SIZE-MISMATCH EFFECTS IN ALLOYS

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INTRODUCTION

In these lectures, we will discuss how to describe solid structures composed of atoms with different sizes. The concepts we will develop are quite general and have important implications in many areas of condensed matter physics. It was first pointed out by Pauling [1] that atoms and ions have certain natural radii that are determined by the local chemistry. For example in semiconductors with the zincblende structure, the ions form sp$^3$ orbitals that bond with one another to give the solid its cohesive energy. The sp$^3$ orbitals on one site are largely unaffected by the nearest or any other neighbors, so that we can regard the atomic

Figure 1. Values of tetrahedral covalent radii for sequences of atoms from the "The Nature of the Chemical Bond" by L. Pauling [1].

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radii as additive. In this way the nearest neighbor distance in a compound AB is given by $r_A^{0} + r_B^{0}$ and in an AC compound by $r_A^{0} + r_C^{0}$. This determines the atomic radii $r_A^{0}$ etc. up to a single additive constant that is rather arbitrary as only sums of radii are meaningful. Pauling made one choice for a reference radius and subsequently other people, most notably Phillips [2], have made other choices. Figure 1 shows the atomic radii for the elements that can form semiconductors.

Of course it is an oversimplification to say that the chemical bond is completely oblivious to its environment as we illustrate in Table 1, also taken from Pauling [1].

Table 1. Showing the experimental values of the Carbon-Carbon single bond distance in various compounds.

<table>
<thead>
<tr>
<th>Substance</th>
<th>C-C distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>1.542</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.533</td>
</tr>
<tr>
<td>Propane</td>
<td>1.54</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1.534</td>
</tr>
<tr>
<td>Neopentane</td>
<td>1.54</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.532</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.53</td>
</tr>
<tr>
<td>Adamantane, C_{10}H_{16}</td>
<td>1.54</td>
</tr>
</tbody>
</table>

It can be seen that the C-C bond is indeed constant to within better than 1%, even in these old measurements. Of course if the local chemistry changes, so does the bond length. A double bond between the carbon atoms C=C is much stronger and has a length that is shorter by about 14% at 1.33Å.

The point here is that the chemical bond can be assigned a natural length that is independent of the environment and this provides an excellent starting point for understanding the actual observed lengths in alloys. In almost all molecules familiar from chemistry, like the benzene ring, each bond can independently take on its natural length, thus leading to an unstrained structure. This is also the case in crystalline semiconductors like GaAs, ZnSe and Si, where each bond can have its natural length. The energy of each individual bond is minimized.
separately, thus ensuring a globally unstrained system and hence a structure with the lowest possible energy.

The situation is very different when a crystalline alloy like Ga$_{1-x}$In$_x$As is formed. The Ga-As bond would like to have a length of 2.448Å, whereas the In-As bond would like to be 2.623Å. Each bond cannot have its natural length as this is not compatible with maintaining the zincblende topology. Therefore the shorter Ga-As bonds are forced to expand a little and the longer In-As bonds contract a little on average. The frustration is shared among the various bonds in a more or less equitable way and the alloy reaches a minimum energy configuration. We shall be studying the detailed properties of this equilibrium structure later in these lectures.

The concepts discussed above are rather general and also apply to layered materials and metallic alloys. However we have used the sp$^3$ orbitals for illustration as they provide a very stable local chemistry. The situation is often more complex, such as in metallic alloys where charge transfer effects are important. If the size-mismatch between the two ions becomes too large, then phase separation occurs. A good empirical rule was given by Hume-Rothery [3] who pointed out that phase separation occurs when the size-mismatch becomes greater than about 15%. Although this "rule" was put forward for metals, it is a rather good guide for most materials.

THE CATCHMENT AREA MODEL

We will begin by discussing a very simple but interesting example of the effects of size-mismatch. During the past decade, many layered compounds have been intercalated with guest species. These layered compounds range from graphite, where the monatomic layers are quite floppy, to clays where the silicate layers are much thicker and therefore

Figure 2. A sketch showing the distortions produced when two kinds of atoms are intercalated into a layered compound.
much more rigid [4]. In these lectures we will be concerned mainly with the structural properties of these layered compounds, when two kinds of atoms or molecules are intercalated to form a 2D alloy. Examples will be given later. To keep a uniform notation, we will refer to these as $A_{1-x}B_x$ alloys. A sketch of the structure is shown in Figure 2.

