Contents

1 Radial Density Function

1.1 Calculation of Distances with Periodicity

Suppose a large chemical structure has uncountably many atoms but the follow a periodic pattern of n atoms every p Angstroms. The atom locations within a period are given by $a_1, a_2, \ldots, a_n$ where $a_i \in \mathbb{R}^3$. The radial density function is the distribution of pairwise distances between these atoms.

The distances d between atoms a_i and a_j where $i \neq j$, atom a_i has been displaced by x, and atom a_j has been displaced by y per the periodicity is

$$
d^2 = \langle a_i + x - (a_j + y), a_i + x - (a_j + y) \rangle
$$
$$
= \langle a_i - a_j, a_i - a_j \rangle + \langle x - y, x - y \rangle + 2 \langle a_i - a_j, x - y \rangle
$$

where $x = (k_1 p, k_2 p, k_3 p)$ for $k_i \in \mathbb{Z}$ and $y = (l_1 p, l_2 p, l_3 p)$ for $l_i \in \mathbb{Z}$. Here $\langle x, y \rangle$ denotes the inner product between x and y.

Suppose D is a random variable that samples at random the distances, d, in the chemical structure. The radial density function is the probability density function of this random variable. This

function can be estimated empirically via a histogram.

The histogram is then normalized by the volume a spherical shell.

$$\frac{4}{3}\pi(r+\Delta r)^3 - \frac{4}{3}\pi r^3$$
$$= \frac{4}{3}(3r^2\Delta r + 3r(\Delta r)^2 + (\Delta r)^3)$$
$$\approx 4\pi r^2 \Delta r$$

where Δr tends to zero.

For a histogram with frequency, f, for bin $[d_i, d_{i+1}]$, we replace f with f/d_i^2. And then normalize the histogram so that the sum over all bins is one.

1.2   Adding Noise For Atom Vibration

Due to the vibrations of the molecules, the radial density function will not be just the equilibrium positions. We can approximate this fluctuation in distances via a Gaussian filter or Weierstrass transform.

$$F(x) = \frac{1}{\sqrt{4\pi t}} \int_{-\infty}^{\infty} f(y) e^{-\frac{(x-y)^2}{4t}} dy$$

Given that the density function is only defined for a finite number of distances, we use a discrete version of the transform making sure to keep the sum of the weights equal to one.

$$F(d_k) = \frac{\sum_{d_i=d_0}^{d_n} f(d_i) \exp\left(-\frac{(d_k-d_i)^2}{4t}\right)}{\sum_{d_i=d_0}^{d_n} \exp\left(-\frac{(d_k-d_i)^2}{4t}\right)}$$

where d_0 is the minimum distance and d_n is the maximum distance.

1.3 Cubane Example

As an example of the above, below are the calculations for cubane (C_8H_8).

Here are the coordinates of the elements in cubane in Angstroms.

```
Element, x, y, z
C, 1.2455, 0.5367,-0.0729
C, 0.9239,-0.9952, 0.0237
C,-0.1226,-0.7041, 1.1548
C, 0.1989, 0.8277, 1.0582
C, 0.1226, 0.7042,-1.1548
C,-0.9239, 0.9952,-0.0237
C,-1.2454,-0.5367, 0.0729
C,-0.1989,-0.8277,-1.0582
H, 2.2431, 0.9666,-0.1313
H, 1.6638,-1.7924, 0.0426
H,-0.2209,-1.2683, 2.0797
H, 0.3583, 1.4907, 1.9059
H, 0.2208, 1.2681,-2.0799
H,-1.6640, 1.7922,-0.0427
H,-2.2430,-0.9665, 0.1313
H,-0.3583,-1.4906,-1.9058
```

