# 6.730

# "Real" Semiconductor Project

# GaAs

# Part 2

Janice Lee
Juan Montoya
Bhuwan Singh
Corina Tanasa

(Friday, March 22, 2001)
Tuesday, April 3, 2001

## 1. How many force constants are required for each bond? Why?

In the Born force constant model, each bond can stretch and bend. These two degrees of freedom correspond to two arbitrary constants. Thus, two force constants are required for each bond. These force constants are $\alpha_S$, the elastic constant for stretching, and $\alpha_\phi$, the elastic constant for bending. Different types of bonds will have different $\alpha_S$ and $\alpha_\phi$ constants, but regardless of the number of different bond types present, there will still be two force constants for each bond.

## 2. What is the energy of a single bond in the Born model?

The energy of a single bond in the Born model, between atom 1 at $\vec{R}$ and atom 2 at $\vec{R} + \vec{a}_1$, is given as

$$E(\vec{R}, \vec{R} + \vec{a}_1) = \frac{1}{2}\alpha_S \left| \vec{a}_1 \cdot \left( \vec{u}[\vec{R} + \vec{a}_1] - \vec{u}[\vec{R}] \right) \right|^2 + \frac{1}{2}\alpha_\phi \left( \left| \vec{u}[\vec{R} + \vec{a}_1] - \vec{u}[\vec{R}] \right|^2 - \left| \vec{a}_1 \cdot \left( \vec{u}[\vec{R} + \vec{a}_1] - \vec{u}[\vec{R}] \right) \right|^2 \right)$$

(1)

where $\alpha_S$ is the elastic constant for stretching of the bond, $\alpha_\phi$ is the elastic constant for bending of the bond, $\vec{a}_1$ is a vector from atom 1 to atom 2, $\vec{R}$ is a vector from the origin to atom 1 (and correspondingly $\vec{R} + \vec{a}_1$ is a vector from the origin to atom 2), and $\vec{u}[\vec{R}]$ and $\vec{u}[\vec{R} + \vec{a}_1]$ are the displacements from equilibrium of atoms 1 and 2, respectively.

## 3. The model assumes that the bond is only slightly displaced from equilibrium. How would you modify the model to make the bond energy more realistically dependent on displacement from equilibrium – what order would the corrections be, and of what sign? Justify your answer physically; include sketches if appropriate.

The Born model implicitly incorporates the assumption that the atoms are only slightly displaced from equilibrium. This assumption affects the expressions for both the bending energy $E_\phi$ and the stretching energy $E_S$. In particular, the expression that was used for $E_\phi$

assumes small angular displacement and the expression for E_S assumes small distance displacement. An exact treatment for the two energies is presented below; these results are then compared to the Born approximation answers.

## Bond Bending

Figure 1 illustrates the bending of a bond. The Born model assumes that for small angles $\phi$, the arc length $s$ can be approximated by the perpendicular distance $x$.
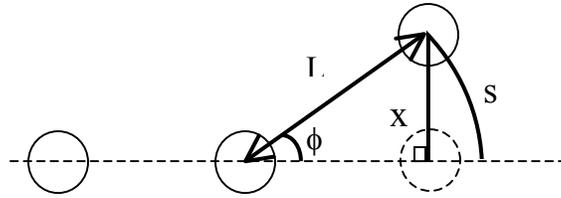


**Figure 1**: *Bond bending*: atom with an equilibrium spacing L is bent by an angle $\phi$

The exact calculation is shown in Eq. (2)

$$\textit{(Exact)} \qquad E_\phi = \frac{1}{2}\alpha_\phi s^2 = \frac{1}{2}\alpha_\phi L^2 \phi^2 \qquad (2)$$

Equations (3) and (4) show the approximation steps used in the Born model

$$\textit{(Born model)} \qquad E_\phi = \frac{1}{2}\alpha_\phi \mid u_{iy} - u_{jy} \mid^2 = \frac{1}{2}\alpha_\phi x^2 \qquad (3a)$$

$$= \frac{1}{2}\alpha_\phi L^2 \sin^2(\phi) \qquad (3b)$$

$$= \frac{1}{2}\alpha_\phi L^2 (\phi - \frac{\phi^3}{3!} + ...)^2 \qquad (3c)$$

$$= \frac{1}{2}\alpha_\phi L^2 (\phi^2 - \frac{\phi^4}{3} + ...) \qquad (4)$$

By comparing Eq. (2) and (4), one can see that the required correction to the bending energy in the Born model is $\frac{1}{2}\alpha_\phi L^2 \frac{\phi^4}{3}$, which is a positive correction to the fourth order in $\phi$.

*Bond Stretching*

Figure 2 illustrates the stretching of a bond.
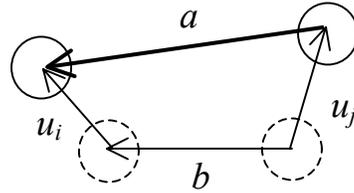


**Figure 2**: Bond stretching: $u_i$ and $u_j$ are the displacements of the atoms.
In the Born model, the component of u perpendicular to the b direction is assumed to be small.

*(Exact)* $$E_S = \frac{1}{2}\alpha_S(|\vec{a}| - |\vec{b}|)^2 = \frac{1}{2}\alpha_S(|\vec{b} + \vec{u}_j - \vec{u}_i| - |\vec{b}|)^2 \qquad (5)$$

*(Born model)* $$E_\phi = \frac{1}{2}\alpha_S[\vec{b} \bullet (\vec{u}_j - \vec{u}_i)] \qquad (6)$$

The stretching energy from the Born model assumes the component $\vec{b} \times (u_j - u_i)$ is small and is therefore ignored. For the exact solution, it has to be incorporated into the calculations.

These corrections make the energy expressions more exact under the assumption that the bonds can be accurately modeled as springs. This approximation may be valid for small displacements, but it is not valid for considerably larger displacements. The actual potential is not harmonic; it just appears harmonic around the minimum of the well.

4. How many force constants will your model require and how large will the dynamical matrix be for nearest-neighbor couplings? What if you use next-nearest neighbor couplings?

If you use nearest neighbor coupling or next-nearest neighbor coupling the dynamical matrix will be a 6x6 matrix. The size of the dynamical matrix is determined by the dimensions in the problem, in this case 3, and the number of atoms per basis in the problem, two in this case.

One bending constant and one stretching constant will be required for the nearest neighbor model since a Ga atom bonding with an As atom will require a spring stretch constant $\alpha_s$ and its associated bending constant $\alpha_\phi$. In contrast, a next-nearest neighbor model in combination with the nearest neighbor model will require a total of six constants. There will be three different types of bonds: Ga-Ga, Ga-As, and As-As. Three of the constants will be due to stretching in the three different types of bonds. The other three constants are associated with the bending of these bonds. The dynamical matrix will still be a 6 x 6 matrix in this case as formerly mentioned.