This is a complex problem, but a simple model describes the experimental data rather accurately. This model was first solved by us using computer simulations [5]. When we saw that it was fitting the experimental data well, we found an exact solution [6]. The model assigns a gallery height $h_A^0$ to the type A intercalant and $h_B^0$ to the type B intercalant. These are the "natural" gallery heights that can be obtained from the pure compounds when $x=0$ or $x=1$, and we regard these as experimentally determined parameters. The natural gallery heights are the analog of the Pauling atomic radii discussed previously. The catchment area model assumes that there is a significant transverse layer rigidity which means that when a single large intercalant atom is present, the gallery height is increased over a catchment area as sketched in Figure 3. This catchment area is similar to poking a finger into a drum membrane so that the height will relax back to normal over some healing length.

As a simple model, we assume that the height is constant over the catchment area. It is convenient to define dimensionless gallery

![Diagram](Image)

**Figure 3.** (a) The solid hexagons contain B ions and the unshaded triangles contain A ions. The partially shaded hexagons contain A ions but are in the catchment area of B ions. The dimensionless size of the catchment area shown is given by $p=7$. (b) A single B is replaced by A, and the B ions in its catchment area are also replaced by A ions to define the reciprocal catchment area of the central A.
heights, \( \langle d_A \rangle \), \( \langle d_B \rangle \) and \( \langle d \rangle \) for the A, B and all sites respectively. These quantities are given by

\[
\langle d \rangle = \frac{h(x) - h(0)}{h(1) - h(0)}
\]

(1)

where \( h(x) \) is the mean gallery height at a concentration \( x \), and \( h(0) = h^0_A \) and \( h(1) = h^0_B \). Similar expressions hold for the mean gallery heights associated with the A and B sites alone. These are related by

\[
\langle d \rangle = (1-x)\langle d_A \rangle + x\langle d_B \rangle
\]

(2)

In order for a particular A ion to have a (dimensionless) height 0 associated with it, the neighboring B ions must be sufficiently far away that their (dimensionless) catchment areas of size \( p \) do not cover the A ion. This defines a reciprocal catchment area around the A ion which also has size \( p \). What happens outside that area is irrelevant for this particular A ion. The probability of a site having such a A ion on it is \( (1-x)^P \) so that

\[
\langle d \rangle = 1 - (1-x)^P
\]

(3)

This result is derived under the assumption that there are only two possible heights for the gallery. Presumably it can be generalized to account for a more gentle height decay away from the large ion, in which case \( p \) would represent some dimensionless mean area surrounding the large

![Figure 4](image_url)

**Figure 4.** A comparison of the catchment area result for the mean gallery height (3) with experimental data as described in [4,7] for various intercalation compounds.
ion. Note that (3) is always superlinear as shown in Figure 4, where the theoretical result is compared with experimental data. It can be seen that the expected trend is found with the transverse layer rigidity \( p \) getting larger as the thickness of the host layers increases from graphite to clay. This is discussed in more detail in the lectures by S. A. Solin [7].

The results above for the mean gallery height are compared with X-ray data with the scattering vector along the c axis perpendicular to the layers. With EXAFS measurements it should be possible to find the mean gallery heights at the A and B sites separately, although no such work has been done to date to our knowledge. Within the catchment area model, the (dimensionless) mean height of a B site is always 1, so that \( <d_B> = 1 \) and from (2)

\[
<d_A> = 1 - (1-x)^{p-1}.
\]

which is illustrated in Figure 5.

![Graph illustrating the mean heights of A and B galleries.](image)

**Figure 5.** The mean heights of the A and B galleries and the overall mean gallery height are shown for various values of \( p \) for the catchment area model. The lower dashed curves are \( <d_A> \) and the upper dashed lines are \( <d_B> \). The solid lines are \( <d> \).

The results shown in Figure 5 are quite distinctive and very different from the \( Z \) plots for semiconductors to be discussed in the next section. In the limit \( p=1 \), we do recover both Vegard's law and the floppy limit where the outer parts of the \( Z \) plot are horizontal.

