values in figure 6-2 can be compensated by adding \( \frac{1}{6} \) and one half the correct value of \( d{\bar{n}}N(0)/dnN \). For \( 0 < t < 1 \), however, a detailed knowledge of \( H_c(T) \) is required to compensate the curves exactly. But, since the curve are basically linear and a different value of \( d{\bar{n}}N(0)/dnN \) will not greatly affect this, it will be enough to pivot a given curve about the \( t = 1 \) point to get the corrected \( t = 0 \) point.
6-5 Discussion and Conclusions

The effect of pressure on the gap edge and thermodynamics of several superconductors has been studied. In three cases, namely, Pb, Pb$_{0.7}$Bi$_{0.3}$, and In, the electron-phonon spectral density obtained from tunneling by McMillan-Rowell inversion has been used. At the same time, a simple model, introduced by Trofimenkoff and Carbott for the change with pressure of $\alpha^2 F(\alpha)$, is also employed with a scaling on the vertical axis (B) considered to be an adjustable parameter and fitted to the observed change with volume of the critical temperature. While the two approaches give qualitatively similar answers for the gap edge, the thermodynamic ratios, and the critical magnetic field deviation function $D(t)$, there are some significant differences. More accurate measurements would allow better testing of the model. At the moment, it is not clear that the tunneling derived results are to be preferred over the model results because small uncertainties in tunneling data (which are not always found to be consistent from one experiment to the other) could account for a great deal of the differences found here.

The same model was used to calculate the volume dependence of the gap edge and the thermodynamics of Nb, Ta, Sn and of Nb$_3$Sn and Nb$_3$Al systems, for which it seems that tunneling data under pressure is unavailable. Definite predictions are made and compared with the little experimental information available in the literature. It should be noted, for such quantities as $\gamma_s (T_c, \Delta_{ACB}(0))^2$, $\Delta C_{V}/\gamma_s T_c$, and $D(t)$, the volume dependence is strictly a strong coupling effect which could not
be calculated without the use of the full Eliashberg equations. Hopefully these calculations can be checked against further experimental results.

Some confidence in the model for the volume dependence of the electron-phonon spectral density comes from section 6-4, in which the effect of uncertainties in \( \frac{\partial \mu}{\partial \text{enV}} \), \( \frac{\partial \text{enT}}{\partial \text{enV}} \) and \( \frac{\partial \text{enN}(0)}{\partial \text{enV}} \) on the predictions are studied. In general, these effects are small and most of the error introduced by these uncertainties can be largely compensated for by the fitting parameter \( B \). While the model \( \alpha^2 F(\Omega) \) will not be correct in every detail, especially if some phonon modes react very differently from others to pressure, these details are not always dominant in getting the right gap edge and thermodynamics. This is clear from Chapters IV and V where the effects of the shape of \( \alpha^2 F(\Omega) \) on the gap ratio \( 2\Delta_0/k_B T_c \) and the thermodynamic ratios \( \Delta C_v/\gamma_s T_c \), \( \gamma_s (T_c/H_c(0))^2 \), and \( D(t) \) is studied. In those chapters, it was found, for a given value of \( T_c \), that the shape of \( \alpha^2 F(\Omega) \) could vary significantly and not change very much the value of the above ratios if \( A, \phi_{\text{en}}^* \) and \( \mu^* \) were fixed. It is only these general features of the model system that need be roughly correct. Further experimental information on the volume dependence of the gap edge and the thermodynamics would make it possible to test the calculations and perhaps indicate the need to refine the model.
Table 6-1. Characteristic data of the zero pressure electron-phonon spectral densities $(\alpha^2 F(\Omega))$ for Pb, Pb$_{0.7}$Bi$_{0.3}$, In, Sn, Nb, Ta, Nb$_3$Sn, and Nb$_3$Al. As well, values of the low temperature average Gruneisen constants $\gamma_0$, and of the compressibilities $\kappa$, for these materials are given.
<table>
<thead>
<tr>
<th></th>
<th>7 ( \frac{mJ}{mol-K^2} )</th>
<th>N ( \times 10^{22} ) cm(^3)</th>
<th>N(0) ( \times 10^{19} ) states(-) meV(-)cm(^3)</th>
<th>T(_c) (K)</th>
<th>( \frac{d\delta nT}{d\delta nV} ) (meV)</th>
<th>A</th>
</tr>
</thead>
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<tr>
<td>Pb</td>
<td>3.00</td>
<td>3.30</td>
<td>0.823</td>
<td>7.19</td>
<td>2.31</td>
<td>4.0320</td>
</tr>
<tr>
<td>Pb(<em>{0.70})Bi(</em>{0.30})</td>
<td>3.64</td>
<td>3.30</td>
<td>0.844</td>
<td>8.45</td>
<td>1.16</td>
<td>4.4624</td>
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<tr>
<td>In</td>
<td>1.70</td>
<td>3.83</td>
<td>0.765</td>
<td>3.40</td>
<td>4.6</td>
<td>2.7409</td>
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<td>Sn</td>
<td>1.78</td>
<td>3.69</td>
<td>0.813</td>
<td>3.72</td>
<td>6.75</td>
<td>3.4181</td>
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<td>Nb</td>
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<td>5.56</td>
<td>4.50</td>
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<td>0.4</td>
<td>7.2469</td>
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<td>Ta</td>
<td>5.84</td>
<td>5.58</td>
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<td>4.39</td>
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<td>0.96</td>
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<td>9.3197</td>
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<td>$\lambda$</td>
<td>$\omega_n$ (K)</td>
<td>$\omega_D$ (meV)</td>
<td>NW</td>
<td>$\mu^*$ (×10$^{-7}$ GPa$^{-1}$)</td>
<td>$\tau_G$</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>----------------</td>
<td>-----------------</td>
<td>----</td>
<td>-------------------------------</td>
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<tr>
<td>Pb</td>
<td>1.5477</td>
<td>56.03</td>
<td>11.0</td>
<td>6</td>
<td>0.1438</td>
<td>2.35</td>
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<tr>
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<td>2.0145</td>
<td>46.55</td>
<td>10.4</td>
<td>6</td>
<td>0.1095</td>
<td>2.35</td>
</tr>
<tr>
<td>In</td>
<td>0.8046</td>
<td>67.70</td>
<td>15.8</td>
<td>6</td>
<td>0.1157</td>
<td>2.3</td>
</tr>
<tr>
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<td>0.7165</td>
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<td>0.1861</td>
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<td>105.16</td>
<td>35.69</td>
<td>6</td>
<td>0.1272</td>
<td>2.0</td>
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Table 6-2  Comparison of the results for the model and measured electron-phonon spectral densities for Pb, Pb$_{0.7}$Bi$_{0.3}$, and In at nonzero pressures. Also included are the zero pressure results and the fitting parameters B and $\beta$ used in the model spectra.
<table>
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<th>Pb0.7Bi0.3 model</th>
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<tr>
<td>Pressure (GPa)</td>
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<tr>
<td>0</td>
<td>12.2</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
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</tr>
<tr>
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</tr>
<tr>
<td>0.75</td>
<td>0</td>
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<tr>
<td>ν</td>
<td>2.70%</td>
<td>2.70%</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2.40%</td>
</tr>
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<td>0.25</td>
<td>2.40%</td>
<td>2.40%</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>2.40%</td>
</tr>
<tr>
<td>0.75</td>
<td>0</td>
<td>2.40%</td>
</tr>
<tr>
<td>Tc (K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.19</td>
<td>6.30</td>
<td>6.30</td>
</tr>
<tr>
<td>8.45</td>
<td>8.23</td>
<td>8.23</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.01660</td>
<td></td>
<td>1.60261</td>
</tr>
<tr>
<td>1.0633</td>
<td></td>
<td></td>
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<td>ω in (K)</td>
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<tr>
<td>56.04</td>
<td>55.57</td>
<td>59.59</td>
</tr>
<tr>
<td>46.55</td>
<td>49.56</td>
<td>49.18</td>
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<tr>
<td>A (meV)</td>
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<tr>
<td>4.032</td>
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<td>ω D (meV)</td>
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<td>10.4</td>
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<tr>
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<td>0.1095</td>
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<tr>
<td>2Δ0/k_BTc</td>
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<td>Hc(0) (Oe)</td>
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</tr>
<tr>
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<td>1007.7</td>
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<tr>
<td>ΔCv/τsTc</td>
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<td></td>
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<td>τs[Tc/Hc(0)]^2</td>
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<td>0.1324</td>
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<tr>
<td>0.1251</td>
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<td>0.1267</td>
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<tr>
<td>-dHc(T)/dT</td>
<td>Tc(0e/K)</td>
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<tr>
<td>239.7</td>
<td>228.6</td>
<td>225.4</td>
</tr>
<tr>
<td>271.4</td>
<td>264.2</td>
<td>262.1</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>model</td>
</tr>
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<td>------------------</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
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<td>$\nu$</td>
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</tr>
<tr>
<td>$T_C$ (K)</td>
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<td>$\beta$</td>
<td></td>
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<td>$\omega_{\nu}$ (K)</td>
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<td>$\mu$</td>
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<td>$2\Delta_0/k_B T_C$</td>
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<td>$H_C(0)$ (Oe)</td>
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<td>1.728</td>
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<tr>
<td>$\tau_{s}[T_C/H_C(0)]^2$</td>
<td>0.1561</td>
<td>0.1584</td>
</tr>
<tr>
<td>$-dH_C(T)/dT</td>
<td>_{T_C}$ (Oe/K)</td>
<td>156.2</td>
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Table 6-3  Model predictions of the volume derivatives of $A$, $\lambda$, $\Delta_0$, $H_c(0)$, $\Delta C_v/\gamma_s T_c$, and $\gamma_s(T_c/H_c(0))^2$ for Pb, Pb$_{0.7}$Bi$_{0.3}$, In, Sn, Nb, Ta, Nb$_3$Sn, and Nb$_3$Al. Also given are the zero pressure values of $\Delta_0$, $H_c(0)$, $\Delta C_v/\gamma_s T_c$, $\gamma_s(T_c/H_c(0))^2$, and $-dH_c(T)/dT|_{T_c}$. The derivatives are calculated from a fit to the values at $\nu = 0\%$, 2.5\%, and 5.0\%. Included are the values of $B$ at $\nu = 2.5\%$, and 5.0\%.
<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Pb$<em>{0.7}$Bi$</em>{0.3}$</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
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<tr>
<td>$B (\nu=2.5%)$</td>
<td>1.01761</td>
<td>1.02545</td>
<td>1.03493</td>
<td>1.01300</td>
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<tr>
<td>$B (\nu=5.0%)$</td>
<td>1.03805</td>
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<td>1.07153</td>
<td>1.02911</td>
</tr>
<tr>
<td>$\frac{d\Delta n}{d\Delta n V}$</td>
<td>4.000</td>
<td>3.664</td>
<td>3.203</td>
<td>3.505</td>
</tr>
<tr>
<td>$\frac{d\Delta n A}{d\Delta n V}$</td>
<td>1.686</td>
<td>1.334</td>
<td>0.928</td>
<td>1.530</td>
</tr>
<tr>
<td>$\Delta_0$ (meV)</td>
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<td>1.8085</td>
<td>0.5553</td>
<td>0.5937</td>
</tr>
<tr>
<td>$\frac{d\Delta x}{d\Delta n V}$</td>
<td>3.649</td>
<td>2.325</td>
<td>5.225</td>
<td>7.280</td>
</tr>
<tr>
<td>$-\frac{dH_c(T)/dT}{H_c(T)}_{T_c}$ (0e/K)</td>
<td>239.7</td>
<td>271.2</td>
<td>156.2</td>
<td>151.0</td>
</tr>
<tr>
<td>$h = H_c(0)$ (0e)</td>
<td>800.8</td>
<td>1053.2</td>
<td>282.9</td>
<td>306.7</td>
</tr>
<tr>
<td>$\frac{d\Delta n h}{d\Delta n V}$</td>
<td>3.889</td>
<td>2.474</td>
<td>5.455</td>
<td>7.559</td>
</tr>
<tr>
<td>$j = \Delta C_v/\gamma S T_c$</td>
<td>2.7666</td>
<td>3.0122</td>
<td>1.7943</td>
<td>1.6734</td>
</tr>
<tr>
<td>$\frac{d\Delta n j}{d\Delta n V}$</td>
<td>2.572</td>
<td>0.984</td>
<td>1.886</td>
<td>2.050</td>
</tr>
<tr>
<td>$r = \gamma S [T_c/H_c(0)]^2$</td>
<td>0.1324</td>
<td>0.1251</td>
<td>0.1561</td>
<td>0.1607</td>
</tr>
<tr>
<td>$\frac{d\Delta n r}{d\Delta n V}$</td>
<td>1.085</td>
<td>0.521</td>
<td>0.685</td>
<td>0.644</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>Ta</td>
<td>Nb₃Sn</td>
<td>Nb₃Al</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>B (ν=2.5%)</td>
<td>1.04693</td>
<td>1.05987</td>
<td>1.05507</td>
<td>1.04627</td>
</tr>
<tr>
<td>B (ν=5.0%)</td>
<td>1.09465</td>
<td>1.10874</td>
<td>1.11176</td>
<td>1.09346</td>
</tr>
<tr>
<td>\frac{\partial \rho}{\partial V}</td>
<td>0.917</td>
<td>0.357</td>
<td>2.996</td>
<td>2.514</td>
</tr>
<tr>
<td>\frac{\partial \rho}{\partial V}</td>
<td>-0.471</td>
<td>-1.127</td>
<td>0.423</td>
<td>0.165</td>
</tr>
<tr>
<td>\Delta_0 (meV)</td>
<td>1.5391</td>
<td>0.6941</td>
<td>3.5500</td>
<td>3.2627</td>
</tr>
<tr>
<td>\frac{\partial n_{\text{ex}}}{\partial V}</td>
<td>1.622</td>
<td>1.252</td>
<td>1.889</td>
<td>1.117</td>
</tr>
<tr>
<td>\frac{\partial H_c(T)}{\partial T}</td>
<td>412.6</td>
<td>332.3</td>
<td>510.2</td>
<td>530.8</td>
</tr>
<tr>
<td>(0e/K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h = H_c(0) (Oe)</td>
<td>1980.1</td>
<td>802.4</td>
<td>4364.5</td>
<td>4154.9</td>
</tr>
<tr>
<td>\frac{\partial \rho_{\text{ex}}}{\partial V}</td>
<td>0.574</td>
<td>1.135</td>
<td>2.015</td>
<td>1.148</td>
</tr>
<tr>
<td>\frac{\partial j}{\partial s_c}</td>
<td>1.9214</td>
<td>1.6221</td>
<td>2.6320</td>
<td>2.6121</td>
</tr>
<tr>
<td>\frac{\partial j}{\partial V}</td>
<td>0.849</td>
<td>0.194</td>
<td>1.352</td>
<td>0.775</td>
</tr>
<tr>
<td>r = \gamma \left[ \frac{T_c}{H_c(0)} \right]^2</td>
<td>0.1527</td>
<td>0.1619</td>
<td>0.1344</td>
<td>0.1338</td>
</tr>
<tr>
<td>\frac{\partial r}{\partial V}</td>
<td>0.221</td>
<td>0.057</td>
<td>0.558</td>
<td>0.335</td>
</tr>
</tbody>
</table>
Table 6-4 Values of $\frac{d\epsilon nA_0}{dP}$, $\frac{d\epsilon n\lambda}{dP}$, and $\frac{d\epsilon nA}{dP}$ for Pb, Pb$_{0.7}$Bi$_{0.3}$ and in calculated using the values given in Table 6-3 and the values of the compressibility given in Table 6-1 and the measured values of these quantities as given in the noted references.
<table>
<thead>
<tr>
<th>Material</th>
<th>$\frac{\Delta n C}{dP} \times 10^{-6}$/GPa</th>
<th>$\frac{\Delta n A_0}{dP} \times 10^{-6}$/GPa</th>
<th>$\frac{\Delta n A}{dP} \times 10^{-6}$/GPa</th>
<th>$\frac{\Delta n A}{dP} \times 10^{-6}$/GPa</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>5.38</td>
<td>8.49</td>
<td>9.31</td>
<td>3.92</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>4.9±0.2</td>
<td>10.1±0.8</td>
<td>18.8±1.9</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>5.3±0.5</td>
<td>8.3±0.3</td>
<td>-</td>
<td>18.8±1.9</td>
<td>55</td>
</tr>
<tr>
<td>Pb$<em>{0.7}$Bi$</em>{0.3}$</td>
<td>3.20</td>
<td>5.39</td>
<td>10.07</td>
<td>3.69</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>-</td>
<td>13.9±0.6</td>
<td>4.8±0.3</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>3.2±0.5</td>
<td>7.6±0.5</td>
<td>-</td>
<td>13.9±0.6</td>
<td>54</td>
</tr>
<tr>
<td>In</td>
<td>11.2</td>
<td>12.72</td>
<td>7.79</td>
<td>2.26</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>12.2±0.6</td>
<td>14.2±1.1</td>
<td>9.4</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td>13.0</td>
<td>8.8</td>
<td>-</td>
<td>57</td>
</tr>
</tbody>
</table>
Table 6-5  A comparison of the model and experimental values of 
$\frac{dH_C(0)}{dP}$ and $\frac{dH_C(T)}{dP}|_{T_C}$ for Pb, In, Sn, Ta, and Nb.