## 5. How many independent elastic constants does your material possess?

For the cubic lattice of GaAs, the elastic response tensor simplifies to only three independent second-order moduli given in Table 1. [1]

**Table 1:** Elastic constants for GaAs at T = 77K and 300K

| Elastic Constants [$10^{10}$dynes/cm$^2$] | Temperature | |
|---|---|---|
| | T = 300K | T = 77K |
| $C_{11}$ | $119.0 \pm 0.1$ | $122.1 \pm 0.3$ |
| $C_{12}$ | $53.8 \pm 0.1$ | $56.6 \pm 0.3$ |
| $C_{44}$ | $59.5 \pm 0.1$ | $59.9 \pm 0.1$ |

How well the Born model predicts the actual elastic constant values is measured by the so-called "Born ratio". In particular, the Born ratio is required to be unity for the GaAs structure, but it turns out to be 1.05 (5% discrepancy). This suggests that the nearest neighbor approach does not provide a general solution for cubic materials. This is because the effect from the remote neighbors in a cubic structure cannot be safely ignored. Firstly, the next-nearest neighbors are in fact not too much further away in position than the nearest neighbors. Secondly, the number of atoms increases significantly as one moves out and counts the nearest, the next-nearest, the next-next nearest neighbors and so on. So even though the next-nearest neighbors may not have as

intimate an effect as the nearest neighbors, the fact that there are more of those types of atoms may still give a significant effect.

1. The attached drawing labels all the atoms in the basis and all their nearest neighbors. For each atom labeled **A-H**, verify that the lattice vectors $\mathbf{R_p}$ to each unit cell, taking atom of type 1 in cell **A** as the origin, is given by the vectors labeled cell B, etc.

GaAs has a zincblende structure, as was discussed in the first part of the project. The lattice is fcc with the cubic lattice constant $a$. Without loss of generality, one can assume that the As atom is at the origin. Around this atom, there are 4 Ga atoms all at an equal distance from the As atom. The coordinates of these Ga atoms as well as the unit vectors from the As atom to the Ga atoms are given in Table 2.

**Table 2**: Positions of Ga atoms neighboring As atom at origin

| Neighboring Atom | x-coordinate ($a$) | y-coordinate ($a$) | z-coordinate ($a$) | Unit vector from As atom to Ga atom |
|---|---|---|---|---|
| 1 | ¼ | ¼ | ¼ | $\bar{a}_A = \dfrac{1}{\sqrt{3}}(\hat{x}+\hat{y}+\hat{z})$ |
| 2 | -¼ | -¼ | ¼ | $\bar{a}_B = \dfrac{1}{\sqrt{3}}(-\hat{x}-\hat{y}+\hat{z})$ |
| 3 | ¼ | -¼ | -¼ | $\bar{a}_C = \dfrac{1}{\sqrt{3}}(\hat{x}-\hat{y}-\hat{z})$ |
| 4 | -¼ | ¼ | -¼ | $\bar{a}_D = \dfrac{1}{\sqrt{3}}(-\hat{x}+\hat{y}-\hat{z})$ |

Around each Ga atom, there are 4 As atoms at an equal distance from the Ga atom. For example, around the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})\cdot a$ Ga atom, there are 4 equally spaced As atoms. The locations of these As atoms as well as the unit vectors from the Ga atom are given in Table 3.

**Table 3**: Positions of As atoms neighboring Ga atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$

| Neighboring Atom | x-coordinate (units of $a$) | y-coordinate (units of $a$) | z-coordinate (units of $a$) | Unit vector from Ga atom to As atom |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | $\bar{a}_E = \dfrac{1}{\sqrt{3}}(-\hat{x} - \hat{y} - \hat{z})$ |
| 2 | ½ | ½ | 0 | $\bar{a}_F = \dfrac{1}{\sqrt{3}}(\hat{x} + \hat{y} - \hat{z})$ |
| 3 | 0 | ½ | ½ | $\bar{a}_G = \dfrac{1}{\sqrt{3}}(-\hat{x} + \hat{y} + \hat{z})$ |
| 4 | ½ | 0 | ½ | $\bar{a}_H = \dfrac{1}{\sqrt{3}}(\hat{x} - \hat{y} + \hat{z})$ |

2. Attached is a general expression for the potential energy of all the atoms in the crystal in terms of their displacements from equilibrium. A Born force model was used which considers only nearest neighbor interactions to simplify this expression.

The basis of the lattice is an As atom at $(0,0,0)\cdot a$ and a Ga atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\cdot a$. The basis is at a location $\bar{R}$ from an arbitrary origin. The following cells will be considered:

(1) cells which have as origins the 4 As atoms specified in Table 3.

These cells will have displacement vectors $\bar{u}_1[\bar{R}]$, $\bar{u}_1[\bar{R} + cell\bar{F}]$,

$\bar{u}_1[\bar{R} + cell\bar{G}]$, and $\bar{u}_1[\bar{R} + cell\bar{H}]$ where $cell\bar{F} = (\frac{1}{2}, \frac{1}{2}, 0)\cdot a = \frac{a}{2}(\hat{x} + \hat{y})$,

$cell\bar{G} = (0, \frac{1}{2}, \frac{1}{2})\cdot a = \frac{a}{2}(\hat{y} + \hat{z})$, and $cell\bar{H} = (\frac{1}{2}, 0, \frac{1}{2})\cdot a = \frac{a}{2}(\hat{x} + \hat{z})$.

(2) cells which contain the 4 Ga atoms specified in Table 2.

The origins of these cells are at $(0,0,0)\cdot a$,

$cell\bar{B} = (-\frac{1}{2}, -\frac{1}{2}, 0)\cdot a = \frac{a}{2}(-\hat{x} - \hat{y})$, $cell\bar{C} = (0, -\frac{1}{2}, -\frac{1}{2})\cdot a = \frac{a}{2}(-\hat{y} - \hat{z})$,

and $cell\bar{D} = (-\frac{1}{2}, 0, -\frac{1}{2})\cdot a = \frac{a}{2}(-\hat{x} - \hat{z})$.