Over 50 years ago, Vegard [8] proposed that the lattice parameter of an alloy should be linear in the composition parameter \( x \). This is obeyed rather closely for some alloys as shown by our discussion of semiconductors in the next section. However it is often violated as seen in Figure
4 for the gallery heights, and almost always violated in close packed metal alloys [9]. We can see from (3) that Vegard’s law is only obeyed if \( p = 1 \), when the catchment area vanishes. Even the case of intercalated graphite, which has the smallest \( p \), is quite far from this limit.

**SPRING MODELS**

A completely different approach starts with a spring model and then minimizes the energy. This approach has been shown to work well in semiconductors [10] and can also be applied to the alloys intercalated between layers discussed in the previous section.

We use a harmonic spring potential first introduced by Kirkwood [11]

\[
V_{\text{harmonic}} = \frac{a}{2} \sum_{\langle ij \rangle} (L_{ij} - L_{ij}^0)^2 + \frac{b}{2} <L>^2 \sum_{\langle ij \rangle} (\cos \theta_{ij} + \frac{1}{3})^2
\]

where the force constants \( a \) and \( b \) are associated with bond stretching and bond bending. The \( L_{ij}^0 \) are the natural (unstrained) bond lengths, which are formed by adding up the appropriate Pauling radii discussed earlier. The quantity \(<L>\) is the mean nearest neighbor distance. It is convenient to include this length in (5) so that the force constants \( a \) and \( b \) both have the same units. We will assume that \( a \) and \( b \) are fixed and do not vary. This is a major assumption that we will return to later.

The mean bond length in the alloy can be found from the following argument. Imagine a (mathematical) plane that goes through the solid. The net tension on this plane must be zero, or else the solid would begin to move spontaneously. This leads to the condition that

\[
(1-x)G(<L_{AC}> - L_{AC}^0) + xG(<L_{BC}> - L_{BC}^0) = 0
\]

for an alloy \( A_{1-x}B_x \). An example of such an alloy would be the semiconductor \( Ga_{1-x}In_x As \). The subscripts \( AC \) and \( BC \) on the lengths in (6) refer to the appropriate nearest neighbor bonds. From (6), we obtain Vegard’s law

\[
<L> = (1-x)L_{AC}^0 + xL_{BC}^0 = (1-x)L_{AC}^0 + xL_{BC}^0
\]

The condition for Vegard’s Law to hold is that the force constants are the same for all bonds in the alloy. This is both a necessary and sufficient condition within this kind of spring model [10]. Using dimensionless lengths similar to (1), we can rewrite (7) as
\( <d> = x \) 

(8)

The other quantities of interest are more difficult to calculate, but can all be expressed in terms of a topological rigidity parameter, which is defined in Figure 6.

![Diagram](image)

**Figure 6.** Showing how the radial forces \( F \) applied to the four nearest neighbors of an atom in the zincblende structure can produce a radial displacement field.

Radial forces \( F \) are applied to the four nearest neighbors of an atom. This opens up a cage and the four nearest neighbors acquire a radial displacement \( u \). If there was no effect from the matrix, the displacement \( u \) is just \( F/a \). But the existence of the matrix makes it harder to open the cage so that the forces needed to produce the displacement \( u \) are

\[
F = \frac{\alpha}{a^*} u
\]

(9)

where \( 0 < a^* < 1 \). The curious notation for the topological rigidity parameter \( a^* \), is used because \( \alpha \) was previously used for a similar quantity involving forces at the end of a single bond [12]. The topological rigidity parameter depends on the ratio \( B/a \) and is in the range 0.7 - 0.8 for all semiconductors which are tetrahedrally coordinated.