The model values of $\frac{dH_C(T)}{dP}|_{T_C}$ are calculated using the 
thermodynamic relation given in equation (6-7). The values 
of $\frac{dH_C(0)}{dP}$ are calculated from the values in Table 6-3 
and the values of $\kappa$ in Table 6-1.
|        | $-\frac{dT_C}{dP}$ | $-\frac{dH_0}{dP}$ | $\frac{dH(T)}{dP}|_{T_C}$ | Ref. |
|--------|-------------------|-------------------|--------------------------|------|
| Pb     | 3.86              | 7.25              | 9.25                     | This work |
|        |                   | 7.3               | 11.7                     | 60   |
|        |                   | 7.8±0.2           | 9.06±0.15                | 61   |
|        |                   | 9.1±0.5           | 10.9±1.1                 | 62   |
|        |                   | 6.3±0.2           | 11.1±1.0                 | 63   |
| In     | 3.81              | 3.76              | 5.95                     | This work |
|        | 4.0±0.2           | 4.8±0.7           | 6.2±0.5                  | 64   |
|        |                   | 3.4±0.5           | 5.8±0.8                  | 63   |
|        |                   | 4.5±0.17          | 5.8±0.43                 | 62   |
|        |                   | 3.8±0.2           | 6.8±0.3                  | 65   |
| Sn     | 4.63              | 4.28              | 7.00                     | This work |
|        | 4.7±0.2           | 4.2±0.6           | 6.9±0.3                  | 64   |
|        |                   | 5.0±1.0           | 6.48±0.14                | 66   |
|        |                   | 3.2±0.6           | 9.1±0.9                  | 62   |
|        | 4.90±0.15         | 4.40±0.13         | 7.27±0.2                 | 67   |
| Ta     | 0.26              | 0.45              | 0.87                     | This work |
|        | 0.26              | 1.1±0.2           | 0.9±0.05                 | 68   |
|        |                   | 0.6±0.1           | 0.8±0.3                  | 69   |
| Nb     | 0.22              | 0.67              | 0.89                     | This work |
|        |                   | 1.2±0.1           | 1.2±0.3                  | 69   |
Table 6-6  A comparison of the effect on the model results of a nonzero value of $d\ln \mu /d\ln V$. Given are values of $B$, $\Delta_0$, $H_C(0)$, and $\Delta_C/\gamma_{sC}$ for Pb at $\nu = 2.5\%$, and 5.0\%, and the associated volume derivatives.
<table>
<thead>
<tr>
<th>( \frac{d\ln u}{d\ln V} )</th>
<th>4.62</th>
<th>2.31</th>
<th>-2.31</th>
<th>-4.62</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (( \nu=2.5% ))</td>
<td>0.9883</td>
<td>1.0026</td>
<td>1.0332</td>
<td>1.0494</td>
</tr>
<tr>
<td>B (( \nu=5.0% ))</td>
<td>0.9795</td>
<td>1.0075</td>
<td>1.0710</td>
<td>1.1067</td>
</tr>
<tr>
<td>( \frac{d\ln \lambda}{d\ln V} )</td>
<td>2.847</td>
<td>2.271</td>
<td>1.096</td>
<td>0.508</td>
</tr>
<tr>
<td>( \frac{d\ln \Delta}{d\ln V} )</td>
<td>5.148</td>
<td>4.579</td>
<td>3.413</td>
<td>2.825</td>
</tr>
<tr>
<td>( \Delta_0 ) (( \nu=2.5% ))</td>
<td>1.2695</td>
<td>1.2710</td>
<td>1.2742</td>
<td>1.2758</td>
</tr>
<tr>
<td>(meV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta_0 ) (( \nu=5.0% ))</td>
<td>1.5391</td>
<td>0.6941</td>
<td>3.5500</td>
<td>3.2627</td>
</tr>
<tr>
<td>(meV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{d\ln \Delta_0}{d\ln V} )</td>
<td>3.752</td>
<td>3.699</td>
<td>3.593</td>
<td>3.539</td>
</tr>
<tr>
<td>( H_c(0) ) (( \nu=2.5% ))</td>
<td>724.0</td>
<td>723.8</td>
<td>730.95</td>
<td>734.7</td>
</tr>
<tr>
<td>(Oe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_c(0) ) (( \nu=5.0% ))</td>
<td>650.4</td>
<td>656.1</td>
<td>668.8</td>
<td>675.8</td>
</tr>
<tr>
<td>(Oe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{d\ln H_c(0)}{d\ln V} )</td>
<td>3.017</td>
<td>3.761</td>
<td>4.118</td>
<td>4.818</td>
</tr>
<tr>
<td>( \Delta C_v/\gamma_{s C} ) (( \nu=2.5% ))</td>
<td>2.5895</td>
<td>2.5987</td>
<td>2.6151</td>
<td>2.6240</td>
</tr>
<tr>
<td>(( \nu=5.0% ))</td>
<td>2.4459</td>
<td>2.4623</td>
<td>2.4980</td>
<td>2.5172</td>
</tr>
<tr>
<td>( \frac{d\ln [\Delta C_v/\gamma_{s C}]}{d\ln V} )</td>
<td>2.804</td>
<td>2.654</td>
<td>2.440</td>
<td>2.322</td>
</tr>
</tbody>
</table>
Table 6-7  A comparison of the effect of $\tau_G$ on the model results of Pb. Given are values of B, $A_0$, $H_c(0)$, $\Delta C_v/\gamma S_T$, and the maximum value of $D(t)$ at $\nu = 2.5\%$, and $5.0\%$, and the associated volume derivatives for $\tau_G = 0.0$, 2.0, 3.0, and 5.0.
<table>
<thead>
<tr>
<th>$T_0$</th>
<th>0</th>
<th>2</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ (ν=2.5%)</td>
<td>0.95133</td>
<td>1.00759</td>
<td>1.03644</td>
<td>1.09538</td>
</tr>
<tr>
<td>$B$ (ν=5.0%)</td>
<td>0.90571</td>
<td>1.01772</td>
<td>1.07634</td>
<td>1.19872</td>
</tr>
<tr>
<td>$\frac{d\epsilon_{nA}}{d\epsilon nV}$</td>
<td>2.008</td>
<td>1.736</td>
<td>1.589</td>
<td>1.286</td>
</tr>
<tr>
<td>$\frac{d\epsilon_{nA}}{d\epsilon nV}$</td>
<td>2.008</td>
<td>3.709</td>
<td>4.528</td>
<td>6.105</td>
</tr>
<tr>
<td>$\Delta_0$ (ν=2.5%) (meV)</td>
<td>1.2923</td>
<td>1.2953</td>
<td>1.2675</td>
<td>1.2529</td>
</tr>
<tr>
<td>$\Delta_0$ (ν=5.0%) (meV)</td>
<td>1.1975</td>
<td>1.1692</td>
<td>1.1570</td>
<td>1.1361</td>
</tr>
<tr>
<td>$\frac{d\epsilon_{nA}}{d\epsilon nV}$</td>
<td>2.981</td>
<td>3.551</td>
<td>3.823</td>
<td>5.260</td>
</tr>
<tr>
<td>$H_c(0)$ (ν=2.5%) (Oe)</td>
<td>742.2</td>
<td>729.4</td>
<td>723.5</td>
<td>712.4</td>
</tr>
<tr>
<td>$H_c(0)$ (ν=5.0%) (Oe)</td>
<td>687.2</td>
<td>665.6</td>
<td>653.6</td>
<td>640.1</td>
</tr>
<tr>
<td>$\frac{d\epsilon_{nH_c(0)}}{d\epsilon nV}$</td>
<td>4.728</td>
<td>4.084</td>
<td>3.687</td>
<td>3.486</td>
</tr>
<tr>
<td>$\Delta_{C/V}/\gamma_{sC}$ (ν=2.5%)</td>
<td>2.6853</td>
<td>2.6450</td>
<td>2.6107</td>
<td>2.5420</td>
</tr>
<tr>
<td>$\Delta_{C/V}/\gamma_{sC}$ (ν=5.0%)</td>
<td>2.6073</td>
<td>2.4720</td>
<td>2.4197</td>
<td>2.3178</td>
</tr>
<tr>
<td>$\frac{d\epsilon[(\Delta_{C/V}/\gamma_{sC})]}{d\epsilon nV}$</td>
<td>1.199</td>
<td>2.009</td>
<td>2.000</td>
<td>3.249</td>
</tr>
<tr>
<td>Max{D(t)} (ν=2.5%)</td>
<td>0.0224</td>
<td>0.0199</td>
<td>0.0187</td>
<td>0.0165</td>
</tr>
<tr>
<td>Max{D(t)} (ν=5.0%)</td>
<td>0.0194</td>
<td>0.0146</td>
<td>0.0124</td>
<td>0.0086</td>
</tr>
</tbody>
</table>
Fig. 6-1 Critical magnetic field deviation function, D(t), curves for the measured and modelled electron-phonon spectral densities $\alpha^2F(\Omega)$ at nonzero pressures along with the zero pressure results. 

a) Pb D(t) curves for measured $\alpha^2F(\Omega)$ at pressure $P = 0$, $\nu = 0.0\%$, (——) and $P = 12.2$ GPa, $\nu = 2.70\%$, (......) and the model $\alpha^2F(\Omega)$ also at $P = 12.2$ GPa, $\nu = 2.70\%$, (———).

b) Same as a) but for Pb$_{0.7}$Bi$_{0.3}$ at $P = 9.5$ GPa, $\nu = 2.40\%$.

c) Same as a) but for In at $P = 10$ GPa, $\nu = 2.42\%$. 
Fig. 6-2  Model predictions of the volume derivative of the critical magnetic field, \( \frac{1}{H_c(0)} \frac{dH_c(T)}{dT} \), plotted against \((T/T_c)^2\) for Sn, In, Pb, Pb\(_{0.7}\)Bi\(_{0.3}\), Ta, Nb\(_3\)Sn, Nb\(_3\)Al, and Nb.
Fig. 6-3  D(t) curves of Pb at zero pressure (-----) and the model
\[ \alpha^2 F(\omega) \] of Pb at \( \nu = 5.0\% \) with \( \mu^* = 0.1277 \) (-----). \( \mu^* = 0.1438 \) (.....) and \( \mu^* = 0.1619 \) (.....).
Fig. 6-4 Variation of $\frac{1}{H_c(0)} \frac{dH_c(T)}{d\mu}$ versus $(T/T_c)^2$ curves with $\mu^*$.

For Pb for $d\mu^*/d\mu = -2.31$ (---), 0.0 (---), and +2.31 (-----).
Fig. 6-5 Variation of the model Pb D(t) curves at $\nu = 5.0\%$ with $\tau_G$, for $2.0 \ (-
)-$, $2.35 \ (.\ ..\ ..\ ..\ )\ and \ 3.0 \ (-\ .\ -\ -\ )$. Also given is the Pb $P = 0$ result (-----).
Fig. 6-6 Variation of $\frac{dH_c(T)}{H_c(0) \frac{d\ln V}{d\ln T}}$ versus $(T/T_c)^2$ curves with $\tilde{T}_G$ for Pb for $\tilde{T}_G = 2.0 (\ldots), 2.35 (- - -), 3.0 (----)$. 
CHAPTER VII
ON THE THERMODYNAMICS OF SUPERCONDUCTING Pb UNDER HIGH PRESSURE

7-1 Introduction

Brandt et al.\(^{[70]}\) obtained critical magnetic field data in Pb under pressures of up to 130 GPa. From this data, they determined that the strength of the electron-phonon coupling decreased under pressure and that the BCS weak coupling limit is reached at approximately 40 GPa. In this chapter, this behaviour will be investigated using the model introduced in the last chapter for changes in the electron-phonon spectral density, \(\alpha^2 F(\Omega)\), with pressure. This model has shown itself to be reliable for simple metals and alloys under low pressures (meaning less than approximately 5% volume change). Brandt's work allows comparison to much higher pressures.

7-2 Comparison to high pressure data

The Eliashberg and free energy equations have been solved numerically for the pressures 19, 40, 61, and 92 GPa, which, from the formula given by Gschneidner\(^{[46]}\) correspond to volume changes of 4.1%, 7.8%, 10.6%, and 13.2% respectively. It should be noted that 92 GPa is roughly three times larger than the maximum pressure used to derive
this formula. For each pressure, $\tau_G$ was taken to be 2.85 (44), and, in addition, $\tau_G = 4.5$ was used for $P = 92$ GPa. This gives an indication of the effect $\tau_G$ has on the model's results at high pressure. Alternately, as was discussed last chapter, in view of the relation $\alpha = 1 + \nu \tau_G$, this also gives an indication of the model's sensitivity to the correct volume change. This is important to know since the pressure to volume change is strictly valid only for low pressures.

Figure 7-1 shows plots of the resultant deviation function, $D(t)$, against reduced temperature for the various pressures. The plots show a tendency to weaker coupling with increasing pressure, as is expected, but not to the extent indicated by Brandt et al., who find that for $P \geq 40$ GPa that the BCS weak coupling limit has been reached. In this limit, $D(t)$ is negative definite everywhere and has a minimum value of -0.037, in contrast to the curve shown in figure 7-1 for the same rough pressure which is still positive definite. As the pressure is increased to 92 GPa, the model $D(t)$ curves do become negative definite, but the minimum is not as deep as experimentally observed.

As for the two $P = 92$ GPa curves, in terms of their difference from the $P = 0$ $D(t)$, they differ by 10%, and the factor $B/\mu^2$ is 7% smaller when $\tau_G = 4.5$ than it is for $\tau_G = 2.85$. This would indicate that variation in $\tau_G$ with pressure is not likely to be solely responsible for the difference between the model results and those of Brandt et al. Also any error in the volume change $\nu$ will be partly, although not entirely, compensated for by the change in $B$.

In table 7-1, calculated values of the zero temperature critical field $H_c(0)$, the electron-phonon mass renormalization, $\lambda$, the
specific heat jump, $\Delta C_v/\gamma_s T_c$, and the ratios $\gamma_s [T_c/H_c(0)]^2$ and $2\Delta_0/k_B T_c$ are given and, where possible, compared to Brandt's work. The ratios $\gamma_s [T_c/H_c(0)]^2$, $2\Delta_0/k_B T_c$, and $\Delta C_v/\gamma_s T_c$ have BCS weak coupling limits of 0.168, 3.53, and 1.43 respectively. $\gamma_s$ is the electronic specific heat constant in the normal state, and $\Delta C_v$ is the difference in the specific heat between the superconducting and normal states. The calculated values of $\gamma_s [T_c/H_c(0)]^2$, $2\Delta_0/k_B T_c$, and $\Delta C_v/\gamma_s T_c$ with increasing pressure, are approaching, but do not reach, their respective BCS limits, as is expected from the behaviour of the calculated $D(t)$ in figure 7-1.

At zero pressure, $N(0)$, the single spin density of electron states is determined from

$$\gamma_s = \frac{2}{3} \pi^2 k_B^2 N(0)(1+\lambda)$$

For Pb, $\gamma_s = 2.98 \text{ mJ/mol} \cdot K^2$. At finite pressure, $N(0)$ is assumed to vary with volume according to the free electron model, $\frac{\text{d}nN(0)}{\text{d}nV} = \frac{1}{3}$. Using this, the calculated values of $H_c(0)$ agree with the experimental results within the experimental accuracy of 1.5%. The calculated and experimentally derived values of $N(0)$, however, disagree; the values at $P \neq 0$ being 10% different. Brandt et al. give their experimental error for $N(0)$ to be 5%. The values of $\gamma_s [T_c/H_c(0)]^2$ also disagree greatly with the experimental values which reach the weak coupling limit. As the values of $[T_c/H_c(0)]^2$ are essentially the same in the theory as in the experiment, the discrepancy must lie with $N(0)(1+\lambda)$. The values of $\lambda$ which Brandt et al. use are only approximate, being determined from
McMillan's equation \(^{(42)}\), but this can only account for part of the difference, as can be seen from table 7-1. Since \(H_c(0)\) is proportional to the square root of \(N(0)\), and since the calculated results match the experiment quite well, it would seem unlikely that the values of \(N(0)\) used in these calculations are not also reasonably accurate. Since the experimental values of \(N(0)\) are derived from \(D(t)\) data, it is quite possible that the error in the experimental \(D(t)\) curves may be higher than that which Brandt et al. have estimated in their paper, and that, at the pressures involved, Pb has not yet reached the weak coupling limit.

7-3 Conclusions

In conclusion, the simple model proposed by Trofimenkoff and Carbotte for the variation of the electron-phonon spectral density with volume gives excellent agreement with experiment for the zero temperature critical magnetic field \(H_c(0)\) and, most likely, other thermodynamic relations as well, provided one assumes that the normal state electronic density of states varies with volume according to free electron theory, and if one treats the electron-ion pseudopotential parameter \(B\) as adjustable such that the model yields the correct critical temperature. The general trend towards a BCS behaviour, observed for the critical magnetic field deviation function \(D(t)\), is confirmed in our calculation but, contrary to experiment, the BCS limit has not yet been reached at pressures of \(P = 92\) GPa. Part of this discrepancy could be due to the difficulty in obtaining accurate data.
on D(t). Certainly the differences found cannot be easily assigned to
the use of either a wrong average Gruneisen $\gamma_G$ or an incorrect volume
change in the theoretical result since it is found that large
variations in $\nu\gamma_G$ give much smaller variations in the thermodynamics as
long as the fitting parameter $B$ is readjusted to match $T_c$. The free
parameter $B$ should absorb much of the uncertainty in the electron-
phonon spectral density introduced by the simplicity of the model
employed for the shift with volume change of that interaction.
Table 7-1  B is the parameter in equation (6-1) fitted to give $T_c$ to within 0.05%. $\lambda$ is the electron-phonon mass enhancement parameter. $N(0)$ is the single spin electronic density of states in units of $10^{34}$ ergs$^{-1}$ cm$^{-3}$. The calculated values of $N(0)$ come from $\gamma_S = 2.98$ mJ mol$^{-1}$ K$^{-2}$ at $P=0$ and from $d\epsilon N(0)/d\epsilon N = \frac{1}{3}$. $\gamma_s$ is the electronic specific heat constant. $H_c(0)$ is the critical magnetic field in Oe. $\Delta_c/\gamma_s T_c$ is the jump in the specific heat which has a BCS limit of 1.43. $\gamma_S [T_c/H_c(0)]^2$ and $2\Delta_0/k_BT_c$ are independent of $N(0)$ (as is the jump) and have BCS limiting values of 0.168 and 3.53 respectively.
<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>0</th>
<th>19</th>
<th>40</th>
<th>61</th>
<th>92</th>
<th>92</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (K)</td>
<td>7.19</td>
<td>6.41</td>
<td>5.70</td>
<td>5.12</td>
<td>4.43</td>
<td>4.43</td>
</tr>
<tr>
<td>$\gamma_G$</td>
<td>2.85</td>
<td>2.85</td>
<td>2.85</td>
<td>2.85</td>
<td>2.85</td>
<td>4.50</td>
</tr>
<tr>
<td>$B$</td>
<td>1</td>
<td>1.03887</td>
<td>1.07699</td>
<td>1.10179</td>
<td>1.10439</td>
<td>1.37895</td>
</tr>
<tr>
<td>$\lambda$ (Brandt)</td>
<td>1.52</td>
<td>1.28</td>
<td>1.16</td>
<td>1.06</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>$\lambda$ (calc.)</td>
<td>1.55</td>
<td>1.29</td>
<td>1.12</td>
<td>1.01</td>
<td>0.90</td>
<td>0.84</td>
</tr>
<tr>
<td>N(0) (exp.)</td>
<td>0.567</td>
<td>0.576</td>
<td>0.575</td>
<td>0.571</td>
<td>0.567</td>
<td>0.567</td>
</tr>
<tr>
<td>N(0) (calc.)</td>
<td>0.513</td>
<td>0.520</td>
<td>0.527</td>
<td>0.533</td>
<td>0.538</td>
<td>0.538</td>
</tr>
<tr>
<td>$H^C_c(0)$ (exp.)</td>
<td>800</td>
<td>659</td>
<td>559</td>
<td>484</td>
<td>399</td>
<td>399</td>
</tr>
<tr>
<td>$H^C_c(0)$ (calc.)</td>
<td>800</td>
<td>664</td>
<td>559</td>
<td>484</td>
<td>404</td>
<td>394</td>
</tr>
<tr>
<td>$\gamma_s \left[ \frac{T_C}{H^C_c(0)} \right]^2$ (exp.)</td>
<td>0.145</td>
<td>0.157</td>
<td>0.162</td>
<td>0.168</td>
<td>0.172</td>
<td>0.172</td>
</tr>
<tr>
<td>$\gamma_s \left[ \frac{T_C}{H^C_c(0)} \right]^2$ (calc.)</td>
<td>0.132</td>
<td>0.139</td>
<td>0.145</td>
<td>0.150</td>
<td>0.154</td>
<td>0.157</td>
</tr>
<tr>
<td>$\Delta C_v / \gamma_s T_c$</td>
<td>2.77</td>
<td>2.48</td>
<td>2.22</td>
<td>2.04</td>
<td>1.88</td>
<td>1.77</td>
</tr>
<tr>
<td>$2\Delta_0 / k_B T_c$</td>
<td>4.50</td>
<td>4.24</td>
<td>4.05</td>
<td>3.94</td>
<td>3.83</td>
<td>3.77</td>
</tr>
</tbody>
</table>
Fig. 7-1 The deviation function $D(t)$, where $t = T/T_c$, for the modelled $\alpha \tilde{F}(\Omega)$. The curves are for the pressures (relative volume decreases) of 0 GPa (0.0%) ———, 19 GPa (4.1%) —.—.—, 40 GPa (7.8%) ————, 61 GPa (10.6%) . . . . . and 92 GPa —.—.—.—. All the curves were calculated with $\gamma_G = 2.85$ except —.—.—.— which used $\gamma_G = 4.50$. 
CHAPTER VIII
A SIMPLE MODEL OF ALLOYS

8-1 Alloys

The effects of alloying on a electron-phonon spectral density is much more complicated than the simple X and Y axes scaling for pressure change used in the last two chapters. First, the introduction of the alloying material is accompanied by new phonon modes proportional in strength to the concentration, thus a simple scaling of one spectrum would not reproduce the physics even roughly. Furthermore, the effects of alloying on the the Coulomb pseudopotential, \( \mu^* \), is not clear. The formula for \( \mu^* \) is

\[
\mu^*(\omega_c) = \frac{\mu}{1 + \mu \text{en}(\epsilon_F/\omega_c)} \tag{8-1}
\]

where \( \mu \) is the average repulsion between electrons, and \( \epsilon_F \) is the energy of an electron at the Fermi surface. The behaviour of \( \mu \) and \( \epsilon_F \) with alloying is, at best, known only roughly.

Obviously, the first step is finding a simple model of alloying changes in \( \alpha^2 F(\Omega) \) is to consider simple binary alloys such as Nb-Ta alloys. Both metals occur in the same column of the periodic table, have the same valence, and have the same bcc crystal structure and
lattice constant. In figure 8-1, the tunneling derived $\alpha^2 F(\Omega)$ for both pure materials has been plotted. It can reasonably be expected that an alloy would have an $\alpha^2 F(\Omega)$ intermediate to these two displaying the characteristics of each in proportion to the alloy concentration.

This can be put on a more rigorous footing by considering the formula for the $\alpha^2 F(\Omega)$ of an alloy

$$
\alpha^2_F(\Omega) = \frac{N(0)}{8\pi^2 R_F^2} \sum_{\ell, \ell'} \frac{d^3 q}{q} v_{\ell}(q)v_{\ell'}(q) e^{-\frac{1}{2}q \cdot (R_\ell - R_{\ell'})} \times \sum_{\alpha, \beta} D_{\alpha \beta}(\ell, \ell'; \Omega) q_{\beta},
$$

(8-2)

where $\alpha$ and $\beta$ are indices of the phonon eigenvectors, $v_{\ell}(q)$ is the Fourier representation of the $\ell$th ion potential with momentum transfer $q$, $R_\ell$ is the position of the $\ell$th atom, and $D_{\alpha \beta}$ is the phonon Green function. By considering a configurational average of all the possible arrangements of host (A) and alloy atoms (B), as is done in Appendix B, it can be shown that

$$
\alpha^2_F(\Omega) = (1-c)\alpha^2_A F(\Omega) + c\alpha^2_B F(\Omega) + c^2(1-c)^2\alpha_{AB}^2 F(\Omega),
$$

(8-3)

where $c$ is the small concentration of introduced atoms, and the single letter subscripts refer to the pure spectra, and the AB to some unknown, possibly concentration dependent, spectra which should be small compared to $\alpha^2_A F(\Omega)$ or $\alpha^2_B F(\Omega)$. Thus in equation 8-3, the last contribution is small and may be neglected at low concentrations.
Clearly it would be preferable to deal only with the known spectra and correct, in a some manner, for not knowing $\alpha_{AB}^2 F(\Omega)$. The model chosen here is

$$\alpha_{AB}^2 F(\Omega) = C[(1-c)\alpha_A^2 F(\Omega) + c\alpha_B^2 F(\Omega)]$$  \hspace{1cm} (8-4)$$

with C an adjustable parameter fitted so that the model will give the correct measured $T_c$ for the particular alloy concentration. Clearly C is approximately unity when $c \ll 1$ or $c \approx 1$. The size of C for intermediate values of c is an indication of how well the model works. If C is much different from unity, then $\alpha_{AB}^2 F(\Omega)$ is making a contribution too large to ignore, and thus the model is too simple.

Of course, there is the added problem of determining $\mu^*$ for the alloy. For the model to be of any use, there can only be the one adjustable parameter C. Thus only a concentration dependent model can be used, the most obvious being

$$\mu^* = (1-c)\mu_A^* + c\mu_B^*$$  \hspace{1cm} (8-5)$$

This is not a totally unreasonable choice, since $\mu^*$ of the pure materials and the alloys should be approximately the same, and the fitting parameter should compensate for most of the error.