The total elastic potential energy for the collection of these cells and atoms will be:

$$V = \frac{1}{2}\alpha_s \left| \bar{a}_A \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R}]) \right|^2 + \frac{1}{2}\alpha_s \left| \bar{a}_B \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{B}]) \right|^2 + \frac{1}{2}\alpha_s \left| \bar{a}_C \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{C}]) \right|^2 +$$

$$\frac{1}{2}\alpha_s \left| \bar{a}_D \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{D}]) \right|^2 + \frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R}] \right|^2 - \left| \bar{a}_A \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{B}] \right|^2 - \left| \bar{a}_B \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{B}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{C}] \right|^2 - \left| \bar{a}_C \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{C}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{D}] \right|^2 - \left| \bar{a}_D \cdot (\bar{u}_1[\bar{R}] - \bar{u}_2[\bar{R} + cell\bar{D}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_s \left| -\bar{a}_B \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{F}]) \right|^2 + \frac{1}{2}\alpha_s \left| -\bar{a}_C \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{G}]) \right|^2 +$$

$$\frac{1}{2}\alpha_s \left| -\bar{a}_D \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{H}]) \right|^2 + \frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{F}] \right|^2 - \left| -\bar{a}_B \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{F}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{G}] \right|^2 - \left| -\bar{a}_C \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{G}]) \right|^2 \right\} +$$

$$\frac{1}{2}\alpha_\phi \left\{ \left| \bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{H}] \right|^2 - \left| -\bar{a}_D \cdot (\bar{u}_2[\bar{R}] - \bar{u}_1[\bar{R} + cell\bar{H}]) \right|^2 \right\}$$

(7)

where the first 4 terms are stretching with the As atom at the origin, the next 4 terms are bending with this atom, the next 3 terms are stretching with the Ga atom, and the last 3 terms are bending with the Ga atom.

3. Use the expression for the potential energy to determine the force on a given atom in the crystal in terms of its displacement and its neighbor's displacements. Check your answers by directly calculating the force from the spring constants and displacements.

Calculating the force on a given atom using the expression for the potential energy requires careful calculation of partial derivatives. In the model that is considered here, it is only necessary that the force on one atom of the basis be calculated with respect to its neighbors, because the force on the other atom of the basis can be determined through symmetry considerations, etc. The force on atom 1 at the origin will be

calculated. Thus, attention will be restricted to those terms in the potential energy that contain $\bar{u}_1[\vec{R}]$. The potential energy is broken up into four separate parts as described earlier. The first part is the stretching energy for atoms connected to atom 1 at the origin. The second part is the bending energy for atoms connected to atom 1 at the origin. The other two terms describe energy due to atom 2 and are therefore unimportant here. In order to compute the force on a given atom by using the potential energy, one needs to take the derivative with respect to the displacement of the atom as given by equation 6.8 in PSSA

$$M \frac{\partial^2}{\partial t^2} u[n] = -\frac{\partial}{\partial u[n]} V(\{u[i]\}) \tag{8}$$

The force contribution from the first part of the potential is given as

$$-\frac{\partial}{\partial u_{1x}[R]}(V_{s1}) = -\frac{4}{3}\alpha_s \cdot u_{1x}[\vec{R}] + \frac{1}{3}\alpha_s \cdot u_{2x}[\vec{R}] + \frac{1}{3}\alpha_s \cdot u_{2y}[\vec{R}] + \frac{1}{3}\alpha_s \cdot u_{2z}[\vec{R}] + \frac{1}{3}\alpha_s \cdot u_{2x}[\vec{R}+\vec{R}_b] -$$

$$\frac{1}{3}\alpha_s \cdot u_{2x}[\vec{R}+\vec{R}_b] + \frac{1}{3}\alpha_s \cdot u_{2x}[\vec{R}+\vec{R}_c] - \frac{1}{3}\alpha_s \cdot u_{2y}[\vec{R}+\vec{R}_c] - \frac{1}{3}\alpha_s \cdot u_{2z}[\vec{R}+\vec{R}_c] + \frac{1}{3}\alpha_s \cdot u_{2x}[\vec{R}+\vec{R}_d]$$

$$-\frac{1}{3}\alpha_s \cdot u_{2y}[\vec{R}+\vec{R}_d] + \frac{1}{3}\alpha_s \cdot u_{2z}[\vec{R}+\vec{R}_d]$$

$$\tag{9}$$

The force contribution due to the second term in the potential is

$$-\frac{\partial}{\partial u_{1x}[R]}(V_{\phi 1}) = -\frac{2}{3}\alpha_\phi \cdot u_{2x}[\vec{R}+\vec{R}_d] + \frac{2}{3}\alpha_\phi \cdot u_{2x}[\vec{R}+\vec{R}_c] + \frac{2}{3}\alpha_\phi \cdot u_{2x}[\vec{R}+\vec{R}_b] - \frac{8}{3}\alpha_\phi \cdot u_{1x}[\vec{R}] + \frac{2}{3}\alpha_\phi \cdot u_{2x}[\vec{R}] +$$

$$\frac{1}{3}\alpha_\phi \cdot u_{2x}[\vec{R}+\vec{R}_c] + \frac{1}{3}\alpha_\phi \cdot u_{2y}[\vec{R}+\vec{R}_c] - \frac{1}{3}\alpha_\phi \cdot u_{2y}[\vec{R}+\vec{R}_b] - \frac{1}{3}\alpha_\phi \cdot u_{2x}[\vec{R}] - \frac{1}{3}\alpha_\phi \cdot u_{2y}[\vec{R}] - \frac{1}{3}\alpha_\phi \cdot u_{2z}[\vec{R}+\vec{R}_d] +$$

$$\frac{1}{3}\alpha_\phi \cdot u_{2y}[\vec{R}+\vec{R}_d] + \frac{1}{3}\alpha_\phi \cdot u_{2z}[\vec{R}+\vec{R}_b]$$

$$\tag{10}$$

The third and fourth terms do not effect the force in the x direction of an atom of type 1.

$$-\frac{\partial}{\partial u_{1x}[R]}(V_{s2}) = 0 \tag{11}$$

$$-\frac{\partial}{\partial u_{1x}[R]}(V_{\phi 2}) = 0$$

(12)

Combining the contribution from the four potentials to find the total force on an atom of type 1 in the x direction results in the following equation

$$f_{1x} = -4\frac{(\alpha_s + 2\alpha_\phi)}{3}(u_{1x}[\vec{R}]) + \frac{(\alpha_s + 2\alpha_\phi)}{3}(u_{2x}[\vec{R}] + u_{2x}[\vec{R} + \vec{R}_b] + u_{2x}[\vec{R} + \vec{R}_c] + u_{2x}[\vec{R} + \vec{R}_d]) +$$

$$\frac{(\alpha_s - \alpha_\phi)}{3}(u_{2y}[\vec{R}] + u_{2y}[\vec{R} + \vec{R}_b] - u_{2y}[\vec{R} + \vec{R}_c] - u_{2y}[\vec{R} + \vec{R}_d]) +$$

$$\frac{(\alpha_s - \alpha_\phi)}{3}(u_{2z}[\vec{R}] + u_{2z}[\vec{R} + \vec{R}_b] + u_{2z}[\vec{R} + \vec{R}_c] + u_{2z}[\vec{R} + \vec{R}_d])$$

(13)

