in subsequent sections, but we point to some of the important aspects here, since many are shared by other diffusion mechanisms. First, it is necessary for an atom to have an adjacent vacancy in order for it to participate in this mechanism. The atom and the vacancy both start and end on lattice sites, but at some point during the jump, the lattice around the jumping atom and vacancy is distorted, and, while this distortion is much less than that needed for two atoms to exchange places, it still represents a high-energy configuration for the lattice, and hence presents an energy barrier which must be overcome for the jump to occur. Similar energy barriers are common to all jump mechanisms. Once the jump has occurred, the vacancy can jump next to any of its nearest neighbors. The atom which has just jumped however, is most likely to jump next by again exchanging with the vacancy, and reversing the effect of the previous jump. Thus two subsequent atomic jumps cancel resulting in a decrease in atomic motion over that of completely uncorrelated jumps. We see later that the correlation of jump direction only changes diffusivities by a small amount for self diffusion, but they can become very important when there exists strong attractive interactions between vacancies and impurities.

![Figure 2.1: Schematic of the vacancy mechanism for an atomic jump.](image)

Atoms which exist as dilute interstitial impurities, such as carbon in iron, can jump from one interstitial site to the next without huge lattice distortions, since the adjacent interstitial sites are most often vacant. This process is shown schematically in Fig. 2.2.

It is possible for an interstitial mechanism to operate for self-diffusion or for impurity atoms which normally reside on lattice sites. Even for host or substitutional impurity atoms, since there will be some (usually small) concentration which reside on interstitial sites. These interstitial atoms can jump to a lattice site, pushing the atom formerly residing there into an adjacent interstitial site. This process is shown in Fig. 2.3.
Chapter 2. Atomistic Mechanisms of Diffusion

Figure 2.2: Schematic of an interstitial atom diffusing in a BCC matrix. Shown are jumps from edge-centered to edge-centered and from edge-center to face-center sites.

Figure 2.3: Schematic of the interstitial diffusion mechanism, where an interstitial atom jumps to a lattice site forcing its occupant to move to an adjacent interstitial site.
A related, and perhaps more common, mechanism is the interstitialcy mechanism. For self interstitials, it is more common for two atoms to share a lattice site, rather than for one to be in an interstitial site while the other resides on the lattice site. This interstitialcy can jump from one lattice site to the next as shown in Fig. 2.4. A related mechanism is known as the crowdion mechanism. Here the extra atom is considered as spread out over a certain length along a row of atoms in the crystal. This extra atom can shuffle along down the row.

![Figure 2.4: Schematic of the interstitialcy diffusion mechanism, where one of two atoms which share a lattice site jumps to share an adjacent lattice site.](image)

The last mechanism we consider is the ring mechanism, originally proposed by Zener. This mechanism requires no defect or vacant sites, but involves the collective motion of several atoms in a ring pattern as shown in Fig. 2.5.

### 2.4 Expression for Diffusivity

By considering these mechanisms we see that we must alter our simple expression for diffusivity $D = a^2 \Gamma / 6$. We propose a more general expression for diffusivity which accounts for some of the factors we have discussed above. The correlation of jump directions must be taken into account. In most mechanisms, there must be adjacent occupied and unoccupied sites, so we must consider the probability that this is so. And we must also consider the rate at which the atom and vacancy on adjacent sites exchange. Considering these factors, as well as geometrical ones we find:

$$D = f(sa_0)^2 \nu pjz$$  \hspace{1cm} (2.5)
component of the jump distance along the direction considered, where $a_0$ is the lattice parameter, $\nu$ is the rate of exchange of the atom and a given vacant site. Here $p$ is the occupational probability, which is the probability that a given atom is residing on the type of site in question, times the probability than a given adjacent site is available for a jump, $z$ is the number of adjacent sites for the atom to jump into, and $j$ is the fraction of them with a component in the direction considered.