In the next section, the model will be solved for 10 concentrations of Nb-Ta alloys and compared to the available experimental data. In the third and last section, the model will be evaluated and conclusions drawn.
8-2 Comparison to experimental results

In this section, the model given in equation 8-4 is used to calculate the ratio \( \frac{2\Delta_0}{k_B T_C} \) and the thermodynamic ratios for Nb-Ta alloys containing 2, 4, 6, 10, 15, 30, 40, 42, 59.5, 86, and 96.3 atomic percent Ta. As well the results for the pure materials are given. In each case, \( C \) was adjusted to give the experimental \( T_C \) within 0.05% with \( \mu^* \) given by equation 8-5. The Coulomb pseudopotential is dependent on the cutoff \( \omega_C \) used. As can be seen from figure 8-1, Ta and Nb have different Debye frequencies, \( \omega_D = 20.9 \text{ meV} \) and \( \omega_D = 28.29 \text{ meV} \) respectively. The model spectra will, of course, have the Nb \( \omega_D \). It would therefore be sensible, though not totally necessary since the fitting parameter \( C \) would compensate, to adjust the \( \mu^* \) for Ta used in equation 8-5 to the cutoff for Nb. Equation 8-1 may be used to derive a formula to calculate the new value

\[
\mu^*(\omega_A) = \frac{\mu^*(\omega_B)}{1 + \mu^*(\omega_B) \ln(\omega_A/\omega_B)} \tag{8-6}
\]

In figure 8-2, the results for \( \frac{[H_C(0)/T_C]^2}{\gamma_s} \), \( \frac{\Delta C}{\gamma_s T_C} \), and \( \frac{2\Delta_0}{k_B T_C} \) are shown. The solid lines are a best fit to the model results. The model points are not shown since the scatter is almost insignificant on the scale used. As might be expected, the model is giving smooth predictable behaviour. The filled circles and triangles are the experimental data of Rollins and Clune(71) and Ohtsuka and
Kimura (72) respectively. The data points have been read from the graphs provided by those authors. As have the error bars. Despite the possible errors this has introduced, it is still quite clear that the two experiments do not totally agree. As well, it appears that the model gives results much closer to data of Rollins and Clune. The data points given for \( \frac{2\Delta_0}{k_B T_C} \) are only approximate as they have been calculated using the Toxen formula (73)

\[
\frac{2\Delta_0}{k_B T_C} = \frac{2T_C}{H_c(0)} \left. \frac{dH_c(T)}{dT} \right|_{T_C}
\]  

(8-7)

which empirically relates the gap edge to the thermodynamic data. Marsiglio et al. (74) have investigated this formula for numerous materials and determined that it works best for weak coupling materials, with significant error being introduced as the strength of the coupling is increased. Ta is a weak coupler but Nb, and at least a few of the alloys examined, are intermediate. Thus there is little useful to say about these results.

The disagreement between the two experiments can also be seen in figure 8-3 where the minimum of the critical magnetic field deviation function (\( D(t) \)) curves have been plotted against concentration. Again the model gives smooth results. And again the experimental points have been read from graphs. The disagreement is even worse when the temperatures at which the minima occurs considered. In the Rollins and Clune data, and in the model, the minima occur at the reduced temperature \( t = 0.7 \). In the Ohtsuka and Kimura data, the
minima occur at \( t = 0.77 \). The fact that neither experiment agrees with the results for the pure materials is puzzling, considering the reasonably good agreement seen in figure 8-2. However, \( D(t) \) is a very sensitive quantity and measurements of it are error prone.

In figure 8-4, the zero temperature critical magnetic field, \( H_c(0) \), has been plotted against concentration. The agreement is quite good between the smooth model curve and the experimental results. The \( \times \)'s are data of Ogasawara et al. (75). The critical field is dependent on the electron density of states. The values of \( N(0) \) used where determined from the measured values of \( \gamma_s \) and the formula

\[
\gamma_s = \frac{2\pi^2 k_B^2}{3} N(0)(1+\lambda)
\]

and where the model values of \( \lambda \) have been used. In figure 8-5, the values of \( \lambda \), and the resultant values of \( N(0) \), are shown. The smooth behaviour of \( \lambda \) is as expected. The bump in \( N(0) \) for alloys with 2 to 10 at.% Ta corresponds to the the behaviour of \( \gamma_s \) measured by Ohtsuka and Kimura. Since the bump is only about 5% higher than the Nb value, and as only the square root of \( N(0) \) enters the formula for \( H_c(0) \), the effect on \( H_c(0) \) is only about 2%. This is the same size as the error of the measurements of \( H_c(0) \) and thus cannot be used as a check on the model.

Also in figure 8-5 is a graph of the fitting parameter as a function of alloy concentration. The curve is approximately parabolic. That \( C \) is fairly smooth and differs from unity by at most 5% is an indication that the model assumptions are reasonable.
8-3 Discussion and conclusions

In Chapter VI, on pressure the effects of $\mu^*$ on the results were studied. It was found, as seen in table VI-6, that though $\mu^*$ could vary by up to 25%, the adjustable parameter compensated for this such that the variation in the gap edge and the thermodynamic ratios was only a few percent. The effects on $D(t)$ were somewhat larger, but not enough to greatly affect figure 8-3. Thus how $\mu^*$ explicitly changes with alloying is largely irrelevant, unless the variation is dramatic, say 50% or more. Anything less would be masked by experimental uncertainties.

Chapters IV and V demonstrate that to within a few percent all the thermodynamics and the gap edge of a superconductor are determined by the set of parameters $T_c$, $\omega_{en}$, $\mu^*$, and $A$ the area of the electron-phonon spectral density. In the model used here, $\omega_{en}$, $\mu^*$, and $A$ are determined from a simple construction of the pure material values. Since the model results generally agree with experiment within the measured uncertainties, this implies that the values of $\omega_{en}$, $\mu^*$, and $A$ used in the model are close to the actual values. However, since $\omega_{en}$ for Ta and Nb is, respectively, 128.4K and 148.9K—a difference of just 14%, and since $A$ should vary smoothly and gently for alloys of such similar metals, getting these results is not a tough test of the model. So far all that has been shown is that a simple model can reproduce the results of a simple system to within experimental uncertainty. A more thorough examination of the model should include a greater variety of
where the pure materials differ considerably in one or more of the following: valence, crystal structure, interatomic distances, and 

Also the discrepancies between the two main sets of experimental data highlights the difficulties in comparing model results to experiment. To resolve which parameters in the model are most important to have right, or which assumptions are incorrect, the experimental data must be accurate and consistent.

In conclusion, a simple model for the electron-phonon spectral density of the simple Nb-Ta alloys, which consists of a concentration percentage sum of the pure material spectra multiplied by a constant fitted to the correct critical temperature, has been studied. The Coulomb pseudopotential \( \mu \) is also treated as a concentration sum of the pure values, but with no other changes. The agreement with experiment is quite good for \( \gamma_s [T_c / H_c(0)]^2 \) and \( \Delta C_v / \gamma_s T_c \), but for D(t) serious discrepancies in the available data make it impossible to draw any firm conclusions. A wider range of calculations and better, consistent, experiments is required to fully investigate the proposed model.
Fig. 8-1  Tunnelling derived electron-phonon spectral density, 
$\alpha^2 F(\Omega)$, for Nb (---) and Ta (.....)
Fig. 8-2

Top) Plot of the alloy model calculated values of
\[ \frac{H(0)}{\frac{1}{T_c}} \left( \frac{c}{T_c} \right)^2 \]
plotted against concentration (smooth curve) and
the experimental data of Rollins and Clune (filled circles)
and Ohtsuka and Kimura (filled triangle).

Middle) Same as top, but for \( \Delta C_v/\gamma_s T_c \).

Bottom) Same as top, but for \( 2\Delta_0/k_B T_c \). Note the data
points were estimated from relation (8-7).
Fig. 8-3  Same as in Fig. 8-2, but for the minimum value of $D(t)$.

the critical magnetic field deviation function.
$\min \{ D(t) \}$

$Ta$ vs $c. (%)$ vs $Nb$
Fig. 8-4  Same as in Fig. 8-2, but for the critical magnetic field, $H_c(0)$. Also included is the experimental data of Ogasawara et al. (x's).
Fig. 8-5

Top) Plot of the scaling factor C in the alloy model given by equation (8-4) plotted versus the alloy concentration.

Middle) Plot of the alloy model value of electron-phonon mass enhancement factor \( \lambda \) against concentration.

Bottom) Plot of the electron density of states for the model.
CHAPTER IX

ON THE RELATIONSHIP BETWEEN THE GAP EDGE
AND THE SPECIFIC HEAT OF A SUPERCONDUCTOR

9-1 Empirical relations

At present, there exist procedures for using thermodynamic data to determine departures of the zero temperature gap $\Delta_0$ to critical temperature $T_C$ ratio $2\Delta_0/k_B T_C$ from the universal BCS value of 3.53. This ratio is often denoted $\alpha$, and this notation will be used in this chapter. In these procedures, it is assumed that it is only through this parameter $\alpha$ that the details of the electron-phonon interaction for a particular material gets reflected in the thermodynamic results. In BCS theory, there is a direct relationship between $\alpha$ and the thermodynamics, and thus simple extensions of BCS theory are often the theoretical bases of such procedures. On the other hand, in Chapters IV and V, it has been shown that certain model systems, with differing electron-phonon spectral densities $\alpha^2 F(\omega)$ but with $2\Delta_0/k_B T_C$ fixed to within 3%, can show large differences in thermodynamic properties. This brings into doubt any scheme based on a single parameter like $2\Delta_0/k_B T_C$. Nevertheless, the value of $2\Delta_0/k_B T_C$ for a given superconductor is a quantity of considerable interest and, as the gap edge at zero temperature is often not known from tunneling or optical absorption experiments, it is desirable to understand if it can be
determined, at least approximately, from the consideration of specific heat data. It is the purpose of this chapter to address this specific question. To begin, it is necessary to review the empirical prescription based on the work of Padamsee et al. (76), as well as other procedures used to extract $\Delta_0$ from experimental data.

The electronic specific heat in the superconducting state ($C_{es}(T)$) at temperature (T) is conveniently normalized to its normal state value at the critical temperature $T_C$, namely, $\gamma_s (T_C) T_C$. Here $\gamma_s (T)$ is the Sommerfeld constant which is temperature dependent when a strong electron-phonon interaction is present (77, 79). To get an estimate of $2\Delta_0 / k_B T_C$ from the normalized $C_{es}(T)$, it has been found convenient to plot the experimental data in the form

$$\left[ C_{es}(T) / \gamma_s(T_C) T_C \right] \times \left( \frac{T}{T_C} \right)^3$$

against temperature $T$, and to compare this to the prediction of Padamsee et al. (76) to extract a value for $2\Delta_0 / k_B T_C$ through a best fit.

Another procedure that has been used to obtain $\alpha$ from specific heat data is to employ the slope of the specific heat curve given on a logarithm plot as a function of $T_C / T$. The motivation for this procedure, reviewed by Stewart and Giorgi (83), is that, in BCS theory, $C_{es}(T)$ is found to be proportional to $\exp( - \frac{\Delta_0}{k_B T_C} \frac{T_C}{T} )$ for $2.5 < T_C / T < 6$ with $\Delta_0 / k_B T_C = 1.44$. This suggests, experimentally, that one could take the measured slope in this temperature range and normalized it by a factor of $2 \times 1.76 / 1.44$ to get $\alpha$. This procedure would give the correct $\alpha$ for a strict BCS superconductor and, perhaps, a reasonable estimate in strong coupling cases. Arguments against this procedure
are advanced by Stewart and Giorgi (83), the foremost of which is the
fact that $\ln C_{es}(T)$ is not linear in $T_c/T$ in that temperature range.
Instead, these authors investigated the method of Grunzweig-Gennosar
and Revzen (86, 87) for materials with larger values of the gap edge than
previously used. They consider the experimental data (in the case of
10 well studied superconductors) for the slope of $\frac{\ln[C_{es}(T)\gamma(T_c/T_c)]}{T}$
versus ($T_c/T$) evaluated at $T_c$ and observe that it agrees well with the
tunneling results for $\Delta_0/k_B T_c$ with three exceptions. On this basis,
they suggest using the slope of $T_c$ in cases when $\Delta_0$ is not known from
other sources. The application of this method to the Mo-Tc alloys
series (83-85), however, does seem to lead to values of $\alpha$ that can
sometimes appear to be too large.

In this chapter, the validity of these empirical procedures is
examined. The Eliashberg equations for an isotropic superconductor are
used with measured electron-phonon spectrum densities to calculate the
superconducting electronic specific heat. Such results are believed to
be accurate and do not suffer from any uncertainty associated with the
subtraction of the lattice contribution from the total specific heat. A
procedure which is necessary when experimental data is used. These
theoretical results are then employed to evaluate the validity of the
proposed procedures described above. Besides using known $\alpha^2 F(\Omega)$'s, it
will be convenient to consider some scaled, as well as model, $\alpha^2 F(\Omega)$'s.
These spectra are the same as the ones used in previous chapters on
$2\Delta_0/k_B T_c$ and the thermodynamic ratios. As in the previous work, only
the case of Pb is studied, but other possible "realistic" shapes of
$\alpha^2 F(\Omega)$ which have, however, the same value of the Allen-Dynes (29)
characteristic phonon energy, \( \omega_{en} \), and the same \( T_c \) are examined. To be more specific, measured spectra for materials other than Pb are rescaled by a constant amount on the vertical and horizontal axes. Since, as it was shown, such rescaled spectra lead to less than 3\% variation in \( 2\Delta/\kappa_B T_c \), they should all give the same specific heat to within that accuracy if any of the empirical prescriptions reviewed above are to hold. More extreme model spectra, involving two delta-functions, will also be considered in an attempt to understand better the limitations of the empirical procedures for extreme shapes of the electron-phonon spectral density. In section 9-2, the methods involving the logarithm of \( C_{es}(T) \) are investigated. In section 9-3, the method of Padamsee et al is examined. Finally in section 9-4, conclusions are drawn.

9-2 Methods for \( \ln C_{es}(T) \)

As explained previously, electronic specific heat difference between superconducting and normal state, \( \Delta C(T) = C_{es}(T)-C_{en}(T) \), is determined from the Eliashberg and free energy formulae for a specific \( \alpha^2F(\Omega) \). To get the actual superconducting state specific heat separately, it is necessary to add on the normal state value. One could approximate the quantity by \( \gamma_s(0)T \) with

\[
\gamma_s(0) = \frac{2}{3} \pi^2 k_B^2 N(0)(1+\lambda) \tag{9-1}
\]

where \( k_B \) is the Boltzmann constant, \( N(0) \) the single spin density of
states at the Fermi energy, and \( \lambda \) the electron-phonon mass renormalization. To get more accurate results, it is better to use the exact expression for \( C_{en}(T) \) given by Griavali\textsuperscript{77,78} which fully includes the electron-phonon renormalization of the specific heat without approximation. In that case

\[
C_{en}(T) = \gamma_s(T)T.
\] (9-2)

with \( \gamma_s(T) \) an effective, temperature dependent, Sommerfeld constant given by \( \gamma_s(T) = \gamma_s(0)(1+\gamma_1(T)/\gamma_s(0)) \) with\textsuperscript{77-79,88}

\[
\gamma_1(T) = \frac{3}{(nk_B T)^2} \int dE \int dE' \frac{\delta f(E)}{\delta E} \frac{\delta f(E')}{\delta E'} \int d\omega \omega^2 f(\omega) \frac{(E-E')^2}{E-E'+\omega}. \quad (9-3)
\]

with the integrals ranging from minus infinity to infinity.

Results for \( C_{es}(T) \), on a logarithm plot, for a select number of materials are shown in figure 9-1 for \( \frac{T_C}{T} \) in the range 1 to 4. It is clear from this figure that the electronic specific heat in the superconducting state is not of the form

\[
\exp\left(-\frac{\Delta_0}{k_B T_C} \frac{T_C}{T}\right). \quad (9-4)
\]

over the entire range of temperature \( \frac{T_C}{T} \) shown. In table 9-1, twice the slope of \( \ln[C_{es}(T)/\gamma_s(T)T_C] \) evaluated at \( T = T_C \) is entered. This is the quantity Stewart and Giorgi\textsuperscript{83-85} take to be a measure of \( \alpha \).
Also entered for comparison is the calculated $2\Delta_0/k_B T_C$ obtained from the Eliashberg programs. It is clear that, in all cases, the slope at $T_C$ very much overestimates the gap to critical temperature ratio. The only exception is Ta, where the agreement between the two values is acceptable. As a more typical example, for Nb₃Sn the calculated slope is 56% larger than $2\Delta_0/k_B T_C$.

Instead of taking the slope of $\ln[C_{es}(T)/\gamma(T_c)T_c]$ versus $T_c/T$ at $T_c$, the average slope in the region $2.6 < \frac{T_c}{T} < 6$ can be measured, as suggested by consideration of the results for a BCS superconductor. While the entire temperature range is not shown in figure 9-1, it can be seen that, even in the more restricted range (2.6 to 4.0), the curves are not quite linear. Nevertheless, the slope between 2.5 and 3.33, has been computed and entered in the fourth column of table 9-1. It is clear that this number is giving acceptable values of $2\Delta(0)/k_B T_c$.

For Pb with a $2\Delta_0/k_B T_C$ value of 4.5, the slope is within 1.8%. In the worst case, Nb, the difference is only 6.5%. It is also clear that the choice of the temperature range, in which the derivative is taken, is fortuitously good. Different choices of temperature range would give different results as it is clear that the slope is varying in this region, although a different choice of scaling might be enough to compensate.

If it were possible to extract a unique value of $\alpha$ from the slope of $\ln[C_{es}/\gamma(T_c)T_c]$ at any point, or, for that matter, from some other property of specific heat curves, it would have to depend only on the value of $\alpha$ and not on other details of the spectral density $\rho^2 F(\Omega)$. 
To shed more light onto the exact relationship between the specific heat and \( \alpha \), model spectra are studied. Following Chapters IV and V, the case of Pb, as an example, is considered. As a model for the \( \alpha^2 F(\Omega) \) of Pb, the known \( \alpha^2 F(\Omega) \) for some other material A is taken and rescaled according to

\[
\alpha^2_n F(\omega) = B \alpha^2_A F(\gamma \omega) \quad (9-5)
\]

where the subscript M stands for model, and B and \( \gamma \) are constant scaling factors which can be chosen uniquely to get the Pb \( T_c \), as well as, the Pb characteristic phonon energy \( \omega_{\text{fn}} \) defined by

\[
\omega_{\text{fn}} = \exp\left[2\int_{\omega} \frac{\alpha^2 F(\omega)}{\omega} \xi n(\omega) d\omega\right] \quad (9-6)
\]

The quantity \( \omega_{\text{fn}} \) is used because it has been found that the ratio \( T_c / \omega_{\text{fn}} \) is a good approximate single measure of the strong coupling effects for a large number of superconductors. With this choice of B and \( \gamma \) in the model spectral density for Pb, given by (9-5), it was found that \( 2\Delta_0 / k_B T_c \) varied by less than 1.5\% for A taken to be Hg, Pb\(_{0.5}\)Bi\(_{0.5}\), In, Tl and Sn and, as well, for a delta-function spectrum. This is confirmed by reference to the second column of table 9-1, where the scaled spectra (A) used are denoted by the name of the origin material, and where the asterisk indicates that the spectrum has been scaled. It then becomes a model for the Pb spectral density with a different shape but with the same \( T_c \), \( \omega_{\text{fn}} \) and, to a good approximation,
the same $\alpha$ value as well. It is clear from an examination of columns 3 and 4 of table 9-1 that the specific heat curves themselves are changed, however. For example, the slope at $T_c$ ranges from $\sim 7.2$ to $\sim 5.8$. Some variation ($\sim 9\%$) is also found in the slope calculated over the temperature interval 2.5 to 3.3, a quantity which is clearly less sensitive to details of $\alpha^2 F(\omega)$ than the slope at $T_c$ is and, moreover, is giving very good estimates of $\alpha$. The complete temperature dependence for $C_{es}(T)/\gamma_3(T_c)T_c$ is given in figure 9-2, where, for later reference, the quantity

$$\frac{C_{es}(T)}{\gamma(T_c)T_c} \frac{\frac{T_c}{T}}{\left(\frac{T}{T_c}\right)^3} \text{ vs } \frac{T_c}{T}$$

is shown. It is clear that $2\Delta_0/k_B T_c$ does not define uniquely the temperature dependence of the electronic specific heat for all $T < T_c$ in the superconducting state even when $T_c$ and $\omega_{\text{en}}$ are fixed. Some of the details associated with the shape of $\alpha^2 F(\omega)$ are strongly reflected in $C_{es}(T)$. On the other hand, there does seem to be a temperature range in which there is a strong correlation. Since the slope varies above and below the range 2.5 to 3.33 used here, it would be necessary, however, to determine the proper scaling factor for each range used.