Recognizing that

$$u_i[\vec{R} + \vec{R}_p] = e^{i\vec{k}\cdot\vec{R}_p}u_i[\vec{R}]$$

(14)

equation (13) can be rewritten as

$$f_{1x} = -4\frac{(\alpha_s + 2\alpha_\phi)}{3}(u_{1x}[\vec{R}]) + \frac{(\alpha_s + 2\alpha_\phi)}{3}(1 + e^{i\vec{k}\cdot\vec{R}_b} + e^{i\vec{k}\cdot\vec{R}_c} + e^{i\vec{k}\cdot\vec{R}_d})(u_{2x}[\vec{R}])$$

$$+\frac{(\alpha_s - \alpha_\phi)}{3}(1 + e^{i\vec{k}\cdot\vec{R}_b} - e^{i\vec{k}\cdot\vec{R}_c} - e^{i\vec{k}\cdot\vec{R}_d})(u_{2y}[\vec{R}])$$

(15)

$$+\frac{(\alpha_s - \alpha_\phi)}{3}(1 - e^{i\vec{k}\cdot\vec{R}_b} - e^{i\vec{k}\cdot\vec{R}_c} + e^{i\vec{k}\cdot\vec{R}_d})(u_{2z}[\vec{R}])$$

From the above equation, it is seen that $f_{1x}$ is in the form shown below

$$f_{1x} = -A(u_{1x}[\vec{R}]) - B(u_{2x}[\vec{R}]) - C(u_{2y}[\vec{R}]) - D(u_{2z}[\vec{R}])$$

(16)

where A, B, C, and D are the elements in the dynamical matrix. This makes intuitive sense in terms of hooks law $F = -kx$. In general then,

$$\begin{bmatrix} f_{1x} \\ f_{1y} \\ f_{1z} \\ f_{2x} \\ f_{2y} \\ f_{2z} \end{bmatrix} = \begin{bmatrix} A & 0 & 0 & B & C & D \\ 0 & A & 0 & C & B & E \\ 0 & 0 & A & D & E & B \\ B^* & C^* & D^* & A & 0 & 0 \\ C^* & B^* & E^* & 0 & A & 0 \\ D^* & E^* & B^* & 0 & 0 & A \end{bmatrix} \begin{bmatrix} u_{1x} \\ u_{1y} \\ u_{1z} \\ u_{2x} \\ u_{2y} \\ u_{2z} \end{bmatrix}$$

(17)

4. The simplified expression for the potential energy was used to calculate the dynamical matrix. Verify from the potential, by explicitly taking the derivatives, the factors in the matrix labeled *A* and *B*.

$$A = \sum_{\overline{R}_p} \left( \frac{\partial^2 V}{\partial u_{i,n}[\overline{R}]\partial u_{i,n}[\overline{R}+\overline{R}_p]} \right)_{eq} e^{-i\vec{k}\cdot\overline{R}_p} \tag{18}$$

where $i$, the index for the type of atom, is 1 or 2 and $n$ is $x$, $y$, or $z$. The only terms in the potential expression that will give nonzero contribution to $A$ are those terms that have squares of $\overline{u}_1[\overline{R}]$ or $\overline{u}_2[\overline{R}]$. For example, the only terms in the potential that contain $u_{1x}^2$ are

$$V = \frac{\alpha_s}{2}(\frac{1}{3}u^2_{1x})\cdot 4 + \frac{\alpha_\phi}{2}(u_{1x}^2 - \frac{1}{3}u_{1x}^2)\cdot 4 \tag{19}$$

Consequently,

$$A = \alpha_s(\frac{1}{3})\cdot 4 + \alpha_\phi(1-\frac{1}{3})\cdot 4 = 4(\frac{\alpha_s + 2\alpha_s}{3}) \tag{20}$$

The same case will hold true for $u_{2x}^2, u_{1y}^2, u_{2y}^2, u_{1z}^2, u_{2z}^2$.

To calculate $B$, observe from its position in the dynamical matrix that

$$B = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{1x}\partial u_{2x}} = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{1y}\partial u_{2y}} = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{1z}\partial u_{2z}} \tag{21}$$

$$B^* = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{2x}\partial u_{1x}} = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{2y}\partial u_{1y}} = \sum_{\overline{R}_p} \frac{\partial^2 V}{\partial u_{1z}\partial u_{2z}} \tag{22}$$

It is necessary to verify Eq. (21). The terms that contribute to B are

$$V = \frac{\alpha_s}{2}(-\frac{1}{3}2u_{1x}[\overline{R}]u_{2y}[\overline{R}]) + \frac{\alpha_s}{2}(-\frac{1}{3}2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{B}])+$$

$$+\frac{\alpha_s}{2}(-\frac{1}{3}2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{C}]) + \frac{\alpha_s}{2}(-\frac{1}{3}2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{D}])+$$

$$+\frac{\alpha_\phi}{2}(-2u_{1x}[\overline{R}]u_{2y}[\overline{R}]-\frac{1}{3}(-2)u_{1x}[\overline{R}]u_{2y}[\overline{R}])+$$

$$+\frac{\alpha_\phi}{2}(-2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{B}]-\frac{1}{3}(-2)u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{B}]) +$$

$$+\frac{\alpha_\phi}{2}(-2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{C}]-\frac{1}{3}(-2)u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{C}])+$$

$$+\frac{\alpha_\phi}{2}(-2u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{D}]-\frac{1}{3}(-2)u_{1x}[\overline{R}]u_{2y}[\overline{R}+cell\overline{D}])$$

(23)

After taking the double derivatives, $B$ becomes

$$B=-(\frac{\alpha_s+2\alpha_\phi}{3})(1+e^{-i\overline{k}\cdot cell\overline{B}}+e^{-i\overline{k}\cdot cell\overline{C}}+e^{-i\overline{k}\cdot cell\overline{D}})$$

(24a)

$$=-(\frac{\alpha_s+2\alpha_\phi}{3})(1+e^{i\frac{(k_x+k_y)a}{2}}+e^{i\frac{(k_y+k_z)a}{2}}+e^{i\frac{(k_z+k_z)a}{2}})$$

(24b)

The occurrence of the complex conjugate in the original B expression when the order of derivation is changed comes from the fact that $cell\overline{F},cell\overline{G},cell\overline{H}$ have signs opposite to $cell\overline{B},cell\overline{C},cell\overline{D}$.

5. Write a Matlab code to find the phonon spectra for general values of your force constants and atomic masses. Plot the phonon dispersion in appropriate units along the Γ–X, X–L, and Γ–L directions using force constants of $\alpha_S=1, \alpha_\phi=0.25$, and $M_1=M_2=1$.

Once the dynamical matrix has been specified, the calculation of phonon dispersion is relatively straightforward. For each value of **k**, the corresponding frequencies are related to the eigenvalues of the matrix $\mathbf{M}^{-1}\mathbf{D}(\mathbf{k})$ (the eigenvalues actually being the squares of the frequencies). In this way, there is a *relation* from **k** to $\omega$. If there were exactly one $\omega$ for each **k**, the relation would simply be a *function*. For a free particle, each **k** corresponds to exactly one frequency $\omega$, and thus $\omega=f(\mathbf{k})$.