The great virtue of this model is that it can be solved exactly, using the linear superposition of the strain fields which is applicable because the force constants \( a \) and \( B \) are fixed [10]. The solutions for the dimensionless lengths are

\[
<d_{AC}^* > = x(1-a^*)
\]

\[
<d_{BC}^* > = 1 - (1-x)(1-a^*)
\]

(10)
and the fluctuations in the nearest neighbor bond lengths are equal and given by

\[
\langle d_{AC}^2 \rangle - \langle d_{AC} \rangle^2 = \langle d_{BC}^2 \rangle - \langle d_{BC} \rangle^2 = x(1-x)\left(\frac{\partial^2 a}{\partial x^2}\right)
\]

where \(\frac{\partial^2 a}{\partial x^2}\) is a derivative of the topological rigidity parameter \(a\) [10]. Thus most quantities of interest can be expressed in terms of a single parameter \(a\) and its derivative. This parameter can either be calculated or fit from experiment. We adopt the later approach here. The strain energy per site \(\varepsilon\) is given by

\[
\varepsilon = \frac{1}{2}G x(1-x)(1-a)\left(L_{BC}^0 - L_{AC}^0\right)^2
\]

As an example of the application of these results, in Figure 7 we show the \(Z\) plot for \(Ga_{1-x}In_x\) in which \(a\) was chosen to be 0.8 to get a good fit. In order to go from the dimensionless lengths \(d\) to the actual observed lengths, the \(d\) are multiplied by \(\left(L_{BC}^0 - L_{AC}^0\right) = 0.175\) Å and added to \(L_{AC}^0 = 2.448\) Å. It can be seen that the fit is excellent.

![Figure 7](image.png)

**Figure 7.** The left panel compares the experimental results [13] (open symbols) for \(Ga_{1-x}In_x\) with simulation results (solid symbols) based on the harmonic potential (5). The straight lines are given in (10). The right panel shows the actual length distributions computed for a sample containing 8,000 atoms [10].

Figure 7 also shows the actual length distributions for the nearest neighbor Ga-As and In-As bonds. These two curves are scaled versions of one another and close to Gaussians [10]. This result is quite surprising, especially in the dilute limit where it still holds. Unfortunately whereas EXAFS experiments can reliably give the mean lengths, they do not
give reliable information about the widths. The approach above can be extended to give the various mean second neighbor distances as shown in Figure 8. The error bars in the experiment are larger but the two sets of parallel straight lines predicted by the theory can be seen emerging from the experimental data. We note that all the results in Figures 7 and 8 are fit with a single parameter $a^{**} = 0.8$.

![Figure 8. The second nearest neighbor distances for $Ga_{1-x}In_xAs$ compared to the experimental results [13].](image)

No existing experimental results for semiconductor alloys are sufficiently good to need improvements beyond the present single parameter theory. For any particular alloy, simulations can be done using more sophisticated potentials, but any deviations found from these straight line Z plots are of dubious significance both experimentally and theoretically. This point is discussed more fully in [10]. We note that as the topological rigidity parameter $a^{**}$ tends to unity, the network becomes floppy and the two outer parts of the Z plot become horizontal as in the first panel of Figure 1. This provides a point of contact between the two very different approaches we have discussed. Because the results of the catchment area model are so very different from the harmonic spring model, it would be especially interesting to have the results of EXAFS experiments available for layered materials.

Similar results can be obtained for the binary alloy $Si_{1-x}Ge_x$ as shown in Figures 9 and 10. We have assumed the Si-Ge bond length to be the arithmetic mean of the Si-Si and Ge-Ge bond lengths as required by using the Pauling type atomic radii. Again all these sets of parallel lines in the two figures are fit with the single topological rigidity parameter $a^{**}$ which in this case is taken to be 0.707. Full details can be found in [10].
Figure 9. Mean nearest neighbor bond lengths for $Si_{1-x}Ge_x$. The open symbols are from computer simulations [14] and the solid symbols are from our simulations [10] using the Kirkwood potential (5). The straight lines are from theory, similar to that described in the text. Good experimental results are not available yet over the complete range of composition.

Figure 10. Similar results to Figure 9, except for mean second neighbor distances. The symbols are from our computer simulations using the Kirkwood potential [10].