Much greater variations for the specific heat than those just described above for scaled spectra can be obtained if less constrained models are used for $\alpha^2 F(\omega)$. In particular, a model, characterized by one delta-function at $\omega_L < \omega_{\text{en}}$ and another at $\omega_G > \omega_{\text{en}}$ with weights uniquely defined if $T_c$ and $\omega_{\text{en}}$ are fixed to the Pb value, demonstrated
this in Chapter V. Results are to be found in table 9-1 and figure 9-3. The first column of table 9-1 identifies the various cases considered according to the notation \( \omega_{\ell n}/\omega_L, \omega_G/\omega_{\ell n} \). Note that the corresponding values for \( 2\Delta_0/k_BT_c \) are nearly all the same while the specific heat slope at \( T_c \) can vary a great deal ranging from 4.0 to 7.1. The average slope for the region (2.5 to 3.33), despite the shape differences, varies much less — from 4.416 to 4.734. Larger differences for the slope at \( T_c \) could be generalized if more extreme models are considered. It is not clear that this would be true for the average low temperature slope. The complete temperature dependence of the specific heat itself is shown in figure 9-3, where it is found to change drastically as the delta-functions are varied through different choices for \( \omega_L \) and \( \omega_G \). Again one is forced to conclude that \( C_{es}(T) \) is not at all uniquely determined by the value of \( 2\Delta_0/k_BT_c \) even when \( T_c \) and \( \omega_{\ell n} \) are additionally constrained, but at low temperatures there is a definite correlation with \( 2\Delta_0/k_BT_c \). As well, the low temperature slope is determining \( 2\Delta_0/k_BT_c \) better than the Toxen's relation as demonstrated in reference (74).

9-3 The method of Padamsee et al.

For a more specific critique of the work of Padamsee et al. (76), the procedure used in the literature to extract \( 2\Delta_0/k_BT_c \) from the temperature variation of \( C_{es}(T) \) is concentrated on. As already described, what is done is that the formulae proposed by Padamsee et al. (76) for the free energy are used to get a family of
which are then labeled by the single strong coupling parameter $\alpha$. These curves are a consequence of the retention, by Padamsee et al., of a BCS quasiparticle excitation spectrum in their approximations but with the BCS value of $2\Delta_0/k_BT_C$ replaced with arbitrary values of $\alpha$. A best fit to the experimental data to one of these curves then determines $2\Delta_0/k_BT_C$ for this material. In figure 9-4, these curves (solid lines) from reference (76), labeled by $\alpha = 3.53, 4.0, 4.5$ and 5.0, are shown. This range of $\alpha$ covers reasonably well the range expected in real materials. On the same figure are shown the results for three scaled spectra, namely, Hg (o's), Pb$_{0.5}$Bi$_{0.5}$ (x's) and In (A's). These systems have basically the same value of $\alpha = 4.5$. While the points for In fall fairly close to the solid $\alpha = 4.5$ curve, the other two do not. While at low temperatures the theoretical results for Pb$_{0.5}$Bi$_{0.5}$ fall close to the $\alpha = 4.0$ curve, at higher temperatures they deviate very substantially from this curve. In fact, in this case, the electronic specific heat clearly varies with temperature in quite a different way from the prediction of reference (76) and could not be fit by any such curve whatever value for $\alpha$ is chosen. Finally, it can be seen from figures XI-2 and -3 that cases could have been chosen in which the temperature variation of $\frac{C_{es}(T)}{\gamma(T/T_C)T} \times \frac{T^3}{T}$ would
differ much more radically from the $\alpha = 4.5$ curve of figure 9-4.

9-4 Conclusions

Three approximate empirical procedures used in the literature to get an estimate of $2\Delta_0/k_B T_c$ from consideration of the temperature variation of the electronic specific heat in the superconducting state have been investigated. It is found that accurate calculations of the specific heat for real materials as well as for some model cases based on Eliashberg theory, do not support two of the proposed procedures, those of Padamsee et al. [76] and of Grunzweig-Genossar and Revzen [86, 87]. The specific heat can vary significantly in temperature dependence at high temperatures as the electron-phonon spectral density $\alpha^2 F(\Omega)$ is changed while keeping fixed the critical temperature $T_c$, the characteristic phonon frequency $\omega_n$, and, as well, the gap to $T_c$ ratio, $2\Delta(0)/k_B T_c$. On the other hand, at low temperatures, there does seem to be a strong correlation to $2\Delta_0/k_B T_c$. In particular, in the range $2.5 < T_c/T < 3.33$, the slope of $\ln C_{es}(T)$ versus $T_c/T$ would appear to equal $\frac{1.44}{1.76} \times 2\Delta_0/k_B T_c$ to within 10% for a wide range of material and model spectra. For different temperature ranges, the strength of the correlation has not been investigated, and the proper scaling factor is unclear. An analytical investigation of the specific heat at low temperature would be necessary to fully investigate this correlation and to determine the scaling factors appropriate to each range.
Table 9-1: Values of $2\Delta_0/k_B T_c$ for a variety of real materials, scaled spectra, and delta-function spectra. The two-delta-function spectra are listed by their values of $(\omega_n/\omega_L, \omega_G/\omega_L)$. Also given are values of the slope of $\ell n C_{es}(T)$ versus $T_c/T$ near $T_c$ denoted $\alpha_1$ and of the average slope of $\ell n C_{es}(T)$ versus $T_c/T$ in the range 2.5 < $T_c/T$ < 3.33 denoted $\alpha_2$. As well, the percentage differences $(2\Delta_0/k_B T_c - \alpha)/2\Delta_0/k_B T_c$ are given.
<table>
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<tr>
<th></th>
<th>(2\Delta_0/K_B T_C)</th>
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<th>% diff.</th>
<th>(\alpha_2)</th>
<th>% diff.</th>
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<tr>
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<tr>
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<td>8.0</td>
<td>4.734</td>
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</tr>
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<td>4.02</td>
<td>10.9</td>
<td>4.592</td>
<td>1.8</td>
</tr>
<tr>
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<td>7.12</td>
<td>57.3</td>
<td>4.447</td>
<td>1.7</td>
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Fig. 9-1. The natural logarithm of $C_{es}(T)/\tau_s(T_c)T_c$ versus $T/T_c$ in the range 1.0 to 4.0. For clarity, only six materials are shown since, for example, Nb$_3$Sn falls close to Pb$_{0.6}Tl_{0.4}$. The insert gives a closeup of the region near $T/T_c = 1$ which is crowded in the main figure. The curves are labeled according to solid line (---) Pb, dotted line (.....) Pb$_{0.6}Tl_{0.4}$, dashed line (-.-.-) NbN, dash triple dotted line (-...-) Nb, dash double dotted line (-..-..) In, and dash dotted line (-.-.-) Ta.
Results for \( \frac{[C_e(T)/\gamma_o(T,T_c)] \times (T_c/T)^3}{T/T_c} \) versus \( T/T_c \) for several scaled spectra, namely \( \text{Pb}_{0.5} \text{Bi}_{0.5}^* \), \( \text{Hg}^* \), \( \text{Sn}^* \), \( \text{In}^* \), and \( \text{Tl}^* \), and for \( \text{Pb} \) and for a delta-function spectrum as labeled in the figure. The starred spectra are taken from the tunneling data on \( \alpha^2 F(\omega) \) for those materials shown but have been rescaled to give the \( \text{Pb} \) value of \( T_c \) and characteristic frequency \( \omega_{\text{en}} \).
Results for \( \frac{C_{es}(T)}{\sigma_s(T_c)T_c} \times (T_c/T)^3 \) versus \( T/T_c \) for a number of two delta function models for the electron-phonon spectral density. The curves are labelled by the position of \( \omega_n/\omega_L \) and \( \omega_G/\omega_n \), the positions of the delta-functions with respect to \( \omega_n \). In all cases, \( T_c \), \( \omega_n \), and (very nearly) \( 2\Delta_0/k_BT_c \) agree with that of Pb. In the work of Padamsee et al., all the curves would collapse into one.
The prediction of Padamsee et al. for $\left[ C_{es}(T)/\gamma_s(T_c)T_c \right] \times (T_c/T)^3$ versus $T/T_c$ (solid lines) for values of $\alpha = 3.53, 4.0, 4.5$, and $5.0$. Also shown are results for the same quantity but calculated in Eliashberg theory for the scaled spectra $Hg^*$, $Pb_{0.5}Bi_{0.5}^*$, and $In^*$. All these have nearly the same $2\Delta_0/k_B T_c = 4.5$, and the points should all fall on the $\alpha = 4.5$ solid line.
CHAPTER X

SOME THERMO DYNAMIC AND OPTICAL PROPERTIES OF NbN

10-1 Introduction

In a recent paper, Kihlstrom et al.\(^{(19)}\) have given results, based on tunneling data, for the electron-phonon spectral density \(\alpha^2 F(\Omega)\) and the Coulomb pseudopotential \(\mu^2\) of films of NbN, which had a critical temperature of 14K. The measured \(\alpha^2 F(\Omega)\) is found to exhibit two fairly distinct peaks, one centered around 15 meV and extending to about 30 meV and the other, of about the same size, centered around 45 meV and extending to the rather large value of 60 meV. Associated with this \(\alpha^2 F(\Omega)\) spectrum is an electron-phonon mass renormalization parameter \(\lambda\) of 1.46. This value is intermediate between Pb (1.55) and Pb\(_{0.6}\)Tl\(_{0.4}\) (1.33). The value \(\lambda = 1.46\) for NbN is much larger than the four recent theoretical estimates which range from a low of 0.87, given by Dacorogna et al.\(^{(89)}\), to a high of 1.23, given by Rietschel et al.\(^{(90)}\). The other two values are close to one another, 0.96 by Glotzel et al.\(^{(91)}\), and 0.93 by Papaconstantopoulos\(^{(92)}\). A discussion of how these results were obtained can be found in the review by Klein and Pickett\(^{(45)}\) where first principle calculations of superconducting parameters are reviewed and compared. Included in the comparison are some transition metals, A-15 compounds, hydrides, and many carbides and nitrides.
Associated with the rather large experimental value for \( \lambda \), compared with theoretical estimates, is a correspondingly large value of the Coulomb pseudopotential found to be 0.33 in the tunneling inversion. This value is to be compared with the more usual values of 0.1 to 0.15 found for the many other systems tabulated by Mitrovic et al.\(^{24}\) and the more recently considered A-15 compounds (Mitrovic, Schachinger and Carbotte\(^{38}\)). Similar values of \( \mu^* \) are also found in the very recent experimental work of Rudman and Beasley\(^{93}\) in NbSn of various compositions and the \( V_3Si \) work by Kihlstrom\(^{18}\). It is important to realize that the large values of \( \mu^* \) in NbN makes the much used approximate equations for \( T_c \)\(^{42,29}\) inapplicable because they were derived for \( \mu^* \) of the order of 0.1. This point is stressed by Geerk et al.\(^{94}\) who consider \( T_c \) for very large values of \( \mu^* \) and find large differences from the McMillan\(^{42}\) equation. For the specific case of NbN, Kihlstrom et al.\(^{19}\) find that the McMillan\(^{42}\) equation underestimates \( T_c \) by 50% while the Allen-Dynes\(^{29}\) equation introduces an even greater error. It is clear that, to get sensible results for the superconducting properties of NbN, it is necessary to numerically solve the full Eliashberg equations. This is what is done in this chapter. From the solutions of the equations, based on the electron-phonon spectral density of Kihlstrom et al.\(^{19}\), the various thermodynamic properties, the gap edge \( \Delta_0 \), the ratio \( 2\Delta_0/k_B T_c \), the coherence distance \( \xi(T) \) as a function of temperature \( T \), the London limit penetration depth, and the jump in the quasiparticle current at the gap voltage will be computed. The results are compared with experiment when possible and with theoretical results for Pb and Pb\(_{0.6}Tl_{0.4}\)
systems which have values of $\lambda$ close to that of NbN.

10-2 Results

Table 10-1 contains characteristic values of some of the material parameters entering the calculations. The first row is the $T_c$ calculated from the imaginary frequency axis equations. For NbN, a cutoff of $N = 4$ times $\omega_{\text{max}} = 60.6$ meV was used. With this cutoff, the value of $\mu^*$ which is needed to get a $T_c = 14K$ from the imaginary axis work is 0.35; this is a little larger than the value found by inversion from tunneling data. Tunneling inversion makes use of the real axis form of the Eliashberg equations and yields 0.33. The difference between the two methods is expected and reflects differences in cutoff, as well as the fact that a sharp cutoff on the imaginary axis does not correspond exactly to a sharp cutoff on the real axis and vice versa. This was discussed by Leavens and Fenton.\(^8\)

Also found in table 10-1 is the electron mass enhancement parameter $\lambda$ and the area under $\alpha^2 F(2)$ denoted by $A$. This last parameter is not as well known as $\lambda$ but has been used in some discussions of superconducting properties.\(^{43}\) Note that $\lambda$ is very large for NbN compared with Pb and would lead to a very large value of $T_c$ if the empirical relationship $T_c = 0.1455 A$ established by Leavens and Carbott\(^{43}\) held. It does not hold, of course, because it applies only for $\mu^* = 0.1$. It is the large size of $\mu^*$ which prevents $T_c$ from being considerably bigger than 14K.

Other entries for NbN in table 10-1 are results for the gap
edge and the ratio $2\Delta_0/k_B T_C = 4.124$ which is close to the experimental value of 4.25(19), and which indicates that the tunneling derived normal state parameters are reasonable and that a large $\mu^*$ is consistent with this data. It must be stressed that in the theoretical work there is no adjustable parameter once $\mu^*$ is fixed to give the correct $T_C$. Also given is $d\Delta_1(\omega)/d\omega\big|_{\Delta_0}$ needed to calculate the ratio of the jump in the current voltage characteristics at the gap edge to its weak coupling value, $J_R'$, as discussed in Chapters II and III.

At this point, it is worthwhile comparing results for NbN with those of Pb and Pb$_{0.6}$Tl$_{0.4}$ systems considered relevant because they have respectively values of $\lambda$ slightly larger and slightly smaller than NbN. This comparison is interesting since $\lambda$ is often taken as an index of "strong coupling effects". It is seen from table 10-1, contrary to what might have been expected, that $2\Delta_0/k_B T_C$ for NbN is lower than that of Pb$_{0.6}$Tl$_{0.4}$ even though its $\lambda$ is smaller. If $2\Delta_0/k_B T_C$ is taken as the strong coupling index, then the systems order differently than when $\lambda$ is chosen. The order given by $2\Delta_0/k_B T_C$ is followed as well when other strong coupling indices are computed as can be seen in table 10-1. These indices are the derivative of the real part of the gap edge at $\Delta_0$ entering $J_R$, the normalized specific heat jump at $T_C$ ($\Delta_C/\tau_s T_C$, where $\tau_s$ is the Sommerfeld constant), and the dimensionless ratio $\tau_s [T_C/H_C(0)]^2$ with $H_C(0)$ the critical magnetic field at temperature $T = 0$. The same holds true for the critical magnetic field deviation function $D(t)$ discussed next.

The critical magnetic field $H_C(T)$ at temperature $T$ can be
determined magnetically or deduced from specific heat data. In Figure 10-1, the magnetic field data in the form of \( D(t) \) is plotted against reduced temperature for NbN (dotted curve) as compared with theoretical results for Pb (dashed curve) and for \( \text{Pb}_{0.6} \text{Tl}_{0.4} \). It is clear, on the basis of \( D(t) \), that it must again be concluded that NbN is a weaker coupling system than is \( \text{Pb}_{0.6} \text{Tl}_{0.4} \) which has a smaller mass enhancement parameter. The solid dots are experimental data points read off the graph from Geibel et al.\(^{(95)} \). The agreement is good. Note, however, that on the whole the data fall a little below the theoretical curve. This conforms with the results of Daams and Carbotte\(^{(17)} \) in many other materials. In general, it is found that the value of \( D(t) \) calculated from Eliashberg theory using the tunneling derived \( \alpha^2 F(\Omega) \) for a given material falls a bit above the experimental curve. This has been interpreted by Daams and Carbotte to be due to anisotropy which is excluded in the isotropic version of the Eliashberg equations employed in the inversion procedure that gives \( \alpha^2 F(\Omega) \). The anisotropy is also left out of the calculations of \( D(t) \) here. A small amount of anisotropy could be introduced that would lead to even better agreement with experiment than is shown in Figure 10-1. This goes beyond the scope of this study, but it should be pointed out that the need to include a small amount of anisotropy is supported by recent very careful measurements on the \( D(t) \) in In and InTl alloys by Niel et al.\(^{(96)} \).

Referring once more to Table 10-1, before going on to the electromagnetic properties, it can be seen that there is also good agreement between theory and experiment for the dimensionless ratios
\[ \Delta C / \gamma S T C \text{ and } \gamma S [T_C / H_C(0)]^2 \] (Giebel et al. (95)). This leaves little doubt that the tunneling data on NbN is consistent with the measured thermodynamics. While the agreement for reduced quantities is good, there remains a problem with the size of the electronic density of states at the Fermi surface that is deduced from the experimental value of the Sommerfeld constant \( \gamma_S \) and the tunneling derived \( \lambda \) of 1.46.

While there can be considerable uncertainty in the measured value of \( \gamma_S \) for systems with high values of \( T_C \) because of the need to extrapolate over a large range (52), for definiteness, it will be assumed that the recent value of Giebel et al. (95) equal to 2.1 mJ/g-mol-K\(^2\) is reliable. In a footnote, Rietschel et al. (90) state that the other data of Roedhammer et al. (97) could be reinterpreted to give instead 2.4 mJ/g-mol-K\(^2\). This difference is quite significant in the comparison with band structure calculations that is about to be made.

The specific heat \( \gamma_S \) is related to the band structure electronic density of states \( N_{BS}(0) \) through

\[ \gamma_S = \frac{2}{3} N_{BS}(0) \pi^2 k_B^2 (1+\lambda) \] (10-1)

with another correction for correlation effects, usually left out, modifying the 1+\( \lambda \) factor. The measured values of \( \gamma_S \) and \( \lambda \) imply a band structure density of states factor of \( N_{BS}(0) \) = 4.94 states/Ryd-atom which is smaller than the presently calculated values. In table 10-2, four recent computed values of \( N_{BS}(0) \) are entered with references and corresponding \( \lambda \) value. It can be seen that the agreement in \( N_{BS}(0) \) between authors is at the 15% level, which is better than in the case...
for corresponding values of $\lambda$. The value found in this study is 15% smaller than the lowest calculated value. While this disagreement is significant, larger deviations between values of $N_{BS}(0)$ derived from specific heat and tunneling data and the band structure results have been noted by Mitrovic et al.\(^{(38)}\) in some A-15 compounds. More accurate band structure calculations or specific heat measurements would be helpful. If $\gamma_s = 2.4 \text{ mJ/g-mol-k}^2$, the disagreement with band theory would be largely resolved.

One further comparison of thermodynamic data is interesting. In a recent paper Mitrovic et al.\(^{(24)}\) and Marsiglio and Carbott\(^{(30)}\) established approximate formulae for various dimensionless ratios of strong coupling parameters involving the parameters $T_C/\omega_{fn}$ which can be found in table 10-1. These are equations (IV-1), (V-1), and (V-2) for the ratios $2\Delta_0/k_B T_C$, $\Delta C_v/\gamma_s T_C$, and $\gamma_s [T_C/\mu_c(0)]^2$ respectively. If these formulae are applied to the case of NbN they give $2\Delta_0/k_B T_C = 4.05$, $\gamma_s [T_C/\mu_c(0)]^2 = 0.149$, and $\Delta C_v/\gamma_s T_C = 2.12$ which agree well with the complete calculations and with experiment. This indicates that these formulae can be applied even for fairly large $\mu^*$ values with about the same accuracy as in the other cases considered in the references just mentioned.

The Matsubara gaps $\tilde{\Delta}(\omega_n)$ and the renormalized frequencies $\tilde{\omega}(\omega_n)$ at temperature $T$ determine directly the coherence length $\xi(T)$ and the local $\lambda_0(T)$ and London limit $\lambda_L(T)$ penetration depths. In a superconductor, the Cooper pairs overlap in space as the approximate distance between members of a Cooper pair is $10^4$ Angstroms which is large on the scale of the separation of atoms in the material. As a
result, the order parameter can vary only over a distance having this range which is called the coherence distance. The electrodynamics are also nonlocal with the electromagnetic coherence distance given by

$$\xi(T) = \frac{\hbar v_p}{2} \left[ \sum_{n \geq 0} \frac{\Delta_n^2}{\omega_n^2 + \Delta_n^2} \right] \left[ \sum_{n \geq 0} \frac{\Delta_n^2}{\omega_n^2 + \Delta_n^2} \right]^{3/2}$$

(10-2)

with $v_p$ the Fermi velocity. The results for the zero temperature limit of $\xi(T)$ in units of $v_p$ are given in table 10-1. It can be seen that NbN when compared to Pb and Pb$_{0.6}$Tl$_{0.4}$ has the smallest value of $\xi(0)/v_p$. Also shown, is the ratio of $\xi(0)$ to its value in BCS theory, namely $\hbar v_p/[\pi \Delta_0 (1+\lambda)]$. The strong coupling correction for NbN is 21%, a little smaller than for the two comparative systems. The full temperature dependence of the coherence distance normalized to its zero temperature value is found in figure 10-2 where it is compared to Pb and Pb$_{0.6}$Tl$_{0.4}$. It is seen that the dotted curve which applies to NbN falls off faster than the other two curves. Of the three cases considered it is the closest to BCS behaviour in which $\xi(T_C)/\xi(0) = 0.76$.

In superconductors surface currents are set up to resist the effects of external magnetic fields. This is the Meisner effect in which the superconductor tries to exclude all flux. As a result, the electromagnetic field decays to zero within a small depth of the surface. Depending on how the field is assumed to decay, different formulae for penetration depths and slightly different depths are
found. The local limit penetration depth is given by

\[
\frac{\lambda_x(T)}{\lambda_x(0)} = \left[ \lim_{T \to 0} \frac{1}{T} \sum_{n \geq 0} \frac{\Delta_n^2}{\omega_n^2 + \Delta_n^2} \right] / \left[ \sum_{n \geq 0} \frac{\Delta_n^2}{\omega_n^2 + \Delta_n^2} \right] \tag{10-3}
\]

from which the London limit follows through the relationship

\[
\frac{\lambda_L^2(T)}{\lambda_L^2(0)} = \frac{\lambda_x^2(T)}{\lambda_x(0)} \cdot \frac{t_0(0)}{t_0(T)} \cdot \frac{\lambda_x^2(T)}{\lambda_x^2(0)} \tag{10-4}
\]

In figure 10-3,

\[
\frac{\lambda_x^2(T)}{\lambda_x(0)^2} - 2 \left[ \frac{1}{\lambda_L^2(0)} \right] - (1 - t^4) \tag{10-5}
\]

for NbN has been plotted versus the reduced temperature \( t = T/T_c \) and compared with the results for Pb and Pb\(_{0.6}\)Tl\(_{0.4}\). The deviation from BCS is largest for Pb (dashed curve) and least for NbN (dotted curve).