To actually obtain the dispersion curves along the desired directions, the path in **k**-space was sampled at a finite number of points. At each sample point, representing a specific **k** value, the eigenvalues of $\mathbf{M}^{-1}\mathbf{D}(\mathbf{k})$ were numerically calculated. Since the matrix is 6x6, there were 6 (perhaps non-distinct) $\omega$ values for each **k**. In this calculation, the physical parameters that are ordinarily material specific are the lattice spacing $a$, the masses of the Ga ($M_1$) and As ($M_2$) atoms, and the spring constants $\alpha_{stretch}$ and $\alpha_{bend}$. In

this part however, the values $M_1=M_2=1$ and $\alpha_{stretch}=1$ and $\alpha_{bend}=0.25$ were used. Since all the groups used the same values for mass and spring constants, this part served as a means of checking the accuracy of the numerical Matlab code. The lattice spacing used here was $a = 5.6325\text{Å}$, the actual value for GaAs. Since units were not specified in the original definition of constants, it was assumed that standard SI units were implied. Thus, the mass of the atoms used in the calculation was (the extremely large value of) 1kg each, and the spring constants used were $\alpha_{stretch}=1$ N/m and 0.25 N/m for $\alpha_{stretch}$ and $\alpha_{bend}$, respectively. The only adjustable parameter in this computation was the number of sample points along the path.

The graph of the dispersion relation is shown in Fig. 3. In this figure, the three different colors represent the three different arcs of the path. The dispersion relation for the arc from $\Gamma$ to $X$ is shown in red. The dispersion relation for the direct path from $X$ to $L$ is shown in green. The arc from $L$ to $\Gamma$ is shown in blue. Notice that although the paths from $\Gamma$ to $X$ and $L$ to $\Gamma$ represent movements along the Brillouin zone, the segment from $X$ to $L$ actually passes through the interior of the Brillouin zone. The portion in green, therefore, does not represent a symmetry direction. It is not surprising therefore that only four lines are seen on the paths from $\Gamma$ to $X$ and $L$ to $\Gamma$ (because the two transverse directions are degenerate) whereas six lines are seen on the $X$ to $L$ path because the symmetry is broken in this direction.

The numbers on the $x$-axis give the total distance traveled in q-space from the starting point at $\Gamma$. Thus, it is clear that the total trip from $\Gamma$ to $X$ to $L$ back to $\Gamma$ is a distance of approximately 2.75 units in q-space. The $y$-axis is frequency. The particular scaling of the frequency axis results from the initial choice of constants and their associated units. The fact that the shape matches the expected shape (as given by the other groups) gives some validation to the Matlab code that generated it and further results. The M-file that calculates phonon spectra for a general values of force constants and atomic masses is called JJCB_B5.m, the first part of the name being the first initials of the group members and the second part for the question.
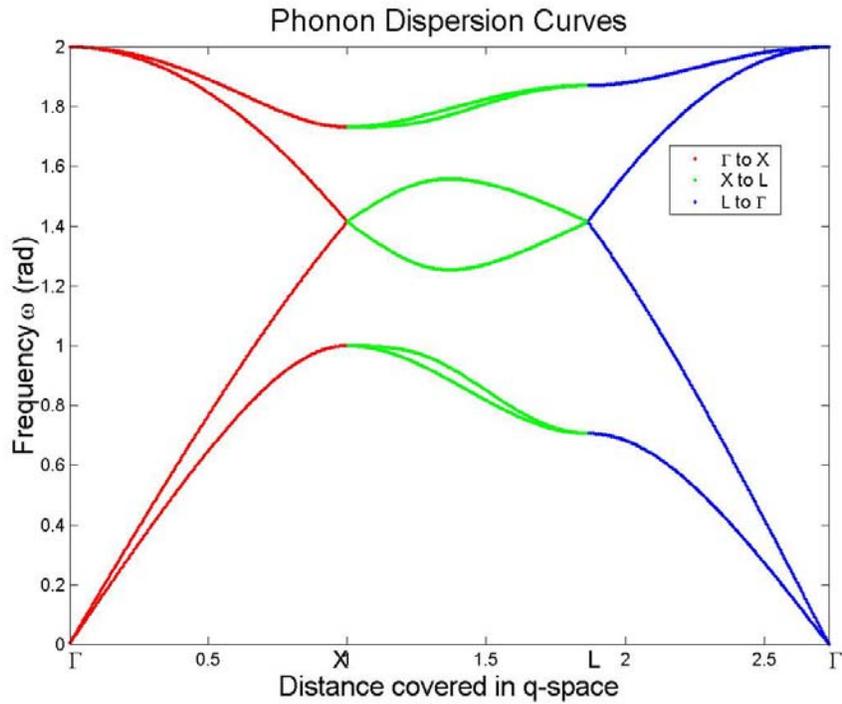
**Figure 3:** Phonon dispersion curves with standard mass and spring coefficients

6.  For these values of force constants and masses, determine the atomic displacements for all the modes at Γ, and for the highest optic and lowest acoustic modes at X and L. Provide drawings of the atomic motion of these modes. How many modes are there at Γ?

Determination of atomic displacements requires that the eigenvectors of $\mathbf{M}^{-1}\mathbf{D(k)}$ be calculated along with the eigenvalues. The results of these calculations are shown in Tables 4, 5, and 6 for the atomic motion at Γ, *X*, and *L*, respectively. The eigenvalues and eigenvectors were calculated in Matlab.

**Table 4:** All frequencies and atomic displacements for phonon modes at Γ

| Freq. $\omega$ (Hz) | $u_{1x}$ | $u_{1y}$ | $u_{1z}$ | $u_{2x}$ | $u_{2y}$ | $u_{2z}$ |
|---|---|---|---|---|---|---|
| 0 | -0.7071 | 0 | 0 | -0.7071 | 0 | 0 |
| 0 | 0 | -0.7071 | 0 | 0 | -0.7071 | 0 |
| 0 | 0 | 0 | -0.7071 | 0 | 0 | -0.7071 |
| 2 | -0.7071 | 0 | 0 | 0.7071 | 0 | 0 |
| 2 | 0 | 0.7071 | 0 | 0 | -0.7071 | 0 |
| 2 | 0 | 0 | -0.7071 | 0 | 0 | 0.7071 |

The first three modes in Table 4 correspond to simple translations and thus do not really represent vibrational modes. The other three modes are optical modes. The movies for these modes can be accessed by running the M-files: Gamma_opt_1.m, Gamma_opt_2.m, and Gamma_opt_3.m, respectively. From the movies, it is clear that the motion of each individual molecule is repeated throughout the crystal, i.e. there is no variation in the motion across the crystal. In the movies, the lines are used to indicate the bonds between the Ga and As atoms when the atoms are in equilibrium and serve to identify an inertial frame.