As an example of the application of Eqn. 2.5 we consider the vacancy mechanism in a FCC lattice. We consider jumps along the [100] type directions. The distance between planes is $a_0/2$ so $s = 1/2$. The probability that a given atom sits on a lattice site is about one, since there are normally few self-interstitials so most all atoms reside on lattice sites. The probability that an adjacent site is available for a jump is just $x_V^o$, the equilibrium concentration of vacancies. For FCC, $z = 12$, and jumps to $1/3$ of the nearest neighbors have a component along a given [100] type direction. For example for an atom at (000) jumping to the a plane lying a distance $a_0/2$ along the [100] direction has available the sites $\frac{a_0}{2}(110)$, $\frac{a_0}{2}(101)$, $\frac{a_0}{2}(110)$, and $\frac{a_0}{2}(101)$. Hence we have for the diffusivity:

$$D = f \left( \frac{a_0}{2} \right)^2 \nu x_V^o \frac{12}{3} = f a_0^2 x_V^o \nu$$

We now turn to a more detailed discussion of the various factors in this equation.
2.5 Equilibrium Concentration of Vacancies

In any crystalline solid, there will be a certain fraction of the lattice sites which are vacant. This results from a balance between the enthalpy cost associated with forming vacancies, and the entropy gained by the ability to arrange the system in more ways as a result of having more vacant sites. We use a thermodynamic approach to find the equilibrium concentration of vacancies by minimizing the free energy. We consider a lattice with a fixed number ($N_L$) of lattice sites and we place $N_V$ vacancies distributed randomly on these sites. Since these vacancies can be arranged in many ways, there is a mixing entropy $\Delta S_m$ associated with their presence. This is given by:

$$\Delta S_m = k_B \ln \Omega$$

(2.6)

where $k_B$ is Boltzman’s constant and $\Omega$ is the number of ways which the vacancies can be arranged. To find $\Omega$ we note that the number of combinations of $N$ objects taken $n$ at a time is:

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

As an example of the use of this formula we calculate the chances of winning the California lottery. Here you must guess six numbers from 1 to 53. The total number of possibilities is then the number of ways of taking 53 objects 6 at a time, or:

$$\binom{53}{6} = \frac{53!}{6!47!} = \frac{53 \cdot 52 \cdot 51 \cdot 50 \cdot 49 \cdot 48 \cdot 47!}{6!47!} = 22,957,480$$

(Note that this does not mean the it would be a good investment to buy a lottery ticket for each combination if the payoff gets larger than 23 million since there can be other winners to share your prize.)

In our problem, we select $N_V$ of the $N_L$ lattice sites and put vacancies on them. So we have for $\Omega$:

$$\Omega = \frac{N_L!}{N_V!(N_L - N_V)!}$$

(2.7)

In Eqn. 2.6, we need $\ln \Omega$, which we can find using Sterling’s approximation:

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$
We find for $\ln N!$:

$$\ln N! \approx N \ln N - N \ln e + \frac{1}{2} [\ln 2\pi + \ln N]$$

The last term is small compared to the others so we ignore it. Applying this to Eqn. 2.7, we find:

$$\ln \Omega = \ln N_L! - \ln N_V! - \ln [(N_L - N_V)!]$$

$$\approx N_L \ln N_L - N_L - N_V \ln N_V + N_V - (N_L - N_V) \ln (N_L - N_V) + N_L - N_V$$

$$= N_L \ln N_L - N_V \ln N_V - (N_L - N_V) \ln (N_L - N_V)$$

(2.8)

We define the mole fraction of vacancies to be given by:

$$x_V = \frac{N_V}{N_L}$$

which gives:

$$1 - x_V = \frac{N_L - N_V}{N_L}$$

Applying this to the second term on the right in Eqn. 2.8, we get:

$$N_V \ln N_V = N_L x_V \ln N_L x_V = N_L x_V \ln x_V + N_V \ln N_L$$

Similarly for the third term:

$$(N_L - N_V) \ln (N_L - N_V) = N_L (1 - x_V) \ln (1 - x_V) + (N_L - N_V) \ln N_L$$

Combining these and simplifying we find:

$$\ln \Omega = N_L \ln N_L - N_L x_V \ln x_V - N_V \ln N_L - N_L (1 - x_V) \ln (1 - x_V) - (N_L - N_V) \ln N_L$$

$$= -N_L [x_V \ln x_V + (1 - x_V) \ln (1 - x_V)]$$

We now plug this into Eqn. 2.6, considering the entropy per lattice site, and find:

$$\Delta S_m = -k_B [x_V \ln x_V + (1 - x_V) \ln (1 - x_V)]$$

This expression is plotted in Fig. 2.6. You can see that the entropy of a mixture is greater than that of the unmixed components.
Figure 2.6: Entropy of mixing as a function of vacancy concentration.