We have also compared this approach with simulation results for amorphous $Si_{1-x}Ge_x$ alloys and find very similar behavior involving straight lines and very minor shifts from the corresponding results for crystalline alloys [10]. This is as expected as the topological rigidity parameter $a^{**}$ is determined by the tetrahedral coordination and not by the crystallinity of the network.
The approach we have described above gives a good account of the experimental results for semiconductor alloys and is intuitively appealing. Differences in force constants \( g \) and \( b \) can be incorporated into this approach via effective medium theory [10]. Very small curvatures in the \( Z \) plots are produced which are just at the limit of observability even in the most favorable case \( Zn_{1-x}Cd_xTe \) [10].

This theory is sufficiently simple that it can be extended to more complex semiconducting alloys like the quaternaries \( A_{1-x}B_xC_{1-y}D_y \) in which both the cations and the anions form random solid solutions. For example the argument we gave that the net tension across a (mathematical) plane must vanish leads to the following generalization of Vegard's law,

\[
<L> = (1-x)r_A^0 + xr_B^0 + (1-y)r_C^0 + yr_D^0
\]

(13)

The partial lengths can also be written down for nearest and next nearest neighbors for the quaternaries [10], where it would be difficult to explore the extensive parameter space with computer simulations.

Lest it should be thought that all alloys exhibit this very simple straight line \( Z \) plot behavior, we note that curvature is the normal situation in fcc metals [9]. This has been well documented for \( Au_{1-x}Ni_x \) alloys using EXAFS [15] and curvature is expected in all cases because of the large differences in force constants and charge transfer effects [9,14]. We note that the topological rigidity parameter \( \alpha^* \approx 0.2 \) in close packed metals, which are much more rigid than semiconductors due to having 12 rather than 4 nearest neighbors. The \( Z \) plot for metals as well as having curvature is therefore much tighter than the rather open \( Z \) plots characteristic of semiconductors.

**LAYERED MATERIALS**

The approach adopted in the previous section can be adapted to layered materials [16]. The input parameters required are the gallery heights \( h_A^0 \) and \( h_B^0 \) for the pure materials, together with the c axis compressibilities \( g_A \) and \( g_B \), all of which can be obtained from experiment. There is an additional parameter \( g_T \) which describes the transverse layer rigidity. This can also be found from experiment by studying the deformations of the layers that are manifested in low frequency phonon modes [17]. Again a better way is to treat \( g_T \) as a fitting parameter. The theory described in the previous section can be applied, and equations
(8), (10)-(12) are valid if the topological rigidity parameter is re-interpreted. For the case when $Q_A = Q_B$, linear superposition of the strain fields holds and the straight line $Z$ plots discussed previously are obtained. The topological rigidity parameter is small when $Q_T \gg Q_A$ and the layers are very rigid as in the clays, leading to a very tight $Z$ plot. On the other hand when $Q_T < Q_A$, the layers are quite floppy as in graphite, and an open $Z$ plot similar to that in semiconductors is obtained. In all cases, we get Vegard's law for the mean gallery height. Vegard's law is always obtained from this model if the spring constant

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11}
\caption{Showing the mean gallery heights. The lower, middle and upper curves in each panel are for the dimensionless heights $<d_A>$, $<d>$ and $<d_B>$. The dashed lines are effective medium theory and the symbols are from computer simulations. The vertical bars represent the widths of the length distribution functions for the A and B intercalants. The parameters used are $Q_T = Q_A$ and $Q_B = 5Q_A$. The three panels are for anticlustering (A), random (R) and clustering (C) arrangements of intercalants [16].}
\end{figure}

$Q_A = Q_B$. This result is independent of the transverse layer rigidity $Q_T$ and of any clustering in the alloy that may be present [15]. Clearly this result is at variance with the experimental results shown in Figure 4. The model can be extended by allowing for different spring constants $Q_A$ and $Q_B$ and also by including anharmonicity as is discussed in the next section.

For different spring constants $Q_A$ and $Q_B$, we have shown that effective medium theory works well, by comparing with the results of computer simulations on the same model. Some sample results are given in Figure 11.
The results in Figure 11 show that different force constants $q_A$ and $q_B$ can produce an upward bowing similar to that seen experimentally in Figure 4, if the larger ion has a smaller compressibility (i.e. a larger spring constant). However the extreme flatness of the $<d>$ curve around $x=1$ is not reproduced by this model, and requires anharmonicity. The catchment area model can be regarded as the limit of a very anharmonic spring model.