**Table 5:** Frequencies and atomic displacements for highest optical and lowest acoustic modes at $X=[1\ 0\ 0]$

| Freq. $\omega$ (Hz) | $u_{1x}$ | $u_{1y}$ | $u_{1z}$ | $u_{2x}$ | $u_{2y}$ | $u_{2z}$ |
|---|---|---|---|---|---|---|
| 1.7321 | 0 | -0.7071 | 0 | 0 | 0 | 0.7071 |
| 1.7321 | 0 | 0 | 0.7071 | 0 | -0.7071 | 0 |
| 1 | 0 | 0 | -0.7071 | 0 | -0.7071 | 0 |
| 1 | 0 | -0.7071 | 0 | 0 | 0 | -0.7071 |

The first two modes in Table 5 are the two (degenerate) highest optical modes. The movies for these modes can be accessed by running the M-files: X_opt_1.m and X_opt_2.m, respectively. The last two modes in Table 5 are the two (degenerate) lowest acoustic modes. The movies for these modes can be accessed by running X_ac_1.m and

X_ac_2.m, respectively. From the movies, it is clear that the motion of the atoms varies across the crystal, in particular along the *x*-direction. The atoms that are at the midpoint in the *x*-direction move in the opposite direction to those that are at the two ends of the *x* axis in the cubic cell.

**Table 6:** Frequencies and atomic displacements for highest optical and lowest acoustic modes

at $L = \begin{bmatrix} \dfrac{1}{2} & \dfrac{\bar{1}}{2} & \dfrac{1}{2} \end{bmatrix}$

| Freq. $\omega$ (Hz) | $u_{1x}$ | $u_{1y}$ | $u_{1z}$ | $u_{2x}$ | $u_{2y}$ | $u_{2z}$ |
|---|---|---|---|---|---|---|
| 1.8708 | 0.5000 | -0.5000 | 0 | 0.5000 | -0.5000 | 0 |
| 1.8708 | -0.2887 | -0.2887 | 0.5774 | -0.2887 | -0.2887 | 0.5774 |
| 0.7071 | -0.5000 | 0.5000 | 0 | 0.5000 | -0.5000 | 0 |
| 0.7071 | 0.2887 | 0.2887 | -0.5774 | -0.2887 | -0.2887 | 0.5774 |

As was true in the previous case, the first two modes in Table 6 are the two highest optical modes. The Matlab files are L_opt_1.m, and L_opt_2.m, respectively. The other two modes are the two lowest acoustic modes. The corresponding movies are in L_ac_1.m and L_ac_2.m, respectively. The variation of the motion across the crystal is considerably more complicated than in previous cases. This fact is to be expected since all components of the **k**-vector are nonzero here.

# Model Optimization and Comparison to Macroscopic Properties

To determine appropriate values for the spring constants, it is necessary to fit some form of calculated data with experimental data. It is known beforehand that the Born model approximation used here cannot match the experimental data perfectly because the model used here has only two adjustable parameters whereas the real crystal has three independent elastic constants. The estimation of the spring constants was done by matching calculated zone edge frequencies with experimental values.

One can observe that all of the terms in the dynamical matrix can be written in terms of the ratio of the two spring constants and a scaling factor. Thus, first the ratio of the spring constants $\frac{\alpha_S}{\alpha_\phi}$ was estimated. This ratio was estimated by searching for the value that minimized the error between the calculated and experimental ratio of frequencies at $L = \begin{bmatrix} \frac{1}{2} & \frac{\bar{1}}{2} & \frac{1}{2} \end{bmatrix}$. At $L$, there are four frequencies. Normalizing these frequencies, the best least squares fit was found for the ratio $\frac{\alpha_S}{\alpha_\phi}$ using a simple search. Once the ratio of the two constants was found, the appropriate scaling factor needed to be determined. To estimate the scaling factor, the magnitude of the highest frequencies at $\Gamma$ and L were used. In the experimental data, there are two optical frequencies at $\Gamma$. However, in the nearest-neighbor model used here, there will always be only one optical frequency at $\Gamma$. Therefore, the average of these two values was used as the experimental optical frequency at $\Gamma$. A least-squares fit gave an estimate for the necessary scaling factor, again using a simple search.

With the scaling factor and the ratio, the two spring constants were determined. With an estimate for these spring constants, other macroscopic properties could be calculated. The calculated and experimental zone-edge frequencies are shown in Table 7. The zone-edge frequencies are calculated from the eigenvalues of $\mathbf{M}^{-1}\mathbf{D}(\mathbf{k})$ for the specific values of $\mathbf{k}$ that correspond to the zone-edges. The table shows that the calculated and experimental values have fairly good agreement, with only one of the entries having a percent difference larger than 20%.

**Table 7:** Measured and calculated zone-edge frequencies

| Mode Description | Meas. Frequency [1] ($10^{12}$ Hz) | Calculated Frequency ($10^{12}$ Hz) | % Difference |
|---|---|---|---|
| Γ — LO | 8.55±0.2 | 8.16 | -4.56% |
| Γ — TO | 8.02±0.08 | 8.16 | 1.74% |
| X — TO | 7.56±0.08 | 7.77 | 2.78% |
| X — LO | 7.22±0.15 | 5.87 | -18.7% |
| X — LA | 6.80±0.06 | 5.66 | -16.8% |
| X — TA | 2.36±0.015 | 2.48 | 5.08% |
| L — TO | 7.84±0.12 | 7.97 | 1.66% |
| L — LO | 7.15±0.07 | 6.62 | -7.41% |
| L — LA | 6.26±0.10 | 4.77 | -23.8% |
| L — TA | 1.86±0.02 | 1.75 | -5.91% |

Three sound velocities were calculated: the longitudinal and transverse sound velocities for waves propagating in the [100] direction and the longitudinal sound velocity for waves propagating in the [111] direction. Here, the sound velocities were calculated in a very simple manner as a two-point finite difference approximation to the derivative in the appropriate direction. The calculated and measured values are shown in Table 8.

**Table 8:** Measured and calculated wave speeds

| Wave direction and character | Chosen $k$ magnitude ($m^{-1}$) | Calculated $\omega$ for chosen $k$ (rad) | Calculated speed ($cm^5$/s) | Meas. Speed at 77K ($cm^5$/s) [1] |
|---|---|---|---|---|
| [100] $v_L$ | 5.58 x $10^7$ | 2.01 x $10^{11}$ | 3.60 | 4.784 |
| [100] $v_T$ | 5.58 x $10^7$ | 1.17 x $10^{11}$ | 2.10 | 3.350 |
| [111] $v_l$ | 5.58 x $10^7$ | 2.40 x $10^{11}$ | 4.30 | 5.447 |

Table 9 shows the calculated and measured elastic constants as well as the formula used for the calculations.