A second aspect of mixing entropy is that the change in entropy associated with the initial addition of a vanishingly small increment of either component (in this case either vacancies or occupied lattice sites) is infinite. This is a consequence of the infinite slope in $\Delta S_m$ at $x_V = 0$ and at $x_V = 1$.

$$\left. \frac{d\Delta S_m}{dx_V} \right|_{0,1} = -k_B \ln \frac{x_V}{1 - x_V} \bigg|_{0,1} = \pm \infty$$

This infinite slope means that you can always lower the free energy ($\Delta G = \Delta H - T\Delta S$) of a perfect vacancy-free crystal by adding some vacancies.

The mixing entropy is not the complete story, there can be additional changes in the entropy associated with the addition of vacancies. If $\Delta S_V$ is the change in entropy associated with the addition of a mole fraction $x_V$ of vacancies, then:

$$\Delta S_V = x_V \Delta S_\nu + \Delta S_m$$

where $\Delta S_\nu$ is the excess entropy due to the change in vibration spectrum of the atoms around the vacancy. Since the atoms around a vacancy have more room to move around, the entropy is increased.

We now can write the change in free energy associated with the addition of vacancies.

$$\Delta G = \Delta H - T\Delta S$$
where $\Delta H_V$ is the enthalpy associated with formation of a vacancy. This is

$$\Delta G_V = x_V (\Delta H_V - T \Delta S_V) + k_B T \left[ x_V \ln x_V + (1 - x_V) \ln (1 - x_V) \right]$$

Rearranging we find:

$$\frac{x_V^o}{1 - x_V^o} = \exp \left( -\frac{\Delta G'_V}{k_B T} \right)$$

where $\Delta G'_V = \Delta H_V - T \Delta S_V$ is the free energy change per vacancy excluding the entropy of mixing term. We find that the equilibrium mole fractions of
vacancies are usually about $10^{-4} - 10^{-5}$ so that the above equation can be written:

$$x_V^0 = \exp \left( - \frac{\Delta G'_V}{k_B T} \right)$$  \hspace{1cm} (2.10)

Our formalism here for calculating the equilibrium concentration of vacancies is applicable to other types of defects as well. For instance, the concentration of self interstitials can be found from an expression similar to Eqn. 2.10, obtained by substituting in the appropriate free energy cost $\Delta G'$ for the formation of the self interstitial, where again, the $\Delta G'$ must not include the configurational entropy term.

### 2.5.1 Measurement of Vacancy Concentration by Dilation and Lattice Parameter

We consider a chunk of material with a fixed number of atoms, $N$. If we raise the temperature we have two effects which change the volume and lattice parameter of the sample.

A. Thermal expansion, causing an increase in length and an increase in lattice parameter.

B. Increase in the number of vacancies, causing increase in length but a decrease in lattice parameter.

Since these two effects affect the lattice parameter and length differently, we can deduce the number of vacancies by measuring the difference between the fractional change in length and the fraction change in lattice parameter.

We examine the effect of creation of vacancies and consider it as a two step process.

1. Remove atoms from interior to create vacancies. Atoms around new vacancies relax inward, strain propagates to surface (Eshleby effect) causing decrease in average lattice parameter and in volume. The change in volume associated with this process is:

$$\Delta V_1 = N_V V_A (f - 1)$$

where $V_A$ is the atomic volume and $fV_A$ is the effective volume of a vacancy.
2. Add the atoms we removed to the surface. The volume change for this process is:

\[ \Delta V_2 = N_V V_A \]

The total volume change for the addition of vacancies is then:

\[ \Delta V_V = N_V V_A f \]

This is a positive volume change, but average lattice parameter still decreases.

We can relate changes in volume to changes in length by:

\[
\frac{\Delta V}{V_0} = \frac{V - V_0}{V_0} = \frac{L^3 - L_0^3}{L_0^3} = \frac{(\Delta L + L_0)^3}{L_0^3} - 1 = \left(1 + \frac{\Delta L}{L_0}\right)^3 - 1 \\
\approx 3\frac{\Delta L}{L_0}
\]

We have \( N \) atoms and at and temperature \( T \), \( N_V(T) \) vacancies. We have \( P \) lattice sites per cell. The volume at any temperature is given by:

\[ V = [N + N_V(T)] \frac{a^3(T)}{P} \]

where \( a(T) \) is the temperature dependent lattice parameter. If we define \( \Delta a = a(T) - a(T_0) \) and \( \Delta N_V = N_V(T) - N_V(T_0) \) where \( T_0 \) is some reference temperature, we have for the fractional change in volume:

\[
\frac{\Delta V}{V_0} = 3\frac{\Delta L}{L_0} = \frac{[N + N_V(T)] a^3(T)}{[N + N_V(T_0)] a^3(T_0)} - 1 \\
= \left(1 + \frac{N_V(T)}{N}ight) \left(1 + \frac{N_V(T)}{N}ight) \left(1 + \frac{\Delta a}{a}\right)^3 - 1
\]
2.6 Atomic Jump Frequency