While the BCS temperature variation is not shown in the graph, it has a minimum around \( t = 0.75 \) of less than -0.21 which falls off the figure. This means that NbN shows considerable departure from a BCS superconductor which is a measurable effect.

10-3 Conclusion

In conclusion, from Eliashberg theory, various thermodynamic
and optical properties of NbN have been calculated from the tunneling derived electron-phonon spectral density $\alpha^2 F(\Omega)$. Good agreement has been found, on comparison wherever possible, with experimental data except perhaps for the Sommerfeld constant $\gamma$, which implies a value of the band structure density of electron states at the Fermi energy about 15% lower than the lowest calculated band theory value. On comparison of results with Pb and Pb$_{0.6}$Tl$_{0.4}$ it is found that NbN is the weakest coupling of all three systems even though it has a larger $\lambda$ than Pb$_{0.6}$Tl$_{0.4}$. A better index for the strength of the coupling is the parameter $T_c/\omega_{\text{en}}$. 
Table 10-1 Various parameters characterizing the electron-phonon spectral density $\alpha^2 F(\omega)$ obtained by Kihlstrom et al. for NbN as well as the results of Eliashberg calculations based on this spectrum. The specific quantities considered are the gap edge ($\Delta_0$) and its derivative, the ratio of $2\Delta_0$ to the critical temperature $T_C$; the normalized specific heat jump $\Delta C_v/T_C$, the ratio $\tau_s [T_C/H_c(0)]^2$ with $H_c(0)$ the zero temperature critical magnetic field, the coherence length $\xi(0)$ at zero temperature in units of $v_F$ times seconds and $\xi(0)/\xi_{\text{BCS}}(0)$. Entries for Pb and Pb_{0.6}Tl_{0.4} systems with nearly the same $\lambda$ as NbN are also entered for comparison as are experimental results.
<table>
<thead>
<tr>
<th></th>
<th>NbN</th>
<th>Pb</th>
<th>Pb\textsubscript{0.6}\textsuperscript{0.4}</th>
<th>NbN (experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>1.2064</td>
<td>0.6196</td>
<td>0.5084</td>
<td>1.2064</td>
</tr>
<tr>
<td>$\omega_{\text{max}}$ (meV)</td>
<td>60.65</td>
<td>11.0</td>
<td>10.9</td>
<td>60.65</td>
</tr>
<tr>
<td>$A$ (meV)</td>
<td>15.168</td>
<td>4.032</td>
<td>.3.346</td>
<td>15.17</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1.473</td>
<td>1.548</td>
<td>1.381</td>
<td>1.46</td>
</tr>
<tr>
<td>$\omega_{\text{en}}$</td>
<td>174.6</td>
<td>56.0</td>
<td>50.0</td>
<td>174.6</td>
</tr>
<tr>
<td>$\frac{T_c}{\omega_{\text{en}}}$</td>
<td>0.080</td>
<td>0.128</td>
<td>0.118</td>
<td>0.080</td>
</tr>
<tr>
<td>$N$</td>
<td>4</td>
<td>6</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>$\mu^{*}$ ($\omega_{\text{c}}$-$\omega_{\text{max}}$)</td>
<td>0.3522</td>
<td>0.1438</td>
<td>0.1252</td>
<td>0.33</td>
</tr>
<tr>
<td>$\Delta_0$</td>
<td>2.488</td>
<td>1.393</td>
<td>1.106</td>
<td>2.56</td>
</tr>
<tr>
<td>$\frac{d\Delta_1(\omega)}{d\omega}</td>
<td>_{\omega=\Delta_0}$</td>
<td>0.0393</td>
<td>0.0631</td>
<td>0.0537</td>
</tr>
<tr>
<td>$2\Delta_0/k_{B}T_c$</td>
<td>4.124</td>
<td>4.495</td>
<td>4.352</td>
<td>4.25</td>
</tr>
<tr>
<td>$\gamma_s [T_c/H_c(0)]^2$</td>
<td>0.1461</td>
<td>0.1324</td>
<td>0.1374</td>
<td>0.147</td>
</tr>
<tr>
<td>$\frac{\Delta_c}{\gamma_s T_c}$</td>
<td>2.162</td>
<td>2.766</td>
<td>2.522</td>
<td>2.09</td>
</tr>
<tr>
<td>$\xi(0)/\nu_F$ (s)</td>
<td>$0.4125 \times 10^{-13}$</td>
<td>$0.7622 \times 10^{-13}$</td>
<td>$0.1004 \times 10^{-13}$</td>
<td>-</td>
</tr>
<tr>
<td>$\xi(0)/\xi(0)_{\text{BCS}}$</td>
<td>1.211</td>
<td>1.29</td>
<td>1.26</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 10-2 Calculated values of the band structure density of states at the Fermi surface and the mass enhancement factor $\lambda$ for NbN.
<table>
<thead>
<tr>
<th>$N_{SS}(0)$</th>
<th>$\lambda$</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.88 states/Ryd-atom</td>
<td>0.87</td>
<td>89</td>
</tr>
<tr>
<td>6.0</td>
<td>1.23</td>
<td>90</td>
</tr>
<tr>
<td>6.8</td>
<td>0.96</td>
<td>91</td>
</tr>
<tr>
<td>6.6</td>
<td>0.93</td>
<td>92</td>
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</table>
Fig. 10-1  The critical magnetic field deviation function $D(t)$ as a function of the square of the reduced temperature, $t=T/T_c$. The calculated result, based on the tunneling inversion of Kihlstrom et al. for $\alpha^2 F(\Omega)$ in NbN, is given by the dotted curve (.....). Also shown for comparison (solid large dots) are the experimental data of Geibel et al. Note that the $D(t)$ curve predicted for Pb (dashed curve ----) and Pb$_{0.6}$Tl$_{0.4}$ (solid curve ---), systems with nearly the same value of the electron-phonon mass renormalization parameter $\lambda$ as NbN.
Fig. 10-2 The temperature dependence of the reduced coherence length \( \xi(T)/\xi(0) \) for NbN (dotted curve \( \cdots \)) compared with the results for Pb (dashed curve \( --\)) and Pb_{0.67.0.4} (solid curve \( ---\)), two systems with nearly the same value of the electron-phonon mass renormalization parameter \( \lambda \) as NbN.
Fig. 10-3 Same as in figure 10-2, but for the square of the London limit penetration depth \( (\lambda_L(0)/\lambda_L(T))^2 \) minus the two fluid model temperature dependence \( 1-t^4 \).
CHAPTER XI
SUPERCONDUCTORS WITH FINITE MASS
PARAMAGNETIC IMPURITIES

11-1 Effects of Paramagnetic Impurities

Electrons in a metal scatter off impurities. When the impurity atom is nonmagnetic (i.e. normal), the electron is scattered from one momentum state to another, \( k \) to \( k' \). In a superconductor, this is of little consequence since the electron has only changed from being a member of one Cooper pair to another. The major effect of the normal impurities is that they alter the structure and hence the phonon distribution, and thus \( \alpha^2 F(\Omega) \). A paramagnetic impurity not only would scatter the electron but would also flip the spin state \( \sigma \) to \(-\sigma\). This destroys Cooper pairs and consequently has a much greater effect on a superconductor than normal impurities. Since it is the spin flipping that is so important, the fact that the electron also changed its momentum state was ignored in the previous work on paramagnetic impurities in superconductors for calculational simplicity. This means that the scattering is assumed to be elastic which, in terms of the paramagnetic impurities, amounts to an assumption that they were infinitely massive. The effects of these infinitely massive paramagnetic impurities on superconductivity have been studied extensively in BCS theory by Abrikosov and Gor'kov\(^{100}\). Ambegaokar
and Griffin\(^{101}\), Skalski et al.\(^{102}\), and others and is reviewed by Maki\(^{103}\). They have also been included in strong coupling theory by Schachinger et al.\(^{104}\). In this chapter, a strong coupling theory of superconductors with paramagnetic impurities which does not require the infinite mass assumption will be derived. Then the effects of this loosened assumption on the behaviour of \(T_C^P\) and of the thermodynamic ratios \(\Delta C_V^P(T)/\Delta C_V^0(T)\) and \([H_{C}^P(0)/T_C^P]^2/[H_{C}^0(0)/T_C^0]^2\) as function of the paramagnetic impurity concentration, are investigated.

In section 11-2, the Eliashberg equations for a superconductor containing low concentrations (< 5 to 10%) of finite mass paramagnetic impurities are derived. In section 11-3, it will be shown that the Bardeen-Stephan equation for the free energy is unchanged when the mass assumption is loosened. In section 11-4, the effects of finite mass paramagnetic impurities on \(T_C^P\), the critical temperature of the superconductor with paramagnetic impurities, and on the thermodynamic ratios \(\Delta C_V^P(T)/\Delta C_V^0(T)\) and \([H_{C}^P(0)/T_C^P]^2/[H_{C}^0(0)/T_C^0]^2\) as functions of \(T_C^P/T_C^0\) are investigated. In section 11-5, conclusions are drawn.

11-2 Formulation of the Basic Theory

The Hamiltonian of the interaction between the electrons and the atoms of the lattice, both host and impurity, is in the second quantization formalism of the form

\[
H_{\text{int}} = \sum_{kk',\sigma,\sigma'} <k'|V(x)|k> C^\dagger_{k',\sigma'} C_{k,\sigma} \tag{11-1}
\]
where \( C_{k,\sigma} \) (or \( C_{k,\sigma}^\dagger \)) destroys (creates) an electron of spin \( \sigma \) in state \( k \).

\[ V(x) = \sum_{\ell=1}^{N} V_\ell(x-R_\ell) \]  

(11-2)

where \( V_\ell(x-R_\ell) \) is the potential due to the atom at \( R_\ell \). This piece of the full Hamiltonian also includes normal state interactions between the electrons and the lattice. \( H_{\text{int}} \) may also be written as

\[ H_{\text{int}} = \sum_{kk',\alpha\alpha'} \sum_{\ell} e^{-i(k'-k)\cdot R_\ell} V_\ell(k'-k) C_{k',\alpha'}^\dagger C_{k,\alpha} \]  

(11-3)

where \( V_\ell(q) \) is the Fourier transform of \( V_\ell(x-R_\ell) \), and where a unit volume is assumed.

Following Abrikosov-Gor'kov (AG) theory, an interaction potential \( V_{\alpha\beta}^\epsilon(x) \) is introduced which describes the scattering of conduction electrons at the \( \ell \)th atom of the lattice by the following formula,

\[ V_{\alpha\beta}^\epsilon(x) = V_{\ell}^N(x) + \frac{1}{2} V_{\ell}^D(x) S_{\alpha\beta} \]  

(11-4)

Here \( V_{\ell}^N(x) \) describes the normal scattering of the electrons off the atoms, which of course does not include any spin-flip. The second term on the right hand side of (11-3) is the paramagnetic or spin flipping
interaction of the electrons, described by the spin matrix $\sigma_{\alpha\beta}^\epsilon$ with a paramagnetic impurity atom of spin $S$. The strength of this interaction is described by $V^P_\epsilon(x)$; if the $\epsilon$th atom is a host atom $V^P_\epsilon(x)$ is zero. The normal part $V^N_\epsilon(x)$ need not be the same for the host as for the impurity.

In order to treat the influence of the impurities on the system, a 4x4 matrix self energy $\Sigma(k,\omega_n)$ is introduced in the momentum ($k$) and frequency ($\omega_n$) space. It is related to the Green function $G(k,\omega_n)$ by the Dyson equation.

$$G^{-1}(k,\omega_n) = G_0^{-1}(k,\omega_n) - \Sigma(k,\omega_n) \quad (11-5)$$

where $G_0(k,\omega_n)$ is the 4x4 matrix Green function of the unperturbed nonsuperconducting material. Infinite order perturbation theory of the usual kind may be used to expand $\Sigma(k,\omega_n)$ in terms of the electron-lattice interaction potential

$$V = \begin{bmatrix} V_{\alpha\beta} & 0 \\ 0 & V_{\alpha\beta}^\dagger \end{bmatrix} \quad (11-6)$$

The Green function of a system with impurities is, in general, not translation invariant. If the impurity atoms are randomly distributed, and if it is assumed that there is no correlation between the spin directions of the paramagnetic impurity atoms, then one may average the Green function over all configurations of impurity sites. As a result, the homogeneity will be restored and the Green function
will again become translation invariant.

The self energy for the superconducting state with impurities is given by

$$Z(k, \omega_n) = \sum_{k', m} \sum_{\ell, \ell'} \frac{1}{\beta} \int_0^\beta d\tau \ e^{-i\omega_{\ell'} \tau} \ e^{-i(k-k') \cdot (R_\ell - R_{\ell'})} \times$$

$$\nu \stackrel{\nu}{\rightarrow} (k-k') \ G(k', \omega_m) \ V_{\ell'}(k'-k)$$  \hspace{1cm} (11-7)

where to get the self energy on the imaginary axis the time variable $t$ has been set to $i\tau$, the imaginary time variable, then a thermal average denoted by $\langle \ldots \rangle$ has been taken, and a Fourier transform to the imaginary frequency axis has been done. The imaginary frequencies are defined

$$\begin{cases} 
\omega_n = \pi(2n-1)/\beta \\
\omega_{\nu} = \pi2\nu/\beta
\end{cases} \hspace{1cm} n, \nu = 0, 1, 2, \ldots \hspace{1cm} (11-8)$$

and $\beta = \frac{1}{k_B T}$ with $k_B$ being Boltzmann's constant. Without loss of generality, one may set $\omega_{\nu} = \omega_n - \omega_m$. The vectors $R_\ell'$ describing atomic positions, are functions of time and are related to the equilibrium positions by

$$R_\ell = R_\ell^0 + u(\ell, t)$$  \hspace{1cm} (11-9)

where $u(\ell, t)$ is the excursion off equilibrium. Making use of the
harmonic approximation

\[ e^{i q \cdot u(1, t)} = 1 + i \sum_{\alpha} q_{\alpha} u_{\alpha}(1, t) \]  \hspace{1cm} (11-10)

the self energy breaks into two parts

\[ \Sigma(k, i \omega_n) = \Sigma_1(k, i \omega_n) + \Sigma_2(k, i \omega_n) \]  \hspace{1cm} (11-11)

The static self energy term is

\[ \Sigma_1(k, i \omega_n) = \sum_{k', \xi, \xi'} \frac{1}{\beta} \int_0^\beta \left[ e^{-i (\omega_n - \omega_m) \tau} e^{-i (k-k') \cdot (R_{\xi}^0 - R_{\xi'}^0)} \right] \times \\
\left[ V_{\xi}^*(k-k') G(k, i \omega_m) V_{\xi'}(k-k') - \overline{V}(k-k') G(k, i \omega_m) \overline{V}(k-k') \right] \]

\[ = \sum_{k', \xi, \xi'} e^{-i (k-k') \cdot (R_{\xi}^0 - R_{\xi'}^0)} \times \\
\left[ V_{\xi}^*(k-k') G(k, i \omega_n) V_{\xi'}(k-k') - \overline{V}(k-k') G(k, i \omega_n) \overline{V}(k-k') \right] \]  \hspace{1cm} (11-12)

where the identity

\[ \delta_{n, m} = \frac{1}{\beta} \int_0^\beta d\tau e^{-i (\omega_n - \omega_m) \tau} \]

has been used. The second term in equation (11-12) is the correction
to remove the effects of the average lattice already in $G^0$. The average potential is

$$\bar{V}(q) = (1-c)V_H(q) + cV_I^N(q), \quad (11-13)$$

where $c$ is the impurity concentration, $V_H(q)$ is the host atom potential, and $V_I^N(q)$ is the normal part of the impurity potential. The dynamic self energy term is

$$Z_2(k, \omega_n) = \sum_{k', m} \sum_{\epsilon \epsilon'} \sum_{\alpha \beta} \frac{1}{\beta} \int_0^\beta \, dr \, e^{-\lambda(\omega_n - \omega_m) r}$$

$$\times (k-k')^\alpha \langle u_{\alpha}^{(\epsilon, r)} u_{\beta}^{(\epsilon', 0)} \rangle (k-k')^\beta$$

$$\times e^{-\lambda(k-k').(R_{\xi}-R_{\xi}')} V_{\epsilon}(k-k') G(k', \omega_n) V_{\epsilon'}(k'-k) \quad (11-14)$$

where $r$ actually refers to the time difference $t-t'$, since the Green functions only depend on this quantity in the restored translationally invariant case. There are no self energies with single $u(\epsilon, t)$ terms since $\langle u(\epsilon, t) \rangle = 0$, that is, on average, the excursion off equilibrium is zero.

The potential can be written in 4-space notation using the direct product between two Pauli matrices, $\tau_i \sigma_j$:

$$2V_{\epsilon}(q) = \tau_1 \cdot V^N_{\epsilon}(q)$$
\[ \tau_3 \cdot \sigma_1 \frac{v^p(q)}{2} S^e_x + \frac{1}{2} \tau_3 \cdot \sigma_2 \frac{v^p(q)}{2} S^e_y + \frac{1}{2} \tau_3 \cdot \sigma_3 \frac{v^p(q)}{2} S^e_z \]  

(11-15)

where \( S^e = (S^e_x, S^e_y, S^e_z) \) is the spin vector of the \( \ell \)th atom. For unpolarized spins, one can write

\[ \langle S^e_\ell \rangle = 0, \quad \langle S^e_\ell S^e_\ell' \rangle = \frac{1}{3} S(S+1) \delta_{\ell \ell'} \delta_{rr} \quad r, s \in x, y, z. \]  

(11-16)

Here \( \langle ... \rangle \) denotes an average over all possible spin directions. The Pauli matrices, and certain identities for them, are given in Appendix C. For \( \Sigma_1(k, i\omega_n) \), the spin average and the impurity configuration average yield the familiar static impurity term,

\[ \Sigma_1(k, i\omega_n) = cN \sum_{k'} |V^r_h(k-k') - V^N_I(k-k')|^2 \tau_3 \cdot 1 \ G(k', i\omega_n) \tau_3 \cdot 1 \]

\[ + cN \frac{S(S+1)}{12} \sum_{k'} \left( |v^p_\ell(k-k')|^2 \right) x \]

\( \{1.\sigma_2 \ G(k', i\omega_n) \ 1.\sigma_2 + \tau_3 \cdot \sigma_1 \ G(k', i\omega_n) \tau_3 \cdot \sigma_1 \)

\[ + \tau_3 \cdot \sigma_3 \ G(k', i\omega_n) \tau_3 \cdot \sigma_3 \} \]

(11-17)
where terms of order $c^2$ and higher have been dropped. There is nothing new in equation (11-17) since the static term is, of course, independent of mass.

For the dynamic term, first note that

$$
\Sigma_2(k, \omega_n) = \frac{1}{\pi \beta} \sum_{k', m} \sum_{\ell, \ell'} e^{-i(k-k').R_{\omega_n}^m} \times
$$

$$
\int_0^{2\Omega} d\omega' \sum_{\ell' \gamma} D_{\ell\ell'}(\ell, \ell'; \Omega) (k-k') \beta \frac{2\Omega}{[\omega_n - \Omega_m^l/H]^2 + \Omega^2} \times
$$

$$
V'^2_{\ell} (k-k') G(k', \omega_m) V_{\ell'} (k'-k) . \quad (11-18)
$$

where

$$
D_{\ell\ell'}(\ell, \ell', t-t') = \frac{2\pi}{\hbar} \langle [u_{\ell}(t), u_{\ell'}(t')] \rangle . \quad (11-19)
$$

A substantial part of the reasoning in deriving equation (11-19) from equation (11-14) is given in Appendix D. Substituting the 4-space form of $V_{\ell}(q)$ given in equation (11-15) into equation (11-18) and averaging over spin directions yields, to first order in $c$,

$$
\Sigma_2(k, \omega_n) = \frac{1}{\pi \beta} \sum_{k', m} \sum_{\ell, \ell'} \int_0^{2\Omega} d\omega' V'^2_{\ell}(k'-k) V_{\ell'}^N (k'-k) \times
$$
\[ \sum_{\alpha \beta} \int \frac{d \omega}{\omega_m} \frac{\omega_\alpha}{\omega_m} \left( k-k' \right) \beta \left[ \frac{\omega_\alpha - \omega_m}{\hbar} \right]^{2+\alpha^2} \]

\[ e^{-i(k-k') \cdot (R^0 - R^0_{1,1})} \{ r_{2,1} G(k', \omega_m) r_{3,1} \}

+ \left( \frac{cN}{\pi \beta} \frac{S(S+1)}{12} \sum_{k,m} \right) |V^0_{I}(k-k')|^2 \times \]

\[ \int d \omega \sum_{\alpha \beta} \frac{(k-k') \alpha}{\omega_m} \frac{\omega_\alpha}{\omega_m} \left( k-k' \right) \beta \left[ \frac{\omega_\alpha - \omega_m}{\hbar} \right]^{2+\alpha^2} \]

\[ (1. \sigma_2 G(k', \omega_m) 1. \sigma_2 + \tau_{3, \sigma_1} G(k', \omega_m) \tau_{3, \sigma_1})

+ \tau_{3, \sigma_3} G(k', \omega_m) \tau_{3, \sigma_3} \}

(11-20)

The first term is the typical result for an alloy. The second part is new and represents the effect of allowing the paramagnetic impurity to have finite mass and thus to interact via lattice vibrations with the electrons. The Feynman diagram leading to such a term is given in figure 11-1. Physically it represents an electron flipping its spin by scattering off a paramagnetic impurity and, as well, using some of the lattice energy (since the impurity can now freely vibrate) to change its momentum state.