In Figure 11, we show the effects of non-random intercalation. We assumed that the intercalation was random in each gallery, but that there were correlations between adjacent galleries. The most likely of these in anticlustering, where a large ion intercalates above a smaller ion in the next gallery etc. This actually leads to a singularity at $x=0.5$, corresponding to a nascent antiferromagnetic type of alternation between large and small ions. Clustering is less likely where a large ion in one gallery has another large ion in an adjacent gallery. Nevertheless, we see from figure 11 that these correlations have a large effect on $<d_A>$ and $<d_B>$, but little effect on the overall mean $<d>$. This is one more reason why EXAFS experiments would give very important information in layered materials.

EFFECTS OF ANHARMONICITY

Effects of anharmonicity on the mean length $<L>$ in 2D and 3D solid solutions can be included by adding an additional cubic term to the potential [see Eq. (5)]

$$V_{\text{anharmonic}} = V_{\text{harmonic}} - \frac{1}{3} \gamma \sum_{i,j} (L_{ij} - L_{ij}^0)^3$$

When both anharmonic and differential compressibility $(q_B - q_A)$ effects are small, deviations from the Vegard's law can be calculated using perturbation theory. For example, for an alloy of the type $A_1-xB_xC$ up to first order we have

$$<L> = (1-x)L_{AC}^0 + xL_{BC}^0 + x(1-x)(1 - a^{**})[\gamma \Delta L/\tilde{G} + \Delta \alpha/\tilde{G}]$$

where $\Delta L = (L_{BC}^0 - L_{AC}^0)$, $\Delta \alpha = q_{BC} - q_{AC}$, and $\tilde{G} = (1-x) q_{AC} + x q_{BC}$ is an average force constant. For systems where $\Delta \alpha = 0$, deviations from Vegard's law arise from anharmonic effects only and since $\gamma$ is usually positive, anharmonicity causes a superlinear behavior.
One can estimate anharmonic effects from the pressure derivative of the bulk modulus which directly gives a useful dimensionless quantity

\[ 1 + 2(\langle \Delta L \rangle / a)/3, \]

(16)

where \( \langle L \rangle \) is the mean bond length. In many 3D solid solutions the above derivative turns out to be remarkably constant from material to material and \( \approx 5 \). Using this we conclude that anharmonic effects will be just about observable for the largest mismatches among the semiconducting compounds (i.e. \( \Delta L / a \approx 0.5 \) for the 8% lattice mismatch in Ga\(_{1-x}\)In\(_x\)As).

Anharmonicity effects in layered intercalation compounds can however be quite significant. In the earlier part of this lecture, the gallery structure of the intercalation compounds was discussed using a simple catchment area model which is essentially anharmonic in nature. The results of this model fitted the experimental data rather well. Later, we discussed the gallery structure using harmonic spring models. Here one can fit the experimental data, although not very well, by assuming that the harmonic spring constant of the larger ion (\( Q_B \)) is considerably larger than that for the smaller ion (\( Q_A \)). One of the fundamental differences between these two models is in the \( x \)-dependence of the normalized average gallery spacing \( \langle d \rangle \) as \( x \to 1 \), the catchment area model gives a nonlinear decrease i.e. \( \langle d \rangle = 1 - (1-x)^p \) (the parameter \( p \) increases with the transverse layer rigidity) whereas the harmonic model gives a linear decrease i.e. \( \langle d \rangle = 1 - m(1-x) \). The slope \( m \) is related to the ratio \( R = Q_A / Q_B \) and the Watson integral \( W \) [see Ref.16 for the definition of \( W \)] which is equivalent to the topological rigidity parameter a discussed earlier by the relation

\[ m = \frac{R}{RW+(W-1)} \]

(17)