**Table 9:** Measured and calculated wave speeds

| Elastic moduli | Formula used for calculation | Calc. Modulus $(10^{10}\,\text{dyne/cm})$ | Meas. Modulus [1] $(10^{10}\,\text{dyne/cm})$ |
|:---:|:---:|:---:|:---:|
| $C_{11}$ | $\rho v_L^2$ | 68.9 | 112.6 |
| $C_{12}$ | $2\rho v_l^2 - 2C_{44} - C_{11}$ | 41.7 | 57.1 |
| $C_{44}$ | $\rho v_T^2$ | 23.4 | 59.5 |

It is clear that the calculated wave speed and elastic moduli are not very close to the measured values. In fact, the calculations consistently underestimate these values. This fact indicates one or more of the following: the spring constants chosen are not the true optimum, the wave speeds are being calculated incorrectly, or the underspecified Born is not useful for accurate estimates of the wave speed.

1. Plot a comparison of your calculated phonon dispersion with theoretical and/or experimental results along the $\Gamma$–$X$, $X$–$L$, and $\Gamma$–$L$ directions.

Fig. 4 shows the calculated phonon dispersion curves; the experimental phonon dispersion curves are shown in: Blakemore, J.S., "Semiconducting and other major properties of gallium arsenide." *J. Appl. Phys.* 53(10), Oct. 1982.
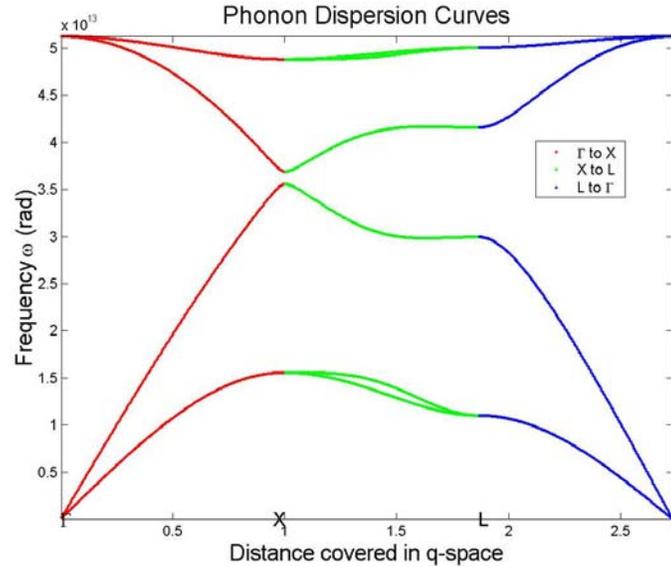
**Figure 4:** Calculated phonon dispersion curves for GaAs

The calculated and experimental phonon dispersion curves have the same general shape and share many features. There is a gap at *X* and the general shape of the Γ-*X* and Γ-*L* regions are the same. The path from *X-L* is not shown because it is not along a symmetry direction as discussed earlier.

## 2. Plot the total density of states (histogram method, include all modes) versus frequency.

Figure 6 shows the total density of states as determined through the histogram method. In order to obtain a total density of states, periodic boundary conditions are applied. The application of periodic boundary conditions discretizes the **k** values and correspondingly the $\omega$ values as well. Thus, to do the actual calculation, the **k**-space is sampled and the $\omega$ values are determined for every sample point. Once one knows all the $\omega$ values, a simple histogram gives the required total density of states.

The density of states shown in Fig. 6 below agrees well with the published experimental figure for the density of states in Blakemore, J.S., "Semiconducting and other major properties of gallium arsenide." *J. Appl. Phys.* 53(10), Oct. 1982.
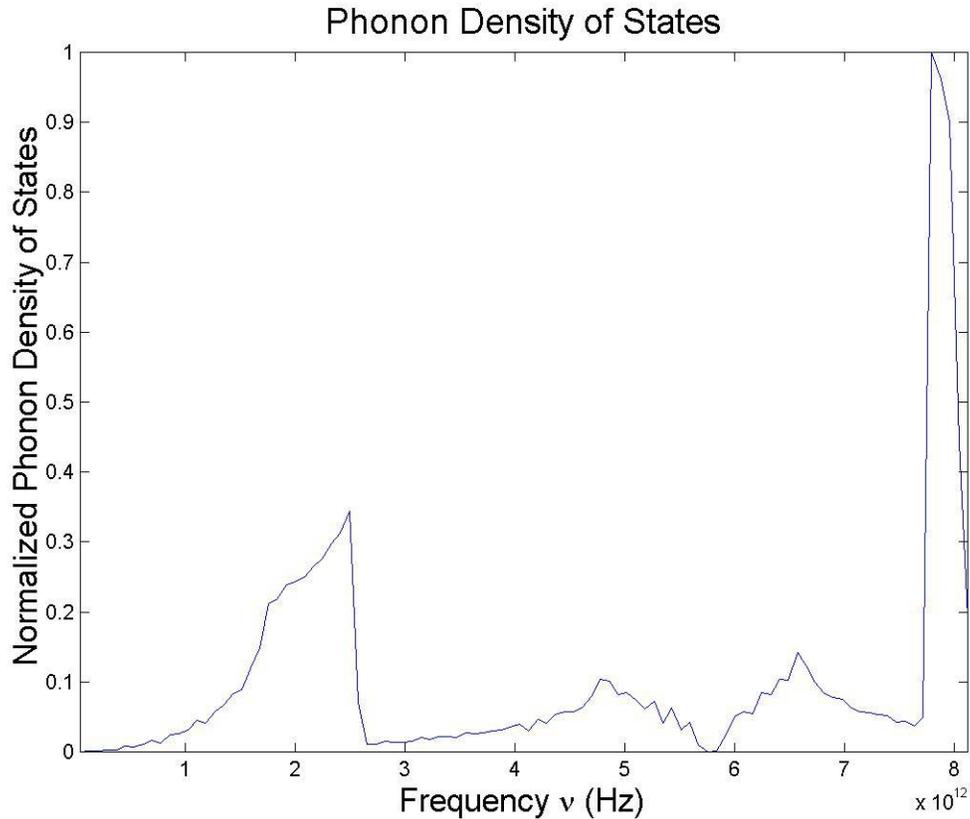
**Figure 6:** Calculated density of states for GaAs

3. Calculate the specific heat of your material versus temperature using (a) your calculated density of states, (b) a Debye model, and (c) a combined Debye-Einstein model. Plot your results for temperatures between 0K and $3\Theta_D$.