Next, assuming an isotropic material, the average self energies given by
\[ Z(\omega_n) = \frac{1}{\sum_k \frac{dS_k}{|v_k|}} \frac{1}{S} \int \frac{dS_k}{|v_k|} Z(k, \omega_n) \] (11-21)

are examined. Where \( v_k \) is the velocity of the electron in state \( k \). As well, the summation over \( k' \) in equations (11-17) and (11-20) can go over to integrals

\[ \sum_{k'} = \frac{1}{(2\pi)^3 \hbar} \int_{-\infty}^{\infty} \frac{d\epsilon'}{2\pi} \int \frac{dS_{k'}}{|v_{k'}|} \]

Also, it is assumed that in the region \( E_F \sim E_D \) to \( E_F \sim E_D \) \( G(k, \omega_n) \) has little or no angular dependence, so that \( G(k, \omega_n) = G(\epsilon, \omega_n) \), and that the other terms are essentially energy independent. It shall also be assumed that the Fermi surface is spherical. Thus

\[ Z_1(\omega_n) = cN \frac{S(S+1)}{12} \frac{N(0)}{8mk_F^2} \int_{<2k_F} \frac{d^3q}{q} |V_1(q)|^2 \times \]

\[ [1.\sigma_2 \int_{\epsilon'G(\epsilon', \omega_n)} 1.\sigma_2 + \tau_2.\sigma_1 \int_{\epsilon'G(\epsilon', \omega_n)} \tau_2.\sigma_1 ] \]

\[ + \tau_2.\sigma_2 \int_{\epsilon'G(\epsilon', \omega_n)} \tau_2.\sigma_3 ] \]

\[ \frac{N(0)}{8mk_F^2} \sum_{\epsilon, \epsilon'} \int_{<2k_F} \frac{d^3q}{q} e^{-i\mathbf{q} \cdot (\mathbf{R}_e - \mathbf{R}_{e'})} (V_{\epsilon}(q) V'_{\epsilon}(q) - |V(q)|^2) \times \]

\[ \]
\[ \tau_{3.1} \int d\epsilon' g(\epsilon', \omega_n) \tau_{3.1} \quad (11-22) \]

This may be written more compactly as

\[ \Sigma_1(\omega_n) = \frac{1}{2\pi^2} \left[ 1.\sigma_2 \int d\epsilon' g(\epsilon', \omega_n) 1.\sigma_2 \right. \]

\[ + \tau_3.\sigma_1 \int d\epsilon' g(\epsilon', \omega_n) \tau_3.\sigma_1 + \tau_3.\sigma_3 \int d\epsilon' g(\epsilon', \omega_n) \tau_3.\sigma_3 ] \]

\[ + \frac{1}{2\pi^N} \left[ \tau_{3.1} \int d\epsilon' g(\epsilon', \omega_n) \tau_{3.1} \right] \quad (11-23) \]

where \( \frac{1}{2\pi^P} \) and \( \frac{1}{2\pi^N} \) are the inverse scattering times for the paramagnetic and normal impurities, respectively, defined

\[ \frac{1}{2\pi^P} = c N \frac{S(S+1)}{12} \frac{N(0)}{8\pi k_F^2} \int_{<2k_F} \frac{d^3q}{q} |V_p(q)|^2 \quad (11-24a) \]

and

\[ \frac{1}{2\pi^N} = c N \frac{N(0)}{8\pi k_F^2} \int_{<2k_F} \frac{d^3q}{q} |\Delta V(q)|^2 \quad (11-24b) \]

where a configurational average has been made of \( \frac{1}{2\pi^N} \) to lowest order.
in c. and $\Delta V(q) = V_H^N(q) - V_i^N(q)$ as shown in Appendix B. Similarly, using the definition of the electron-phonon interaction spectral density of an alloy.

$$\alpha^2_F (\Omega) = \frac{N(0)}{8\pi^2 k_F^2} \sum_{\epsilon, \epsilon'} \int_{<2k_F} \frac{d^3q}{q} V_\epsilon^N(q) V_{\epsilon'}^N(q) \times$$

$$\sum_{\alpha\beta} \gamma_{m2,\alpha\beta}(\epsilon, \epsilon'; \Omega) q_\beta e^{iq \cdot (R_{\epsilon} - R_{\epsilon'})} \quad (11-25)$$

and defining a new spectral density for the finite mass paramagnetic impurity term

$$\alpha^2_{SF}(\Omega) = c N \frac{S(S+1)}{4} \frac{N(0)}{8\pi^2 k_F^2} \int_{<2k_F} \frac{d^3q}{q} |V_\epsilon^p(q)|^2 \times$$

$$\sum_{\alpha\beta} \gamma_{m2,\alpha\beta}(I, I; \Omega) q_\beta \quad (11-26)$$

the dynamic part of the self energy may be written as

$$\Sigma_2(\omega_n) = \frac{1}{3\beta} \sum_{m} \tilde{\lambda}_{SF}(n-m) \left[ 1 \cdot \sigma_2 \int d\epsilon' G(\epsilon', \omega_m) 1 \cdot \sigma_2 \right.$$ \nonumber

$$+ \tau_3 \cdot \sigma_1 \int d\epsilon' G(\epsilon', \omega_m) \tau_3 \cdot \sigma_1 + \tau_3 \cdot \sigma_3 \int d\epsilon' G(\epsilon', \omega_m) \tau_3 \cdot \sigma_3 \left]$$
\[ + \frac{1}{\beta} \sum \lambda(n-m) \left[ \tau_{2,1} \int_{e'} G(e', i\omega_m) \tau_{2,1} \right] \]  

(11-27)

where

\[ \lambda(n-m) = \int_0^\infty d\Omega \alpha^2 \rho(\Omega) \frac{2\Omega}{(\omega_n - \omega_m)^2 + \Omega^2} \]  

(11-28)

and where \( \lambda_{SP}(n-m) \) is similarly defined.

At this point, the standard self energy term for the effects of the short range Coulomb repulsion on the pairing self energy

\[ \Sigma_C(i\omega_n) = -\frac{1}{\beta} \sum \mu^z \Theta(\omega_n - |\omega_m|) \tau_{2,1} \int_{e'} G(e', i\omega_m) \tau_{2,1} \]  

(11-29)

is introduced, where \( \mu^z \) is the Coulomb pseudopotential for some cutoff on the summation. \( \omega_c \). It is assumed that alloying does not affect this term. Thus the full self energy of superconducting state is

\[ \Sigma(i\omega_n) = \Sigma_1(i\omega_n) + \Sigma_2(i\omega_n) + \Sigma_C(i\omega_n) \]  

(11-30)

Making the standard ansatz that

\[ G^{-1}(e,i\omega_m) = Z(i\omega_m) \omega_m \tau_{1,1} - Z(i\omega_m) \Delta(i\omega_m) \tau_{2,1} \sigma_2 - e \tau_{2,1} \]  

(11-31)

the total self energy can then be written as
$$\Sigma(i\omega_n) = [1-Z(i\omega_n)]i\omega_n 1 + Z(i\omega_n)\Delta(i\omega_n) \tau_2 \cdot \sigma_2 \quad (11-32)$$

Equation (11-31) may be inverted to get an expression for $G$

$$G(\epsilon, i\omega_n) = \frac{-1}{Z(i\omega_n)} \frac{i\omega_n 1 + \Delta(i\omega_n) \tau_2 \cdot \sigma_2 + [\epsilon/Z(i\omega_n)] \tau_3 \cdot 1}{[\omega_n^2 + \Delta^2(i\omega_n)] + [\epsilon/Z(i\omega_n)]^2} \quad (11-33)$$

so that the energy integrals in equations (11-23), (11-27) and (11-29) may be trivially integrated. Along with the definition of the total self energy (11-30), this yields the Eliashberg equations for a superconductor with finite mass paramagnetic impurities

$$\omega_n Z(i\omega_n) = \omega_n + n k_B T \sum_m \left[\lambda(n-m) + \lambda_{SF}(n-m)\right] \frac{\omega_m}{\sqrt{\omega_n^2 + \Delta^2(i\omega_n)}}$$

$$+ \left(\frac{1}{2r_N^N} + \frac{1}{2r_P^P}\right) \frac{\omega_n}{\sqrt{\omega_n^2 + \Delta^2(i\omega_n)}} \quad (11-34a)$$

and

$$Z(i\omega_n)\Delta(i\omega_n) = n k_B T \sum_m \left[\lambda(n-m) - \lambda_{SF}(n-m) - \mu \theta(\omega_c - |\omega_m|)\right] \frac{\Delta(i\omega_m)}{\sqrt{\omega_n^2 + \Delta^2(i\omega_n)}}$$

$$+ \left(\frac{1}{2r_N^N} - \frac{1}{2r_P^P}\right) \frac{\Delta(i\omega_n)}{\sqrt{\omega_n^2 + \Delta^2(i\omega_n)}} \quad (11-34b)$$
Thus the mathematical effect of letting the paramagnetic impurities have finite mass is to introduce a paramagnon-like term into the Eliashberg equations.

11-3 The Free Energy Equation

The thermodynamics of a system are calculated from the grand thermodynamic potential \( \Omega(\beta, \mu, V) \), which is related to the grand partition function \( Z_G(\beta, \mu, V) \) by

\[
Z_G(\beta, \mu, V) = \exp(-\beta \Omega(\beta, \mu, V)) ,
\]  

(11-35)

where \( \mu \) is the chemical potential and \( V \) is the volume of the system. Luttinger and Ward\(^{105}\) have given a first principles calculation of \( \Omega \) in the case of an isotropic system of spin \( \frac{1}{2} \) particles interacting via an instantaneous two-body potential. Eliashberg\(^{106}\) extended this work to include phonon contributions and the noninstantaneous electron-phonon interaction. The grand thermodynamic potential per unit volume can be written

\[
\Omega = -\frac{2}{\hbar} \sum_P \text{exp}(i \omega_n \epsilon_i) \left\{ \ln \left| \text{det} G^{-1}(P) \right| + \Sigma(P) G(P) \right\} 
\]

\[
+ \frac{1}{2\hbar} \sum_Q \text{exp}(i \omega_j \epsilon_j) \left\{ \ln \left| \text{det} D^{-1}(Q) \right| + \pi(Q) D(Q) \right\}
\]

\[
+ \sum_P \Sigma(P) G(P)
\]

(11-36)
where

\[ P = (k, \omega_n), \quad \omega_n = \pi(2n-1)/\beta \]
\[ Q = (q, \omega_\nu), \quad \omega_\nu = \pi2n/\beta \]
\[ \Sigma = \Sigma \Sigma \Sigma \Sigma \]
\[ P \quad k \quad n \rightarrow \infty \quad Q \quad q \quad n \rightarrow \infty \]

The phonon polarization index on the phonon thermodynamic Green function \( D(Q) \) have been suppressed. The polarization part, \( \pi(Q) \), is defined by

\[ D^{-1}(Q) = D_0^{-1}(Q) - \pi(Q) \]  (11-38)

What has been tried to be made clear in writing equation (11-36) is that the form of the equation is independent of whether the two-body interaction is instantaneous or not. All corrections and assumptions modify the Green function and the self energy, not the equation itself. Thus equation (11-36) is the grand thermodynamic potential for the normal state when only the normal state Green functions and self energies are considered. Including the self energies, as given in section 11-2, yields the correct value for the superconducting state. Then the free energy difference \( \Delta F(T) = \Omega_s - \Omega_n \), from which the thermodynamic ratios of interest may be calculated, is,

\[ \Delta F(T) = -\frac{1}{\beta V} \sum_P \left\{ \chi_n \left[ \frac{\phi_n(P)}{\phi_n(P)} \right] + \Sigma_{s}(P)G_s(P) - \Sigma_n(P)G_n(P) \right\} \]  (11-39)
where $\phi$ is the determinant of $G$ in the appropriate state. It has been implicitly assumed that $D_{s}(P)=D_{n}(P)$ i.e. that there is little difference in the phonons between the superconducting and normal states. This is a general formula for the free energy difference. The superconducting terms can be found in terms of $\omega_{n}$, $Z(\omega_{n})$, $\Delta(\omega_{n})$, and $\epsilon$ from equations (11-32) and (11-33). Expressions for the normal state terms can also be had from these equations with $\Delta(\omega_{n})$ set to zero and $Z(\omega_{n})$ replaced by $Z_{n}(\omega_{n})$. $Z_{n}(\omega_{n})$ is in turn found from equation (11-34a) with $\Delta(\omega_{n}) = 0$. Making the appropriate substitutions, equation (11-39) becomes

$$\Delta F(T) = -\frac{1}{\beta} \sum_{p} \left\{ \frac{Z_{n}^{2}(\omega_{n})(\omega_{n}^{2}+\Delta_{n}^{2}(\omega_{n})) + \epsilon^{2}}{Z_{n}^{2}(\omega_{n})\omega_{n}^{2} + \epsilon^{2}} \right\}$$

$$-\frac{Z_{n}^{2}(\omega_{n})(\omega_{n}^{2}+\Delta_{n}^{2}(\omega_{n})) - \omega_{n}^{2}Z_{n}(\omega_{n}) + i\omega_{n}(1-Z_{n}(\omega_{n}))\epsilon}{Z_{n}^{2}(\omega_{n})(\omega_{n}^{2}+\Delta_{n}^{2}(\omega_{n})) + \epsilon^{2}}$$

$$-\frac{Z_{n}^{2}(\omega_{n})\omega_{n}^{2} - \omega_{n}^{2}Z_{n}(\omega_{n}) + i\omega_{n}(1-Z_{n}(\omega_{n}))\epsilon}{Z_{n}^{2}(\omega_{n})\omega_{n}^{2} + \epsilon^{2}}$$

(11-40)

The summation over $k$ in $P$ can be converted to an integral over $\epsilon$

$$\Delta \tilde{\Sigma} = \sum_{p} \sum_{k n \rightarrow \infty} \frac{d^{3}k}{(2\pi)^{3}} \int_{n \rightarrow -\infty}^{+\infty} \epsilon \left\{ \frac{d^{3}k}{(2\pi)^{3}} \int_{n \rightarrow -\infty}^{+\infty} \epsilon \right\} = \int_{n \rightarrow -\infty}^{+\infty} \epsilon \left\{ \frac{d^{3}k}{(2\pi)^{3}} \int_{n \rightarrow -\infty}^{+\infty} \epsilon \right\} \text{d}N(0)$$

where $N(0)$ is the normal state single spin electron density of states.
Doing the integrals, and making certain rearrangements, the Bardeen-Stephen equation for the free energy difference is arrived at

\[
\Delta F(T) = 2\pi N(0)T \sum_{n>0} \left[ 2 \left\{ \left( \omega_n^2 + \Delta_n^2 \right)^{1/2} - \omega_n - \frac{1}{2} \frac{\Delta_n^2}{\sqrt{\omega_n^2 + \Delta_n^2}} \right\} - \left( \omega_n^0 - \omega_n^0 \right) \left\{ \frac{\omega_n}{\sqrt{\omega_n^2 + \Delta_n^2}} - 1 \right\} \right]
\]

where for economy of space the definitions \( \omega_n^0 = \omega_n Z(\omega_n) \), \( \omega_n^0 = \omega_n Z(\omega_n) \), and \( \Delta(\omega_n) = \Delta(\omega_n) Z(\omega_n) \) have been used. Calculating the free energy difference is simple once the solutions of equations (11-34a) and (11-34b) are known. The particular quantities of interest \( H_c(0) \) and \( \Delta C_v(T) \) are determined from the thermodynamic relations \( H_c(T) = \sqrt{8\pi \Delta F(T)} \) and \( \Delta C_v(T) = T \frac{d^2 \Delta F(T)}{dT^2} \). Hence it is now possible to present results.

11-4 Results

In this section, the effects of \( \alpha_{St}^2 F(\Omega) \) on the critical temperature, \( T_c^p \), on the jump in the specific heat \( \Delta C_v(T_c^p) \), and on the ratio \( \left[ \frac{H_c(0)}{T_c^p} \right]^2 \) as a functions of paramagnetic impurity concentration will be investigated. The critical temperature may be determined from equations (11-34a) and (11-34b) in the limit with
\[ \omega_n Z(\omega_n) = \omega_n + \frac{\pi k_B T_c^P}{2} \sum_m \frac{[\lambda(n-m)+\lambda_{SP}(n-m)]}{\omega_m} \omega_n \]

\[ + \left( \frac{1}{2r_N^N} + \frac{1}{2r_F^F} \right) \frac{\omega_n}{\omega_n^N} \]  \hspace{1cm} (11-42a)

and

\[ Z(\omega_n) \Delta(\omega_n) = \pi k_B T_c^P \sum_m \frac{[\lambda(n-m)-\lambda_{SP}(n-m)-\mu g/|\omega_n|]}{\omega_m} \Delta(\omega_n) \]

\[ + \left( \frac{1}{2r_N^N} - \frac{1}{2r_F^F} \right) \frac{\Delta(\omega_n)}{|\omega_n|} \]  \hspace{1cm} (11-42b)

The normal impurity scattering lifetime \( \frac{1}{r_N^N} \) has no effect on the critical temperature at low concentrations, since it disappears if equations (11-42a) and (11-42b) are combined into one equation. The main effect on \( T_c^P \) from the normal part of the impurity scattering is that of the change of \( \gamma F(\Omega) \). However, compared to the drastic effects of paramagnetic impurities, the effect is slight so that, in calculations, \( \gamma F(\Omega) \) may be taken to be that of the pure material at all the concentrations examined. For definiteness, Pb will be considered as the host material. The imaginary part of the pure material phonon Green function is given by (107)
\[ \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \right. \left. \r
\[ \alpha_{SP}^2(\Omega) = c \frac{S(S+1)}{4} \frac{1}{N_M} \frac{N(0)}{E \pi r^2} \int_{<2k_F} \frac{d^3q}{q} |v_I^P(q)|^2 \times \]

\[ \frac{1}{N} \sum_{\lambda, p} q_\lambda \varepsilon_{\lambda}(p, \lambda) \varepsilon_{\rho}(p, \lambda) q_\rho \frac{\delta(\Omega - \Omega(p, \lambda))}{2\varepsilon(p, \lambda)} \]  

(11-46)

This differs from the formula for \( \alpha_H^2(\Omega) \) of the host in the weighting given to each frequency. Thus equation (11-46) can be written in a simpler form

\[ \alpha_{SP}^2(\Omega) = c \frac{S(S+1)}{4} \frac{N_H}{N_M} R(\Omega) \alpha_H^2(\Omega) \]  

(11-47)

Note that \( \alpha_{SP}^2(\Omega) \) is zero if \( N_M \) is infinite. Since \( R(\Omega) \) cannot be evaluated, it will instead be assumed that it is roughly constant for all \( \Omega \). In such a case, \( R \) may be calculated by taking the first moment with respect to \( \Omega \) of both sides of equation (11-47). The delta-function enables the integral to be done and, using the closure property of the polarization vectors, yields

\[ R = \frac{\int qd^3q |v_I^P(q)|^2}{\int qd^3q |v_I^H(q)|^2} \]  

(11-48)

For calculational purposes, \( \frac{1}{2\pi r^2} \) is dealt with rather than \( c \), and, rather than the form given in equation (11-47).
\[ \alpha^2_{SF}(\Omega) = B \frac{1}{2\pi \rho^2} \alpha^2_F(\Omega) \]  

(11-49)

is dealt with, where \( \frac{1}{2\pi \rho} \) has units of meV and \( B \) of meV\(^{-1}\). The Eliashberg equations have been solved for the values of \( B = 0.0, 0.05, 0.25, \) and \( 1.0 \) (\( B = 0.0 \) being the static case). It is assumed that \( \mu^* \) does not vary with \( c \).

In figure 11-2, results for the ratio of the critical temperature to its pure value versus the ratio of the impurity scattering lifetime to its critical value, \( \frac{1}{2\pi \rho_{crit}} \), are presented. The critical value is the amount required to destroy the superconducting state. For the values of \( B \) used, the extrapolated critical values are \( \frac{1}{2\pi \rho_{crit}} = 0.275, 0.262, 0.224, \) and \( 0.150 \) meV respectively. Thus the spin-flip spectra, in essence, makes paramagnetic impurities even more effective is destroying superconductivity. The curves in figure 11-2 show significant departures from the static (\( B = 0.0 \)) case with increasing \( B \). Note that the AG curve approximately coincides with the \( B = 0.25 \) curve; the dynamic spin-flip term is masking strong coupling effects.

In figures 11-3 and 11-4, the effects on the thermodynamic ratios \( \Delta C_v(T_c)/\Delta C_v(T_c^0) \) and \( [H_{c}(0)/T_c^0]^2/[H_c^0(0)/T_c^0]^2 \) are shown along with the AG results as plotted against \( T_c^P/T_c^0 \). The portions of the curves below \( T_c^P/T_c^0 = 0.1 \) are extrapolated. From these it can be seen that as \( B \) increases, the strong coupling results approach the AG results and can pass beyond, as they did for \( T_c^P \). The size of \( B \) needed to mask
strong coupling effects here is approximately 1.0 and 0.25 for respectively. Clearly the size of the effect depends on the quantity being considered.