In the floppy layer limit, \( W = 1 \), \( m \) becomes 1, i.e. we have Vegard's law. In the limit \( R = 0 \), i.e. when the smaller atom is infinitely compressible, \( m = 0 \) as long as we have finite transverse layer rigidity (\( W > 1 \)). What this means physically is that the smaller atoms do not contribute to the layer spacing as soon as the local height becomes larger than their natural height. This is true in the catchment area model. Thus to relate the spring model to the catchment area model we must take the harmonic spring constant of the smaller ion \( Q_A = 0 \) and treat the many defect problem exactly.
An alternate way to tackle the anharmonicity problem is to take a realistic anharmonic interaction between the intercalants and host and also to allow for the anharmonic terms in the transverse layer distortion energy [18]. We have studied the effects of anharmonicity on the mean gallery spacing by taking a Lennard Jones interaction between the host and the intercalants, and treating the layer distortion energy in the harmonic approximation. As expected from physical grounds, we find anharmonicity effects are important especially in the limit of small concentration of smaller intercalants (x < 1), particularly when the transverse layer rigidity is large. In this limit the interaction between the larger intercalants and the host layer can be treated adequately by a harmonic model but for the smaller intercalant anharmonicity is crucial. Even if the harmonic parts of the interaction are the same for both types of intercalants one sees deviations from Vegard's law. The deviation increases with anharmonicity and for a given anharmonicity, it increases with the transverse layer rigidity.

Finally, we can compare the results of computer simulation studies using LJ potentials with those obtained in the catchment area model. In the LJ model there are two fundamental parameters, \( R = \frac{A_A}{A_B} \) and \( \frac{g_T}{g_B} \). In Figure 12, we give the simulation results for four different values of R (0.1, 0.07, 0.05, 0.02) and for a given value of the transverse layer rigidity \( g_T/g_B = 0.1 \), which corresponds to a reasonably rigid layer. We plot <d>, <d_B> and <d_A> and fit <d> with the curve \( 1 - (1-x)^2 \) (dashed curve) and <d_A> with the curve \( 1 - (1-x)^3 \) (dotted curve). These analytic forms were obtained in the catchment area model (with \( p' = p-1 \)) and <d> fitted the experimental results rather well. We find that the mean gallery separation <d> obtained in the LJ model (simulation results) fits the \( 1 - (1-x)^2 \) curve very well, the simulation results are slightly below the analytic curve for values of x > 0.5. Furthermore the simulation results for <d_A> fit rather well the analytic form \( 1 - (1-x)^3 \) with \( p' = p-1 \) again justifying the validity of the simple catchment area model for these layered intercalation systems [see Eqs. (3) and (4)]. However the results for <d_A> differ near the x = 1 region. The parameter p increases with decrease in R and for a fixed R increases with the transverse layer rigidity. Thus the catchment area model somehow incorporates two important physical effects, the compressibility ratio of the two ions and the transverse layer rigidity. However it is strictly valid in the limit \( R = 0 \). For finite R, <d_B> deviates from 1 and <d_A> is less than 1 in the limit x = 1 and these deviations become less significant as
the layers become more rigid. As discussed before, by carefully measuring local heights one should be able to shed some light on the roles of anharmonicity, differential compressibility, and the transverse layer rigidity.

EFFECTS OF PRESSURE

Finally we would like to make some brief remarks on the effect of external pressure on the structural properties of size mismatched alloys. For the layered solids because of the large elastic anisotropy, external hydrostatic pressure usually transforms to uniaxial pressure perpendicular to the layers. Thus one expects to see changes in the gallery

![Graphs showing the effects of pressure on gallery height](image)

**Figure 12.** Average gallery height for an anharmonic bilayer using Lennard Jones interaction between intercalants and the host gallery [18]. The symbols are simulation results for $\langle d \rangle$, $d_A^*$ and $d_B^*$. The dashed and dotted lines are the results from the catchment area model (see text).
structure under the action of external pressure. In the limit when both
the intercalants have the same compressibility, the effect of external
uniaxial force is to shift the d-spacing by a constant amount. Thus in
the scaled (dimensionless) form one cannot see the effect of external
pressure. However if the two intercalants have different compres-
sibilities, one expects to see changes in the x-dependence of all three
quantities \(<d>, \ <d_B>, \text{ and } \ <d_A\). These have to be worked out using the
effective medium theory which we have developed in the case of zero ex-
ternal pressure [10,16]. In the 3D solid solutions, particularly the
semiconducting alloys where the compressibilities of the different bonds
are nearly the same we expect an overall rigid shifting of the \(z\) plots.

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