Figure 8 shows the specific heat calculated using all these methods. The specific heat can be determined from the calculated density of states as given in PSSA 6.209

$$C_v = \frac{1}{4k_B T^2} \sum_\sigma \int (\hbar\omega)^2 g_\sigma(\omega) \operatorname{cosech}^2\left(\frac{\hbar\omega}{2k_B T}\right) d\omega \tag{25}$$

When this specific heat is actually calculated, the integral becomes a summation over bins. The $g_\sigma(\omega)d\omega$ term is simply the number of states in each bin with center at $\omega$. The center frequency is used for the quadratic term and the hyperbolic cosecant term.

For the Debye model, the equation for the specific heat is given as below

$$C_v = 9nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4}{4} \mathrm{cosech}^2\left(\frac{x}{2}\right) dx \qquad (26)$$

The Debye temperature for GaAs is approximately 345 K [1]. The integral given in Eq. (26) can be found tabulated in [2] for $T$ between 0 and $\Theta_D$. For the range beyond $\Theta_D$ a straight line approximation was made from $T = \Theta_D$ to $T = 3\Theta_D$, where at $T = 3\Theta_D$, $C_v$ was set to 2, corresponding to the high temperature approximation that $C_v = 3nk_BT$ ($n$ referring to density of atoms here).

For the combined model, the Debye equation is used for the acoustic modes and the Einstein specific heat is used for optical modes. The Einstein approximation for the specific heat is given as

$$C_v = \frac{(\hbar\omega_o)^2}{4k_BT^2} \mathrm{cosech}^2\left(\frac{\hbar\omega_o}{2k_BT}\right) \qquad (27)$$

To use this approximation, a specific frequency $\omega_o$ needs to be chosen, that will be used to represent all the optical modes. It makes sense to choose the frequency that has the highest density of modes, which is what has been done here. In this combined model, since the Debye approximation is only being used for the acoustic modes, the specific heat just due to the Debye part should be half of what it was earlier.
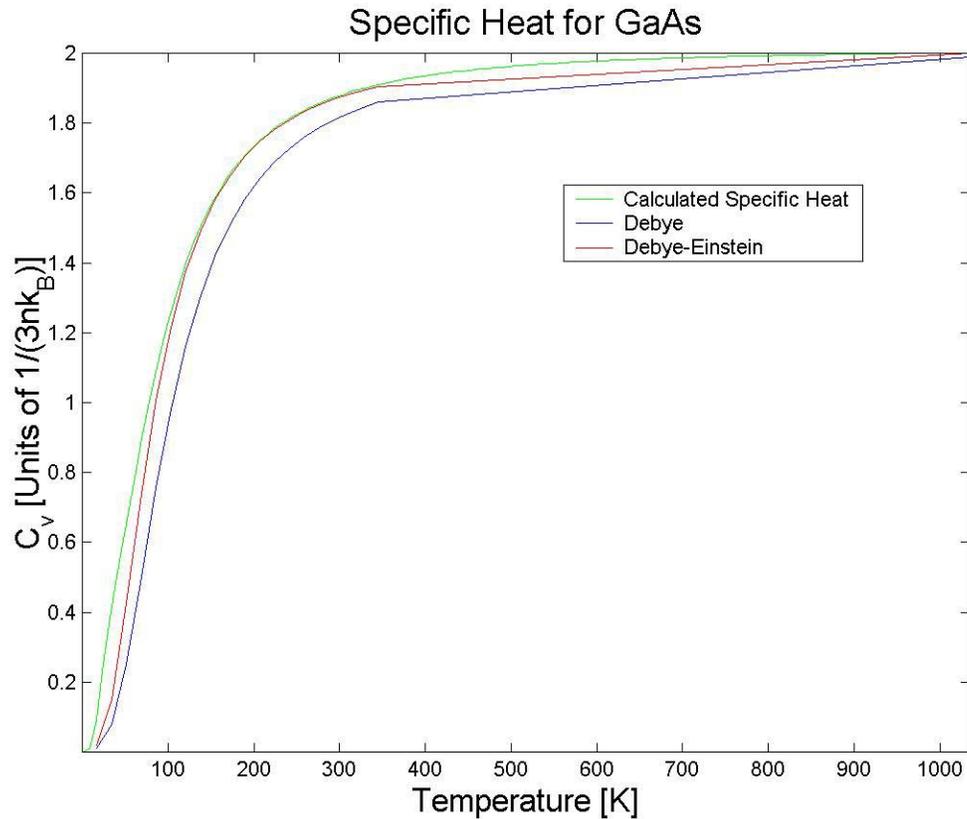
**Figure 8:** Specific heat calculated a number of ways.

(Note that *n* refers to the density of molecules, not atoms.)

It can be seen that both the Debye alone and the combined Debye-Einstein approximations match up very closely with the calculated specific heat using the calculated density of modes. Starting at $T \approx 0$, it is clear that the calculated specific heat does not display the $T^3$ dependence that actually exists. This dependence is correctly captured by both the Debye and the Debye-Einstein models. The general shape of all the curves is the same and all come very close to the high temperature limit value of $C_v = 2$ (for the units chosen on this plot). The Debye model underestimates the specific heat throughout the entire temperature range. This result is in fact to be expected because the Debye model cannot take into account the peak in the density of modes at a large $\omega$ value. The Debye-Einstein model on the other hand does a much better in this respect. Since the mode chosen for the Einstein model was at a very high frequency, adding in the

Einstein model increases the estimate of the specific heat. From the author's perspective, the only thing really surprising about Fig. 8 is that the approximations seem to match up *too* well to the calculated specific heat. It is not clear to this author why the agreement should be so good when it seems that the approximations made are rather crude in some sense!

# References

[1] Blakemore, J.S. Semiconducting and other major properties of gallium arsenide. J.
Appl. Phys. 53(10), Oct. 1982.

[2] Ashcroft, Mermin, Solid State Physics. Harcourt: 1976.

# Appendix

Files on accompanying disk:

| | |
|---|---|
| Gamma_opt_1.m | M-file for animation of 1st optical mode at $\Gamma$ |
| Gamma_opt_2.m | M-file for animation of 2nd optical mode at $\Gamma$ |
| Gamma_opt_3.m | M-file for animation of 3rd optical mode at $\Gamma$ |
| L_ac_1.m | M-file for animation of one lowest acoustic mode at $L$ |
| L_ac_2.m | M-file for animation of other lowest acoustic mode at $L$ |
| L_opt_1.m | M-file for animation of one highest optical mode at $L$ |
| L_opt_2.m | M-file for animation of other highest optical mode at $L$ |
| X_ac_1.m | M-file for animation of one lowest acoustic mode at $X$ |
| X_ac_2.m | M-file for animation of other lowest acoustic mode at $X$ |
| X_opt_1.m | M-file for animation of one highest optical mode at $X$ |
| X_opt_2.m | M-file for animation of other highest optical mode at $X$ |
| JJCB_B5 | M-file for calculating (and graphing) phonon dispersion relation for arbitrary mass and spring constant values |