The next step in our exploration of diffusivity is to examine the atomic jumping frequency $\nu$. This is the rate that an atom jumps to an adjacent available site. A schematic of this process for the case of vacancy diffusion in a close-packed plane is shown in Fig. 2.8. Here we see that the initial and final states have the atoms sitting in different equilibrium positions. However to get from one equilibrium position to another, the atom must pass through a non-equilibrium position which distorts considerably the positions of adjacent atoms. This distortion will have an energy cost, so the energy will have a maximum as the atom moves from one lattice point to another. This is shown schematically in Fig. 2.9, where the free energy is plotted as a function of some coordinate which measures the configuration of the system.

We would like to know how often this jump occurs. In fact one may ask why it occurs at all if it involves raising, even temporarily, the energy of the system. The answer can be found by examining the nature of the state where the atom is between the lattice sites. This state, known as an activated complex, is thermodynamically unstable since any small excursion
CHAPTER 2. ATOMISTIC MECHANISMS OF DIFFUSION

Figure 2.8: Schematic of the atomic jump process.

Figure 2.9: Schematic of free energy as a function of reaction coordinate as an atom moves from one lattice site another. In this case the reaction coordinate corresponds to the distance along the path connecting the lattice positions.
along the reaction path will lower the energy of the system. Formation and decomposition of this activated state corresponds to an atom jump. Statistical mechanics treatments of this process yield a remarkably simple result. Since the statistical mechanics used is somewhat beyond the scope of this course, we instead present plausible physical arguments to arrive at the same result.

We consider that the activation complex is thermodynamically unstable so that any motion along the reaction path will result in its decomposition and the completion of an atomic jump. The rate of atomic jumping will be given by the product $\nu_0 n_{ac}$, where $\nu_0$ is the frequency which the atom will vibrate along the reaction path, and $n_{ac}$ is the number fraction of atoms in activated complexes. We calculate the number fraction of activated complexes using the same thermodynamic treatment we used to calculate the equilibrium concentration of vacancies. One might question how we can apply thermodynamics to an unstable configuration such as the activated complex. Formally this is justified by removing from the activated complex the degree of freedom corresponding to motion along the reaction path. With respect to other coordinates, the activated complex is stable, so that the energy of the system has a saddle point at the configuration corresponding to the activated complex. Hence thermodynamics can be performed on this reduced system and the number of complexes calculated. We then find:

$$\nu = \nu_0 \exp \left( \frac{-\Delta G_M'}{k_B T} \right)$$

(2.12)

where $\Delta G_M'$ is the free energy associated with formation of an activated complex less the configurational entropy part, as in our expression for the number fraction of vacancies. As such it is the free energy associated with migration and is known as a migration free energy. This expression, Eqn. 2.12, is characteristic of thermally activated processes. The quantity $\Delta G_M'$ is an activation free energy, and we see that it comes into the expression from the minimization of the energy of the system with respect to the formation of activated complexes. It is the mixing or configurational entropy which drives the formation of these activated complexes, and as temperature increases, the importance of this entropy contribution also increases. In this sense, the process is said to be thermally activated.

Let’s now consider the diffusivity for a vacancy mechanism. We have:

$$D = f a_0^2 \nu^2 \nu = f a_0^2 \nu_0 \exp \left( \frac{-\Delta G_M' - \Delta G_V'}{k_B T} \right)$$
\[ f a_0^2 \nu_0 \exp \left( \frac{\Delta S_M + \Delta S_V}{k_B} \right) \exp \left( \frac{-\Delta H_M - \Delta H_V}{k_B T} \right) \]
\[ = D_0 \exp \left( \frac{-Q}{k_B T} \right) \] (2.13)

where \( Q = \Delta H_V + \Delta H_M \) is the activation energy consisting of formation and migration contributions. Quantities which can be described by an equation such as Eqn. 2.13 are said to follow Arrhenius behavior. A plot of the log of the diffusivity versus \( 1/T \), known as an Arrhenius plot, will have \( Q \) as the slope, and \( \ln D_0 \) as the intercept. Note that for this diffusion mechanism, both formation of the vacancy and formation of the activated complex have an effect on the activation energy.