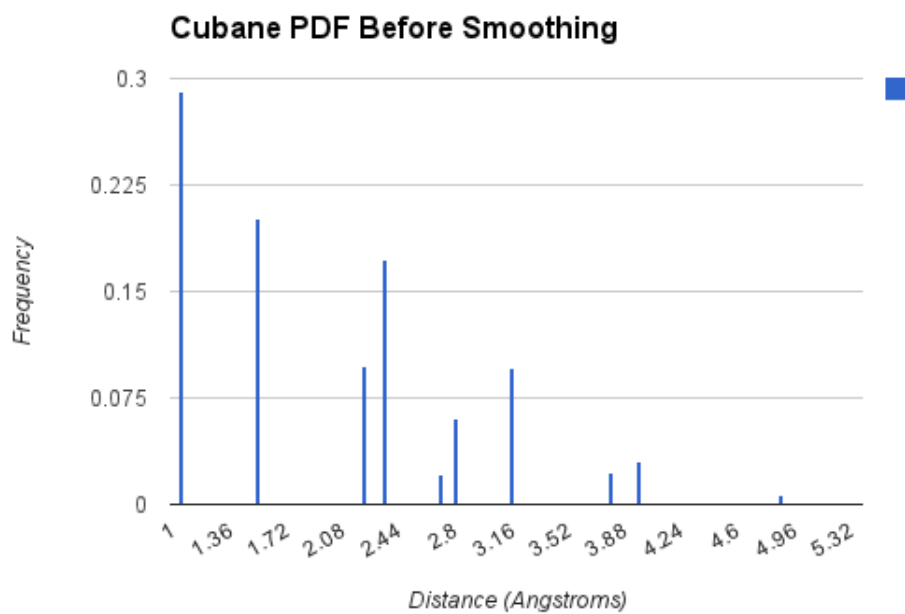### 1.3.1 Cubane Radial Density Functions
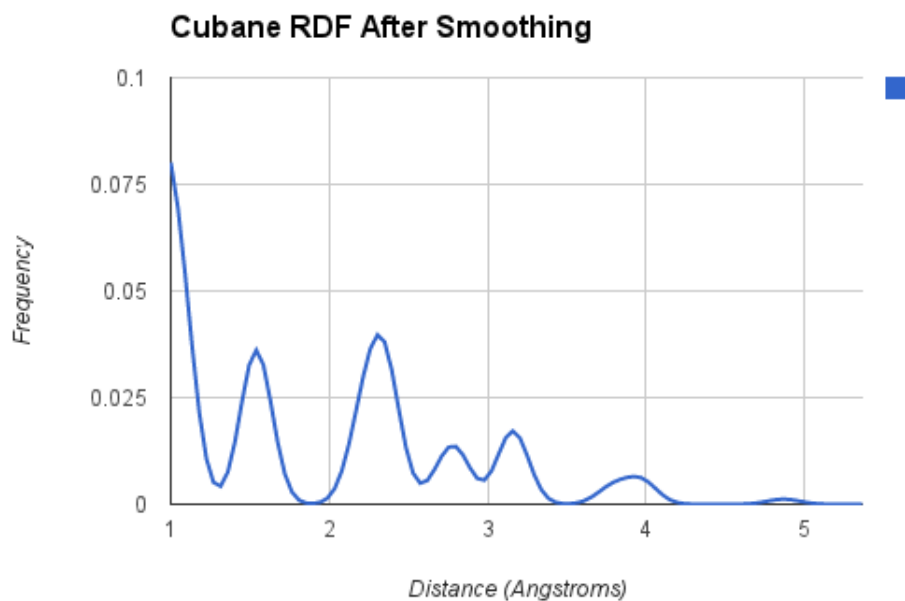
Figure 1: Before Smoothing

Figure 2: After Smoothing

1.4 Experimental and Theoretical RDFs for Known Structures

For some structures, we are able to theoretically calculate the RDF from atom locations and also have the experimental RDF from Xray scattering. These known matches provide some insight into understanding how the experiments and theory align. The RDF comparison are shown below.

Outside of these structures, there are not many other known matches. There are a few reasons for this. First, if a structures is already known at the atomic level then there is no need to run an xray diffraction experiment. Second, if a structure is periodic as in a lattice, the atomic structure can be determined by xray diffraction which is easier and cheaper than xray scattering.

1.4.1 Ga As

Experimental Data: Pair Distribution Functions Analysis, Valeri Petkov
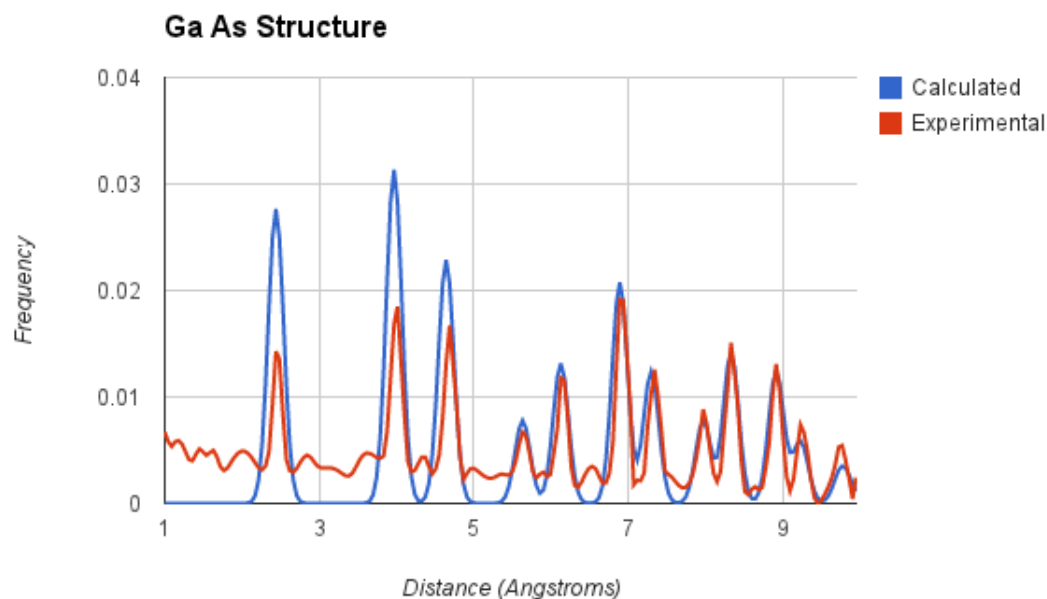Calculated Data: Maria Chan