11-4 Discussion and Conclusions

One would naturally like to be able to estimate the size of the effects of the spin flip term from a knowledge of $S$ and $c_{\text{crit}}$ and from a rough knowledge of the comparative sizes of $V^p_I(q)$ and $V^p_H(q)$. This can be done realizing that

$$\frac{B}{2\pi c_{\text{crit}}} = \frac{S(S+1) M_H}{4 M_I} R$$

so that $\frac{S(S+1) M_H}{4 M_I} R$ can be plotted versus $c_{\text{crit}}$ for the three values of $\frac{B}{2\pi c_{\text{crit}}}$ that have been calculated. This is done in figure 11-5. If $\frac{M_H}{M_I}$ is approximately unity for some alloy with a $c_{\text{crit}}$ of several percent and a reasonably large value of $S$ then values of $B$ of 0.25 or greater are possible. Hence the finite impurity mass effects may be observable.

In strong coupling superconductors, the difference of the curves in figures 11-2, 11-3, and 11-4 for various values of $B$ and the $\Delta G$ curves is a competition between the finite impurity mass effects and the strong coupling effects. Therefore differences in these curves for weak coupling superconductors, which normally would be expected to
follow AG theory closely, would give a much better idea of the value of B, and hence of R, involved. Since \( V_I^P(q) \) undoubtedly varies with the impurity species, careful measurement may give an indication of relative size of this potential amongst the various impurity species tested.

In conclusion, paramagnetic impurities of finite mass have been introduced into strong coupling theory. The effect is to introduce a paramagnon like term \( \lambda_{SP}(n-m) \) into the Eliashberg equations. The term is, for the small concentrations of paramagnetic impurities needed to destroy superconductivity, proportional to the inverse scattering lifetime \( \frac{1}{2\pi n} \). The overall strength of the contribution \( \lambda_{SP}(n-m) \) would depend on the strength of the paramagnetic impurity potential compared to the host atom potential and on the spin. If the impurity and host potentials are approximately the same, there could be observable effects in the curves of \( \frac{T_c^P}{T_c^0} \) versus \( \tau_{\text{crit}}/\tau \) and of \( \Delta C_\nu^P(T)/\Delta C_\nu^0(T) \) and \( [H_c^P(0)/T_c^P]^2/[H_c^0(0)/T_c^0]^2 \) as function of \( \frac{T_c^P}{T_c^0} \). If such effects are observed, it may be possible to roughly compare the size of one impurity potential to another.
Fig. 11-1  Feynman diagrams for the self energy of an electron for the interactions considered in this chapter. These interactions are impurity scattering a) and b), electron-phonon interactions c) and d), and Coulomb repulsion e). The right hand interactions involve spin $\sigma$ and spin flipping. Figure d) is the dynamic or inelastic scattering self energy, as explained in this chapter.
Fig. 11-2  Ratio of the critical temperature of a dilute alloy to the pure material value, $T^P/T^0_C$, plotted against fractions of the inverse paramagnetic impurity scattering lifetime $1/2\pi\tau^P_{\text{crit}}$ required to destroy superconductivity for $B = 0.0$ (—), 0.05 (....), 0.25 (- - -), and 1.0 (---). The $B = 0.0$ curve is the static (AG) limit for a strong coupling superconductor. The (---) curve is the static AG limit for a weak coupling superconductor.
Fig. 11-3  Ratio of the values of the thermodynamic quantity $\Delta C(T_C)$ for a dilute alloy to the pure material value plotted against $T^P_C/T^0_C$ for various values of $B$. Same notation as Fig. 11-2.
Fig. 11-4  Ratio of the values of the thermodynamic quantity 
$[H_c(0)/T_c]^2$ for a dilute alloy to the pure material value plotted against $T^p_c/T^0_c$ for various values of $B$. Same notation as Fig. 11-2.
Fig. 11-5  Plot of $\frac{S(S+1)}{4} \frac{M_H}{M_I}$ versus the critical concentration of
paramagnetic impurities for $B = 0.05$ (-----), $B = 0.25$
(-----), and $B = 1.0$ (-----).
CHAPTER XII
SUMMARY

Rather than recapitulate what has been said in the concluding remarks of the previous ten chapters, this summary will, instead, deal with some of the aspects of the strong coupling theory of superconductivity as shown in those chapters that demonstrate its uses and versatility.

A good deal of that versatility lies in the availability of computer programmes that solve the nonlinear equations involved quickly and accurately, and in the existence of a varied selection of accurate tunneling derived electron-phonon spectral densities. Chapter II illustrates the accuracy of the programmes, and, thereby, of strong coupling theory, by showing how well such fine details as $\frac{d\Delta_1(\omega)}{d\omega}$ may be calculated when one has accurate spectral densities. Conversely, the accuracy of a measured spectrum can be checked by comparing the results of the programmes for tunneling, thermodynamic, and electromagnetic quantities to experiment, as was done in Chapter X for NbN. This is not inconsequential as tunneling results can be quite misleading. As an example, two recent tunneling experiments on $V_3Si^{(17,18)}$ have yielded spectra with widely different values of $\lambda$ and $\mu$. Subsequent calculations$^{(109,110)}$ revealed that the more conventional spectrum results were in much better agreement with other available experiments. $V_3Si$ is an interesting material to many in the
field but difficult to work with in tunneling experiments. Chapter X confirmed that NbN, also interesting yet difficult to experiment on, has a novelly large value of $\mu^*$. Confirming this point is important since few such high $\mu^*$ systems are known.

The speed of the programs and the accurate spectra allow systematic studies of empirical relations, as for $J_R$ in Chapter II and as between thermodynamic quantities and $2\Delta_0/k_B T_c$ in Chapter IX. Thus the accuracies of the relations may be checked, highlighting where they may not be applicable.

Furthermore, this speed allows investigation of which features of a spectra, the $\alpha^2 F(\Omega)$, are important to such measured quantities as $\Delta_0/k_B T_c$ using model spectra, either scaled tunneling derived spectra or more unphysical shapes such as delta functions. Chapters IV and V show that many superconducting properties do indeed depend almost completely on a few parameters of the spectrum such as the area and $\omega_n$. The main hope of such an investigation is that it may be easier to get a qualitative and quantitative microscopic understanding of these parameters than of $\alpha^2 F(\Omega)$ which would in turn lead to the fabrication of materials with desirable characteristics. As well, it indicates important ingredients for any successful description of the effects of pressure (Chapters VI and VII) and alloying (Chapter VIII) and the like.

Turning from the numerical possibilities of strong coupling theory, it is also possible to use the identified major parameters to analytically establish useful approximate formulae, as was done in
Chapter II for $\frac{1+\lambda}{\lambda} \frac{d\Delta_1(\omega)}{d\omega} \mid \Delta_0$ as a function of $\frac{T_c}{\Delta_0}$ in the background. Of course, is the numerical data often needed to fit parameters. In this way, the accuracy of the approximate equations can be estimated. And, in turn, the accuracy highlights the importance of the chosen parameter and the correctness of the assumptions on which the approximations were based.

The last point brought out in this thesis is that strong coupling theory is not a complete theory of all superconducting systems, but one in which new physics, such as the dynamic paramagnetic impurities of Chapter XI, may be incorporated. Often this may be done by extensions along well established methods and forms. On the other hand, mysteries abound in this field, the most notorious of late being the heavy fermion systems. Indeed, very recent experiments (111) on thin Pb films, perhaps demonstrate systems in which strong coupling theory will need major revision to apply if at all. One can be confident that the field of superconductivity will remain a good source of doctoral dissertations for years to come.
APPENDIX A

DERIVATION OF AN APPROXIMATE

ANALYTIC FORMULA FOR J_R

The starting point of the derivation is the zero temperature Eliashberg equations written on the real axis:

\[ \Delta(\omega)Z(\omega) = \int_{0}^{\infty} d\omega' \text{Re} \left( \frac{\Delta(\omega')}{\sqrt{\omega'^2 - \Delta^2(\omega')}} \right) \left[ \bar{K}_+(\omega, \omega') - \mu(\omega_c) \theta(\omega - \omega_c) \right] \]  \hspace{1cm} (A-1a)

\[ Z(\omega) = 1 - \frac{1}{\omega} \int_{0}^{\infty} d\omega' \text{Re} \left( \frac{\omega'}{\sqrt{\omega'^2 - \Delta^2(\omega')}} \right) \bar{K}_-(\omega, \omega') \]  \hspace{1cm} (A-1b)

where

\[ \bar{K}_+(\omega, \omega') = 2 \int_{0}^{\infty} d\Omega \alpha_F^2(\Omega) \frac{(\Omega + \omega')}{(\Omega + \omega')^2 - \omega'^2} \]  \hspace{1cm} (A-2)

and

\[ \bar{K}_-(\omega, \omega') = -2 \int_{0}^{\infty} d\Omega \alpha_F^2(\Omega) \frac{\omega}{(\Omega + \omega')^2 - \omega'^2} \]  \hspace{1cm} (A-3)
The first approximation is to ignore the imaginary part of $\Delta(\omega)$ and $Z(\omega)$. Then taking the derivative of equations (A-1a) and (A-1b), evaluating at $\omega = \Delta_0$, and rearranging yields

$$\frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega=\Delta_0} = \frac{1}{Z(\Delta_0)} \int_{\Delta_0}^\infty d\omega' \, \text{Re} \left( \frac{\Delta(\omega')}{\sqrt{\omega'^2 - \Delta^2(\omega')}} \right) \frac{\delta K_1(\omega,\omega')}{\delta \omega} \bigg|_{\Delta_0}$$

$$+ \frac{\Delta_1(\Delta_0)}{Z(\Delta_0)} \int_{\Delta_0}^\infty d\omega' \, \text{Re} \left( \frac{\Delta(\omega')}{\sqrt{\omega'^2 - \Delta^2(\omega')}} \right) \frac{\delta K_1(\omega,\omega')}{\delta \omega} \bigg|_{\Delta_0} \quad (A-4)$$

The next assumption is to set $\Delta(\omega') = \Delta_0$ inside the integrals in equation (A-4). As well, it will be assumed that all the important phonon frequencies in $\alpha^2 F(\Omega)$ are much larger in energy than the gap.

These assumptions reduce (A-4) to a much simpler form

$$\frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega=\Delta_0} = -\frac{4\Delta_0}{Z(\Delta_0)} \int_0^\infty d\Omega \, \alpha^2 F(\Omega) \int_{\Delta_0}^\infty d\omega' \, \frac{\Delta_0}{\sqrt{\omega'^2 - \Delta_0^2}} \frac{1}{(\omega' + \Omega)^3}$$

$$+ \frac{4\Delta_0^2}{Z(\Delta_0)} \int_0^\infty d\Omega \, \alpha^2 F(\Omega) \int_{\Delta_0}^\infty d\omega' \, \frac{\omega'}{\sqrt{\omega'^2 - \Delta_0^2}} \frac{1}{(\omega' + \Omega)^4} \quad (A-5)$$

which can be further reduced to
\[
\left. \frac{d\Delta_1(\omega)}{d\omega} \right|_{\omega=\Delta_0} = -\frac{4\Delta_0}{Z(\Delta_0)} \int_0^\infty d\Omega \frac{\alpha^2_F(\Omega)}{\Omega^3} \left[ -\frac{3}{2} \ln(\frac{\Delta_0}{\Omega}) - \frac{1}{6} \ln(\frac{\Delta_0}{2\Omega}) \right] \\
+ \frac{4\Delta_0^2}{Z(\Delta_0)} \int_0^\infty d\Omega \frac{\alpha^2_F(\Omega)}{\Omega^3} \frac{13}{6} \ln(\frac{\Delta_0}{\Omega}) 
\]
(A-6)

Following Marsiglio and Carbotte\(^{(30)}\), the final integrals over \(\alpha^2_F(\Omega)\) are approximated by

\[
\int_0^\infty d\Omega \frac{2\alpha^2_F(\Omega)}{\Omega^3} \ln(\frac{\Delta_0}{\Omega}) \approx \alpha_1 \frac{\ln(\frac{2\Delta_0}{\Omega})}{\ln(\frac{\Delta_0}{\Omega})} 
\]
(A-7)

and

\[
\int_0^\infty d\Omega \frac{2\alpha^2_F(\Omega)}{\Omega^3} \approx \alpha_2 \frac{\ln(\frac{\Delta_0}{\Omega})}{\ln(\frac{\Delta_0}{\Omega})} 
\]
(A-8)

with \(\alpha_1\) and \(\alpha_2\) to be treated later as parameters to be fitted to the exact data for \(J_R\).

An expression for \(Z(\Delta_0)\) has been worked out in the paper by Mitrovic, Zarate and Carbotte\(^{(24)}\) which contains a strong coupling correction, but this is not needed here since, in equation (A-6), each term is already proportional to a strong coupling correction which will be taken to be small. To be consistent, \(Z(\Delta_0)\) is replace by its approximate value \(1+\lambda\). This leads to a final formula of the form

\[
\left. \frac{d\Delta_1(\omega)}{d\omega} \right|_{\omega=\Delta_0} = \frac{\lambda}{1+\lambda} \left[ 2\alpha_2 \frac{\Delta_0}{\ln(\frac{\Delta_0}{2\Omega})} + \frac{22}{3} \alpha_1 \left( \frac{\Delta_0}{\ln(\frac{\Delta_0}{\Omega})} \right)^2 \right] 
\]
(A-9)
Finally, in equation (A-9), $\Delta_0$ is changed to $T_c$ using the BCS relation $2\Delta_0/k_B T_c = 3.53$; and two new parameters $a$ and $b$ are introduced to get the simple form

$$\frac{1+\lambda}{\lambda} \frac{d\Delta_1(\omega)}{d\omega} \bigg|_{\omega=\Delta_0} = a \left(\frac{T_c}{\omega_{\text{en}}}\right)^2 \ln \left(\frac{\omega_{\text{en}}}{bT_c}\right)$$

which is the final expression.
APPENDIX B
CONFIGURATIONAL AVERAGES

An alloy is a unique arrangement of host and impurity atoms located in the lattice. As the location of impurities is random translational invariance is lost. To restore the invariance one considers an ensemble of alloys containing all the possible arrangements and deals with the average. Invariance is thus restored since every lattice position is now occupied by an "average" atom. Summations over the lattice positions, as in equation (11-12), are then solvable by considering the probabilities of a particular sort of atom being at a given position.

The first step in doing actual configurational averages is to define the quantity \( \sigma(R_\xi) = -1 \) \((-1\) if \(R_\xi\) is a host (impurity) site. The next step is to consider averages of the following sort \( \langle \sigma(R_\xi) \rangle_{CA^*} \) \( \langle \sigma(R_\xi) \sigma(R_{\xi'}) \rangle_{CA^*} \) and so on. Thus, for an alloy \( A_{1-c} B_c \) where the B atoms are the impurities,

\[
\langle \sigma(R_\xi) \rangle_{CA} = (1-c)(+1) + c(-1)
\]

\[
= 1 - 2c
\]

is the configurational average weighting given to each lattice site. Calculating \( \langle \sigma(R_\xi) \sigma(R_{\xi'}) \rangle_{CA} \) requires more care. When \( \xi = \xi' \), the
answer is clearly \( \langle \sigma^2(R_\ell) \sigma(R_{\ell'}) \rangle_{CA} = 1 \). When \( \ell \neq \ell' \), the four possible combinations of types of atoms at \( R_\ell \) and \( R_{\ell'} \), must be considered. For example, the probability that there is an A atom at \( R_\ell \) is \( 1-c \); the probability that there is a second A atom at \( R_{\ell'} \) is slightly lower, \( \frac{(1-c)N - 1}{N - 1} \). The possible combinations then give

\[
\langle \sigma(R_\ell) \sigma(R_{\ell'}) \rangle_{CA} = \left[ (1-c) \left( \frac{(1-c)N - 1}{N - 1} \right) (+1)(+1) + c \frac{cN}{N - 1} (-1)(-1) + (1-c) \frac{cN}{N - 1} (+1)(-1) \right. \\
\left. + c \frac{(1-c)N}{N - 1} (-1)(+1) \right] (1 - \delta_{\ell,\ell'}) + \delta_{\ell,\ell'} \quad \cdot \quad (B-2)
\]

Rearranging the right hand side gives the expression

\[
\langle \sigma(R_\ell) \sigma(R_{\ell'}) \rangle_{CA} = (1-2c)^2 \frac{2}{N - 1} \frac{N}{N - 1} + \frac{1}{N - 1} + 4c(1-c) \frac{N}{N - 1} \delta_{\ell,\ell'} \quad \cdot \quad (B-3)
\]

which is as far as is necessary to go to do a configurational average of \( \frac{1}{2\pi r_N^2} \). In the limit of large \( N \), as is the case for alloys, equation (B-3) reduces to

\[
\langle \sigma(R_\ell) \sigma(R_{\ell'}) \rangle_{CA} = (1-2c)^2 + 4c(1-c) \delta_{\ell,\ell'} \quad \cdot \quad (B-4)
\]

Recalling, from equation (11-22).
\[
\frac{1}{2\pi r^N} = \frac{N(0)}{8\pi k_B T} \sum_{\epsilon, \epsilon'} \int \frac{d^3q}{q} \epsilon q \cdot (R_\epsilon - R_{\epsilon'} \cdot [V^N_\epsilon(q) V^N_{\epsilon'}(q) - \bar{V}^2(q)] \tag{B-5}
\]

It can be seen that it is necessary to calculate \(\langle V^N_\epsilon(q) V^N_{\epsilon'}(q) \rangle_{CA} \). To do so note that

\[
V^N_\epsilon(q) = \left[ \frac{1 - \sigma(R_\epsilon)}{2} \right] V_H(q) + \left[ \frac{1 - \sigma(R_\epsilon)}{2} \right] V_I(q)
\]

\[
V_H(q) - \left[ \frac{1 - \sigma(R_\epsilon)}{2} \right] (V_H(q) - V^N_I(q)) \tag{B-6}
\]

and thus

\[
V^N_\epsilon(q) V^N_{\epsilon'}(q) = V^2_H(q) - \left[ \frac{1 - \sigma(R_\epsilon)}{2} \right] (V_H(q) - V^N_I(q)) \cdot V_H(q);
\]

\[
- \left[ \frac{1 - \sigma(R_{\epsilon'})}{2} \right] (V_H(q) - V^N_I(q)) \cdot V_H(q)
\]

\[
+ \left[ \frac{1 - \sigma(R_\epsilon)}{2} \right] \left[ \frac{1 - \sigma(R_{\epsilon'})}{2} \right] (V_H(q) - V^N_I(q))^2 \tag{B-7}
\]

The configurational average is then

\[
\langle V^N_\epsilon(q) V^N_{\epsilon'}(q) \rangle_{CA} = V^2_H(q) - \left[ \frac{1 - \langle \sigma(R_\epsilon) \rangle_{CA}}{2} \right] \Delta V(q) \cdot V_H(q)
\]

\[
- \left[ \frac{1 - \langle \sigma(R_{\epsilon'}) \rangle_{CA}}{2} \right] \Delta V(q) \cdot V_H(q)
\]
\[ + \left\{ \frac{1 - <\sigma(R_{\ell})^2>_{CA} - <\sigma(R_{\ell})>_{CA}}{4} \right\} [\Delta V(q)]^2 \]

\[ + \left\{ \frac{<\sigma(R_{\ell})>_{CA} - <\sigma(R_{\ell})>_{CA}}{4} \right\} [\Delta V(q)]^2 \]

\[ (B-8) \]

where \( \Delta V(q) = V_H(q) - V_I^N(q) \). Next, using the results (B-2) and (B-4), this reduces to, after some rearrangement,

\[ <V_{\ell}^N(q)V_{\ell'}^N(q)>_{CA} = V_H^2(q) + 2c \Delta V(q) V_H(q) \]

\[ + [c^2 + c(1-c)\delta_{\ell, \ell'}] [\Delta V(q)]^2 \]

\[ (B-9) \]

Recalling that \( \bar{V}(q) = (1-c)V_H(q) + cV_I^N(q) \), equation (B-9) may also be written as

\[ <V_{\ell}^N(q)V_{\ell'}^N(q)>_{CA} = \bar{V}^2(q) + c(1-c)[\Delta V(q)]^2 \delta_{\ell, \ell'} \]

\[ (B-10) \]

Thus the configurational average of \( \frac{1}{2\pi^2} \) is

\[ \frac{1}{2\pi^2} < V^N_{\ell} >_{CA} = \frac{c(1-c)}{\pi N^2} \sum \int \frac{d^3q}{q} e^{i\bar{q} \cdot (R_{\ell} - R_{\ell'})} [\Delta V_{\ell}(q)]^2 \delta_{\ell, \ell'} \]

\[ (B-11) \]

which, to first order in \( c \), is
\[
\left< \frac{1}{2\pi^2} \frac{\hbar^2}{CA} \right> = \frac{c}{N} \frac{N(0)}{8\pi^2k_F^2} \int_{<2k_F} \frac{d^3q}{q} [\Delta V_{\xi}(q)]^2
\]

(b-12)

Configurational averages can also be used to expand the \( \alpha^2_F(\Omega) \) of an low concentration alloy in terms of the spectra of the host and impurity materials. The \( \alpha^2_F(\Omega) \) of an alloy\(^{(26)}\) is

\[
\alpha^2_F(\Omega) = \frac{1}{N^2} \frac{N(0)}{8\pi^2k_F^2} \sum_{\ell, \ell'} \int_{<2k_F} \frac{d^3q}{q} V_N^{q}(q) V_{\ell'}^N(q) \times
\]

\[
\sum_{\alpha \beta} \delta_{\alpha \beta} \delta_{\ell, \ell'; \Omega} q_{\beta} e^{iq \cdot (R_{\ell}^0 - R_{\ell'}^0)}
\]

(b-13)

To approximate \( \alpha^2_F(\Omega) \) the phonon structure, as given by \( D(\ell, \ell'; \Omega) \), is ignored and only the configurational average \( <V_N^q(q)V_{\ell'}^N(q)>_{CA} \) is considered. Note first, however, that equation (b-10) can be written as

\[
<V_N^{q}(q)V_{\ell'}^{N}(q)>_{CA} = (1-c)V_B^2(q) + cV_I^2(q)
\]

\[+ c(1-c) [\delta_{\ell, \ell'; -1}] [\Delta V(q)]^2
\]

(b-14)

Then equation (b-13) can be written as

\[
<\alpha^2_F(\Omega)>_{CA} = \frac{1-c}{N^2} \frac{N(0)}{8\pi^2k_F^2} \sum_{\ell, \ell'} \int_{<2k_F} \frac{d^3q}{q} V_{\ell}^2(q) \times
\]

\[
\sum_{\alpha \beta} \delta_{\alpha \beta} \delta_{\ell, \ell'; \Omega} q_{\beta} e^{iq \cdot (R_{\ell}^0 - R_{\ell'}^0)}
\]
\[
\sum_{\alpha\beta} \sum_{\epsilon', \epsilon} \sum_{\Omega} \frac{e^{i \mathbf{q} \cdot (\mathbf{R}_{\epsilon} - \mathbf{R}_{\epsilon'})}}{\mathbf{q}} \epsilon \epsilon' \Omega \mathcal{Q}_{\epsilon} \mathcal{Q}_{\epsilon'} (R_{\epsilon} - R_{\epsilon'})
\]

+ \frac{c}{N^2} \frac{N(0)}{8\pi^2 k_F^2} \sum_{\epsilon', \epsilon} \int_{<2k_F} \frac{d^3q}{q} V_1^2(q) \times

\sum_{\alpha\beta} \sum_{\epsilon', \epsilon} \sum_{\Omega} \frac{e^{i \mathbf{q} \cdot (\mathbf{R}_{\epsilon} - \mathbf{R}_{\epsilon'})}}{\mathbf{q}} \epsilon \epsilon' \Omega \mathcal{Q}_{\epsilon} \mathcal{Q}_{\epsilon'} (R_{\epsilon} - R_{\epsilon'})

+ \frac{c(1-c)}{N^2} \frac{N(0)}{8\pi^2 k_F^2} \sum_{\epsilon', \epsilon} \int_{<2k_F} \frac{d^3q}{q} [\delta_{\epsilon, \epsilon'} \epsilon] \Delta V^2(q) \times

\sum_{\alpha\beta} \sum_{\epsilon', \epsilon} \sum_{\Omega} \frac{e^{i \mathbf{q} \cdot (\mathbf{R}_{\epsilon} - \mathbf{R}_{\epsilon'})}}{\mathbf{q}} \epsilon \epsilon' \Omega \mathcal{Q}_{\epsilon} \mathcal{Q}_{\epsilon'} (R_{\epsilon} - R_{\epsilon'})
\]

(B-15)

Again ignoring phonon structure, equation (B-15) can be approximated as

\[
\langle \alpha^F(\Omega) \rangle_{CA} = c \alpha^2_F(\Omega) + (1-c) \alpha^F_1(\Omega) + c(1-c) \alpha^2_{HI} F(\Omega)
\]

(B-16)

where the third term \( \alpha^2_{HI} F(\Omega) \) should be small in comparison to \( \alpha^2_F(\Omega) \) or \( \alpha^F_1(\Omega) \) because \( \Delta V(q) \) is small since \( V_H(q) \) and \( V_1(q) \) are approximately the same size.
APPENDIX C

PAULI MATRICES

The Pauli \( \tau \) matrices are 4\( \times \)4 matrices and are given by

\[
\begin{align*}
\tau_0 &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & \tau_1 &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\
\tau_2 &= \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}, & \tau_3 &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\end{align*}
\tag{C-1}
\]

where each element of the matrix is a 2\( \times \)2 matrix. The Pauli \( \sigma \) matrices are defined

\[
\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_2 = \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}, \quad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\tag{C-2}
\]

The \( \tau_1 \sigma_j \) matrices have the elements of the \( \tau_1 \) matrices multiplied by the \( \sigma_j \) matrices. The \( \tau_1 \sigma_j \) matrices of interest are

\[
\begin{align*}
\tau_3 \cdot 1 &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \\
1 \cdot \sigma_2 &= \begin{bmatrix} \sigma_2 & 0 \\ 0 & \sigma_2 \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & i & 0 \end{bmatrix}
\end{align*}
\tag{C-3}
\]
\[ r_3 \cdot \sigma_1 = \begin{bmatrix} \sigma_1 & 0 \\ 0 & -\sigma_1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \]  
(C-5)

\[ r_3 \cdot \sigma_3 = \begin{bmatrix} \sigma_3 & 0 \\ 0 & -\sigma_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \]  
(C-6)

\[ r_2 \cdot \sigma_2 = \begin{bmatrix} 0 & -i\sigma_2 \\ i\sigma_2 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} \]  
(C-7)

As well there are certain identities of use

\[ r_3 \cdot 1 \ r_2 \cdot \sigma_2 \ r_3 \cdot 1 = -r_2 \cdot \sigma_2 \]  
(C-8)

\[ r_3 \cdot \sigma_1 \ r_2 \cdot \sigma_2 \ r_3 \cdot \sigma_1 = r_2 \cdot \sigma_2 \]  
(C-9)

\[ r_3 \cdot \sigma_3 \ r_2 \cdot \sigma_2 \ r_3 \cdot \sigma_3 = r_2 \cdot \sigma_2 \]  
(C-10)

\[ 1 \cdot \sigma_2 \ r_2 \cdot \sigma_2 \ 1 \cdot \sigma_2 = r_2 \cdot \sigma_2 \]  
(C-11)
APPENDIX D

RELATION BETWEEN THE TIME CORRELATION FUNCTION AND THE ALLOY PHONON GREEN FUNCTION

Much of what follows in this appendix is a simple extension of Appendix 2 of Doniach and Sondheimer (107) to the case for an alloy. The starting point is to consider the definition of the correlation function given by the thermal average

$$<u_{\alpha}(\epsilon,t)u_{\beta}(\epsilon',0)> = Z^{-1} \ Tr(e^{-\alpha H}e^{iHt}u_{\alpha}(\epsilon,0)e^{-iHt}u_{\beta}(\epsilon',0))$$  \hspace{1cm} (D-1)

where

$$Z=\text{Tr}(e^{-\alpha H})$$

is the partition function. Note that the Heisenberg picture is being used so that the time dependence of an operator is given by

$$A(t) = e^{iHt}A(0)e^{-iHt}$$  \hspace{1cm} (D-2)

If it is supposed that the system with Hamiltonian \(\mathcal{H}\) has a complete set of eigenstates \(\{\psi_n\}\) such that \(\mathcal{H}\psi_n\psi_n\), equation (D-1) can be written as

$$<u_{\alpha}(\epsilon,t)u_{\beta}(\epsilon',0)> = Z^{-1} \sum_n<\psi_n|e^{-\alpha H}e^{iHt}u_{\alpha}(\epsilon,0)e^{-iHt}u_{\beta}(\epsilon',0)|\psi_n>$$  \hspace{1cm} (D-3)
To extract the time dependence a complete set \( |m\rangle (\sum_m |m\rangle <m| = 1) \) is inserted to obtain

\[
\langle u_\alpha(\tau, t) u_\beta(\tau', 0) \rangle
\]

\[
= Z^{-1} \sum_{n,m} \langle n | u_\beta(\tau', 0) e^{-\Delta E |m\rangle <m | e^{i \omega t} u_\alpha(\tau, 0) e^{-\omega t} | n \rangle
\]

\[
= Z^{-1} \sum_{n,m} \langle n | u_\beta(\tau', 0) |m\rangle <m | u_\alpha(\tau, 0) \rangle | n \rangle e^{i (E_n - E_m) t} \quad (D-4)
\]

where the identity \( \text{Tr}(AB) = \text{Tr}(BA) \), with \( A \) and \( B \) matrices, has been used to shift the location of \( u_\beta(\tau', 0) \) in the summation. The fact that only the time difference is important with the correlation functions can be demonstrated by considering \( \langle u_\alpha(\tau, 0) u_\beta(\tau', -t) \rangle \)

\[
\langle u_\alpha(\tau, 0) u_\beta(\tau', -t) \rangle
\]

\[
= Z^{-1} \sum_{n,m} \langle n | e^{-\Delta E} u_\alpha(\tau', 0) |m\rangle <m | e^{-\omega t} u_\beta(\tau, 0) e^{\omega t} | n \rangle
\]

\[
= Z^{-1} \sum_{n,m} \langle n | u_\beta(\tau', 0) |m\rangle <m | u_\alpha(\tau, 0) \rangle | n \rangle e^{i (E_n - E_m) t} \quad (D-5)
\]

It becomes clear upon inspection that equations (D-4) and (D-5) differ only in the dummy counting variables used, hence

\[
\langle u_\alpha(\tau, t) u_\beta(\tau', 0) \rangle = \langle u_\alpha(\tau, 0) u_\beta(\tau', -t) \rangle \quad (D-6)
\]
The Fourier transform of \( u_\alpha(t) u_\beta(t',0) \) is

\[
J_{\alpha \beta}(t,t';\Omega) = \int_{-\infty}^{\infty} u_\alpha(t) u_\beta(t',0) e^{i\Omega t} \, dt
\]

\[
= 2\pi \sum_{n,m} e^{-\beta E_n} \langle n | u_\beta(t',0) | m \rangle \langle m | u_\alpha(t,0) | n \rangle \delta(E_m - E_n + \Omega). \tag{D-7}
\]

In the same way, it may be found that

\[
J_{\alpha \alpha}(t',t;\Omega) = \int_{-\infty}^{\infty} u_\alpha(t',0) u_\alpha(t,0) e^{i\Omega t} \, dt
\]

\[
= 2\pi \sum_{n,m} e^{-\beta E_n} \langle n | u_\alpha(t',0) | m \rangle \langle m | u_\alpha(t,0) | n \rangle \delta(E_m - E_n + \Omega). \tag{D-8}
\]

Since the \( \delta \)-function is nonzero only for \( E_n = E_m + \Omega \), (D-8) can be written

\[
J_{\alpha \alpha}(t',t;\Omega)
\]

\[
= 2\pi \sum_{n,m} e^{-\beta (E_n + \Omega)} \langle n | u_\alpha(t',0) | m \rangle \langle m | u_\alpha(t,0) | n \rangle \delta(E_m - E_n + \Omega),
\]

\[
e^{-\beta \Omega} J_{\alpha \beta}^1(t,t';\Omega) \tag{D-9}
\]

\( J_{\alpha \beta}^1(t,t';\Omega) \) is the spectral density function associated with the time
correlation function \( u_\alpha(\ell, t) u_\beta(\ell', 0) \). It is also a real function. This can be seen on noting that, since the displacement is a real quantity, the phase angle of \( \text{im}u_\beta(\ell', 0) \) is exactly the opposite of \( \text{im}u_\alpha(\ell, 0) \) and hence cancels out in the product of the two.

The next step is to consider the alloy phonon Green function defined in equation (11-19).

\[
D_{\alpha\beta}(\ell, \ell'; t) = 2\pi \langle [u_\alpha(\ell, t), u_\beta(\ell', 0)] \rangle
\]

\[
\begin{align*}
D_{\alpha\beta}^R(\ell, \ell'; t) & \quad t > 0 \\
D_{\alpha\beta}^A(\ell, \ell'; t) & \quad t < 0
\end{align*}
\]  

(D-10)

Now

\[
D_{\alpha\beta}^R(\ell, \ell'; t) = i2\pi \theta(t) \{ \langle u_\alpha(\ell, t) u_\beta(\ell', 0) \rangle - \langle u_\beta(\ell', 0) u_\alpha(\ell, t) \rangle \}
\]

\[
= i\theta(t) \int_{-\infty}^{\infty} \left( j_{\alpha\beta}(\ell, \ell'; \omega) - j_{\beta\alpha}(\ell', \ell; \omega) \right) e^{-i\omega t} \, d\omega
\]

\[
= i\theta(t) \int_{-\infty}^{\infty} \left( 1 - e^{-\omega} \right) j_{\alpha\beta}(\ell, \ell'; \omega) e^{-i\omega t} \, d\omega ,
\]

(D-11)

where the inverse transforms of equations (D-7) and (D-8) have been used. Next, a complex Fourier transform of (D-11) is taken where \( \Omega \) is regarded as a complex variable with a nonzero (but infinitesimal)
imaginary part. The imaginary part must be chosen negative for \( t < 0 \) and positive for \( t > 0 \). This yields

\[
D_{\alpha\beta}^{R}(\ell, \ell'; t) = i \int_{-\infty}^{\infty} \frac{(1 - e^{-\alpha \omega})}{\omega - \omega + i \eta} J_{\alpha\beta}^{1}(\ell, \ell'; \omega) \times \int_{0}^{\infty} e^{\ell(\Omega - \omega + i \eta) t} dt d\omega. \tag{D-12}
\]

Doing the last integral yields

\[
D_{\alpha\beta}^{R}(\ell, \ell'; t) = -\left[ \int_{-\infty}^{\infty} \frac{(1 - e^{-\alpha \omega})}{\omega - \omega + i \eta} J_{\alpha\beta}^{1}(\ell, \ell'; \omega) \right]. \tag{D-13}
\]

Making use of the identity

\[
\frac{1}{\omega + i \eta} = \mathcal{F}\left(\frac{1}{x}\right) - i \pi \delta(x) \tag{D-14}
\]

and recalling that \( J_{\alpha\beta}^{1}(\ell, \ell'; \Omega) \) is real, one has the relation

\[
j_{m} D_{\alpha\beta}^{R}(\ell, \ell'; \Omega) = \pi \left(1 - e^{-\alpha \Omega}\right) J_{\alpha\beta}^{1}(\ell, \ell'; \Omega) \Omega > 0. \tag{D-15}
\]

In a similar fashion, for

\[
D_{\alpha\beta}^{A}(\ell, \ell'; t) = i 2\pi \theta(t) \langle u_{\alpha}(\ell, t) u_{\beta}(\ell', 0) \rangle
\]
it is found that

$$J_{\alpha \beta}^{A}(\varepsilon, \varepsilon'; \Omega) = (1 - e^{-\Omega t}) J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; \Omega) \quad \Omega < 0.$$  \hspace{1cm} (D-17)

It will be useful here to consider how $J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; \Omega)$ and $J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; -\Omega)$ are related. Now, from equation (D-7),

$$J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; -\Omega) = \int_{-\infty}^{\infty} <u_{\alpha}(\varepsilon, t) u_{\beta}(\varepsilon', 0)> e^{-i\Omega t} dt.$$  \hspace{1cm} (D-18)

Making a change of variable from $t$ to $-t$, and making use of fact that only the time difference is of importance,

$$J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; \Omega) = - \int_{-\infty}^{\infty} <u_{\alpha}(\varepsilon, 0) u_{\beta}(\varepsilon', t)> e^{i\Omega t} dt.$$

$$= - 2\pi Z^{-1} \sum_{n,m} e^{-\beta_{n}} <m|u_{\alpha}(\varepsilon', 0)|m> <m|u_{\beta}(\varepsilon, 0)|m> \delta(E_{m} - E_{n} - \Omega).$$  \hspace{1cm} (D-19)

Since the $J_{\alpha \beta}^{1}(\varepsilon, \varepsilon'; \Omega)$ is real, one may take the complex conjugate of the right hand side of equation (D-19). Doing this, and using the hermicity of the displacement operator, yields

$$J_{\alpha \beta}^{1}(\varepsilon', \varepsilon; -\Omega).$$
\[-2\pi^{-1} \sum_{n,m} e^{-\beta \mu_n} \langle n | u_\rho(\epsilon', 0) | m \rangle \langle m | u_\alpha(\epsilon, 0) | n \rangle \delta(E_n - E_m - \Omega) \]

\[-J^2_{\alpha \rho}(\epsilon, \epsilon'; \Omega)\]

\[-e^{-\beta \Omega} J^1_{\alpha \rho}(\epsilon, \epsilon'; \Omega)\]  \hspace{1cm} (D-20)

Thus the equation for \(J^D_{\alpha \rho}(\epsilon, \epsilon'; \Omega)\) may be written as

\[J^D_{\alpha \rho}(\epsilon, \epsilon'; \Omega) = \pi (1 - e^{-\beta \Omega}) J^1_{\alpha \rho}(\epsilon, \epsilon'; \Omega) \quad \Omega < 0. \]  \hspace{1cm} (D-21)

and, by extension,

\[J^D_{\alpha \rho}(\epsilon, \epsilon'; \Omega) = J^D_{\alpha \rho}(\epsilon, \epsilon'; \Omega) + J^D_{\alpha \rho}(\epsilon, \epsilon'; \Omega)\]

\[= \pi (1 - e^{-\beta \Omega}) J^1_{\alpha \rho}(\epsilon, \epsilon'; \Omega)\]  \hspace{1cm} (D-22)

which is symmetric about \(\Omega\).

The final point of interest is that temperature Green functions are also determined by the spectral density functions, and hence by the imaginary part of \(D(\epsilon, \epsilon'; \Omega)\), as is shown next. Consider

\[D_{\alpha \rho}(\epsilon, \epsilon'; \tau) = -2\pi \langle \langle T[u_\alpha(\epsilon, \tau), u_\rho(\epsilon', 0)] \rangle \rangle\]

\[= -2\pi \theta(\tau) \langle u_\alpha(\epsilon, \tau) u_\rho(\epsilon', 0) \rangle\]
\[ + 2\pi \theta(-\tau) \langle u_\rho(\epsilon',0)u_\alpha(\epsilon,\tau) \rangle \quad \text{(D-23)} \]

where \( T \) is the imaginary time ordering operator. Proceeding, as in the case of the real time correlation function, one finds

\[ \langle u_\alpha(\epsilon,\tau)u_\rho(\epsilon',0) \rangle \]

\[ = Z^{-1} \sum_{n,m} e^{-\phi_n} \langle n | u_\rho(\epsilon',0) | m \rangle \langle m | u_\alpha(\epsilon,0) | n \rangle e^{(E_m - E_n)\tau} \quad \text{(D-24)} \]

and

\[ \langle u_\rho(\epsilon',0)u_\alpha(\epsilon,\tau) \rangle \]

\[ = Z^{-1} \sum_{n,m} e^{-\phi_n} \langle n | u_\rho(\epsilon',0) | m \rangle \langle m | u_\alpha(\epsilon,0) | n \rangle e^{(E_m - E_n)\tau} \quad \text{(D-25)} \]

From this, using Fourier transforms appropriate to the \( \omega_\nu \) and \( \tau \) variables, one finds

\[ D_{\alpha\delta}(\epsilon,\tau;\omega_\nu) = \frac{1}{\beta} \int_0^\beta d\tau' e^{-i\omega_\nu \tau'} D_{\alpha\delta}(\epsilon,\epsilon';\tau) \]

\[ = -\frac{2\pi}{\beta} \int_0^\beta d\tau' e^{-i\omega_\nu \tau'} \langle u_\alpha(\epsilon,\tau)u_\rho(\epsilon',0) \rangle \]
\[ v = -\frac{2\pi}{\hbar^2} \sum_{n,m} \left< n \left| u_\alpha(\ell',0) \right| m \right> \left< m \left| u_\alpha(\ell,0) \right| n \right> \frac{e^{-\beta E_n} - e^{-\beta E_m}}{E_n - E_m - i\omega_N} \]  

(D-26)

This may be related to \( J^{\perp}_{\alpha\beta}(\ell,\ell';\Omega) \) through the simple integration

\[ D_{\alpha\beta}(\ell,\ell';\omega_N) = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \left( 1 - e^{-\beta\Omega} \right) \frac{J^{\perp}_{\alpha\beta}(\ell,\ell';\Omega)}{\Omega - i\omega_N} \, d\Omega \]  

(D-27)

which, using the definition given in (D-21) and changing the range of the integral, is

\[ \frac{2\pi}{\hbar} \int_{0}^{\beta} dr \, e^{-i\omega_N r} \left< u_\alpha(\ell,r) u_\beta(\ell',0) \right> \]

\[ = \frac{2}{\hbar} \int_{0}^{\infty} d\Omega \, J^{\perp}_{\alpha\beta}(\ell,\ell';\Omega) \frac{2\Omega}{\Omega^2 + \omega_N^2} \]  

(D-28)

which is the identity needed in Chapter 11.
REFERENCES


(9) J.M. Rowell, W.L. McMillan and R.C. Dynes, a tabulation of spectral densities, private communication.


(41) F. Marsiglio, J.P. Carbotte and E. Schachinger, accepted by J. Low Temp. Phys.


(49) P. Hermans, J.C. Ho, J. Boyer and N.E. Phillips, Jour. de Phys. 39, C6, 477 (1978). I would like to thank Dr. Phillips for bringing this paper to my attention.


(51) J.W. Garland and K.H. Bennemann, in Superconductivity in d- and


(60) G.K. White, Phil. Mag. 7, 271 (1962).


(69) G.K. White, Cryogenics 2, 292 (1962).


(74) F. Marsiglio, J.M. Coombs and J.P. Carbotte, accepted by *Phys. Rev. B*.


(98) S.B. Nam, Phys. Rev. 156, 470 (1967); 156, 487 (1967).


Vol. 2.