Figure 3: Ga As

1.4.2   In As

Experimental Data: Pair Distribution Functions Analysis, Valeri Petkov
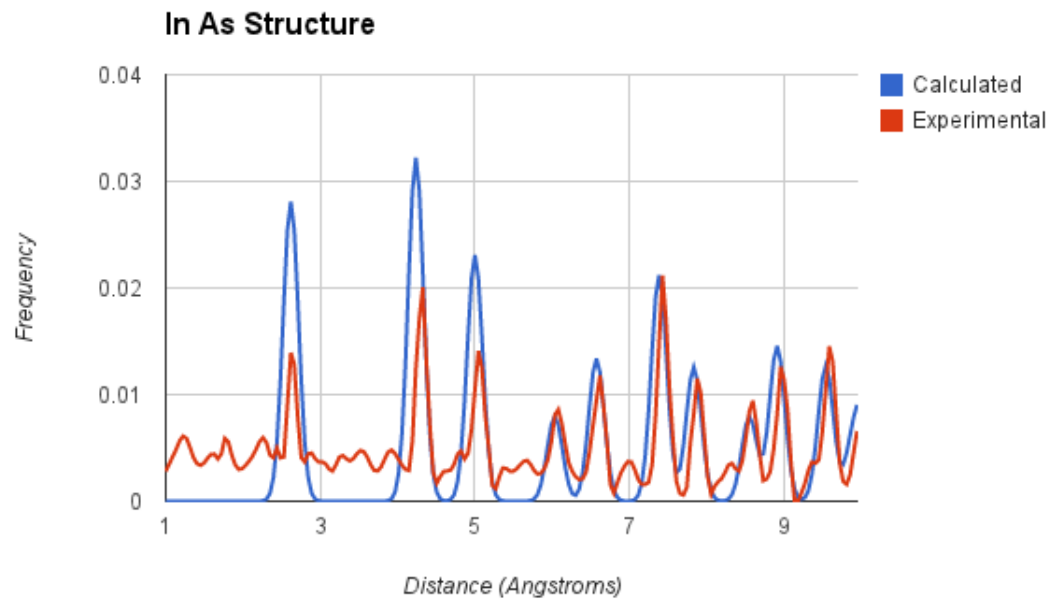
Calculated Data: Maria Chan

Figure 4: In As

1.4.3   Si Lattice

Experimental Data: J. AM. CHEM. SOC. VOL. 133, NO. 3, 2011, P: 503-512

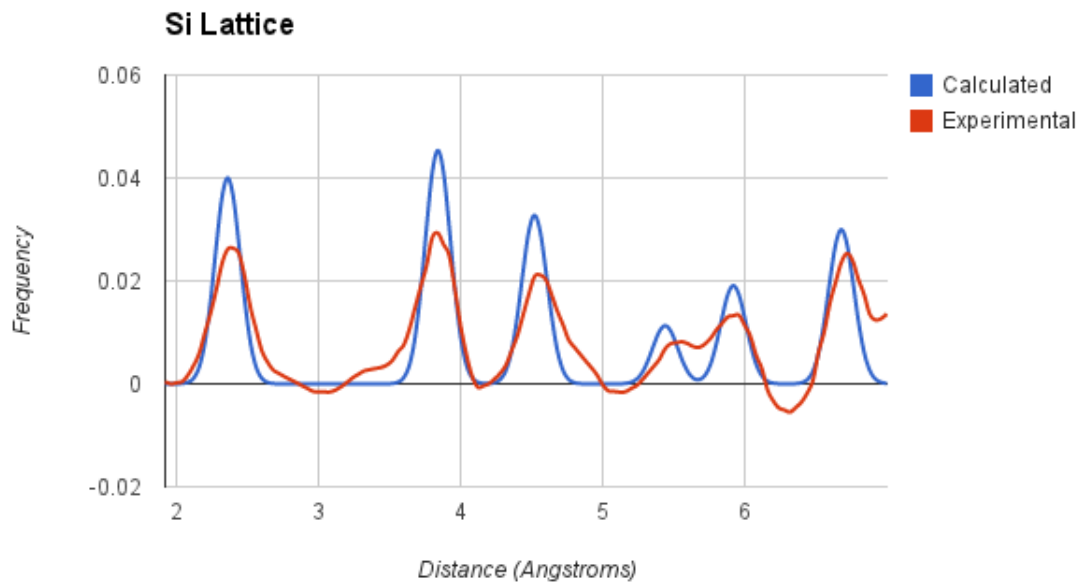Calculated Data: http://materialsproject.org/materials/mp-149/

Figure 5: Si Lattice

2 Sources

http://en.wikipedia.org/wiki/Atom_vibrations

http://en.wikipedia.org/wiki/Radial_distribution_function

http://en.wikipedia.org/wiki/Weierstrass_transform