### 2.7 Correlation Coefficient

We next consider the correlation coefficient \( f \) which accounts for the correlation between directions of subsequent jumps. We illustrate this effect by considering a two-dimensional close-packed array with a tracer \( A^* \) diffusing in an otherwise identical host \( A \). Referring to Fig. 2.10, we consider the situation where the tracer at 7 has just jumped with the vacancy at 6. We wish to determine the degree to which the direction of the next jump of the tracer will be correlated with that of the jump which has just occurred. In fact, we see that the next tracer jump is most likely going to be an exchange with the vacancy, jumping from 7 back to 6. This jump will reverse the previous jump. This violates our assumption that the jumps are random in direction. There will be more atomic motion than we would measure by just investigating the rearrangement of tracer atoms, since many jumps would be ineffective in movement of tracer atoms. In contrast, the vacancy can jump to any of its nearest neighbors with equal probability, so there is no correlation between the direction of its next jump and that of its last. We define the correlation coefficient as:

\[ f = \lim_{n \to \infty} \frac{\langle R_n^2(A^*) \rangle}{\langle R_n^2(V) \rangle} = \frac{D_{A^*}}{D_A} \] (2.14)

where \( \langle R_n^2(A^*) \rangle \) is the averaged square displacement of the tracer atom after \( n \) jumps, and \( \langle R_n^2(V) \rangle \) is the similar quantity for the vacancy. The quantity \( D_{A^*} \) is the tracer diffusivity and \( D_A \) is the self diffusivity, which just a measure of the rate of jumping of atoms, and does not take into account the effectiveness of the jumps in rearranging the atoms, since for self diffusivity
we only consider one type of atom. The last equality in Eqn. 2.14 results from the observation that the diffusion distance is proportional to the square root of the diffusivity, so the ratio of the diffusivities will be proportional to the ratio of the square of the diffusion distances.

\[
\begin{array}{cccccccc}
\bigcirc & \bigcirc & \bigcirc & 1 & 2 & \bigcirc & \bigcirc & \bigcirc \\
\bigcirc & \bigcirc & \bigcirc & 6 & 7 & 3 & \bigcirc & \bigcirc \\
\bigcirc & \bigcirc & \bigcirc & 5 & 4 & \bigcirc & \bigcirc & \bigcirc \\
\end{array}
\]

Figure 2.10: Two-dimensional close-packed array with tracer and vacancy. The tracer has just jumped with the vacancy, so the last tracer jump was from 6 to 7.

Since the vacancy has random jump directions we see from Eqn. 2.4 that:

\[
\langle R_n^2(V) \rangle = na^2
\]

so that we find for \( f \):

\[
f = \lim_{n \to \infty} \left( 1 + \frac{2}{n} \left\langle \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \cos \theta_{i,i+j} \right\rangle \right)
\]

which, since the average of a sum is a sum of average, can be written as:

\[
f = \lim_{n \to \infty} \left( 1 + \frac{2}{n} \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \langle \cos \theta_{i,i+j} \rangle \right)
\]

so the problem of calculating the effect of the correlations in jump directions comes to finding the average of the cosine of the jump angle for the diffusing particles.

Recall that the quantity \( \theta_{i,i+j} \) is the angle between the \( i \)th jump and the \((i + j)\)th jump. Recall also that we are considering vacancy-tracer jumps which occur between a tracer and vacancy which are on nearest neighbor lattice sites. In a crystal, all such site pairs are indistinguishable save for orientation, so that the average cosine of the angle cannot depend on the
initial orientation. That is, \( \langle \cos \theta_{i,i+j} \rangle \) is independent of \( i \). Hence we define a new quantity \( \langle \cos \theta_j \rangle \) which is the average of the cosine of the angle between any jump and a jump \( j \) jumps later. In terms of this we see:

\[
\sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \langle \cos \theta_{i,i+j} \rangle = \sum_{j=1}^{n-1} (n-j) \langle \cos \theta_j \rangle
\]

so that the task of finding \( f \) is reduced to finding the average of the cosine of the angle between jumps. It is possible to show that:

\[
\langle \cos \theta_j \rangle = \langle \cos \theta \rangle^j
\]

where \( \theta \) is just the angle between successive jumps (\( \theta = \theta_1 \)). With this we now find for \( f \):

\[
f = \lim_{n \to \infty} \left[ 1 + \frac{2}{n} \sum_{j=1}^{n-1} (n-j) \langle \cos \theta \rangle^j \right] \tag{2.15}
\]

The sums in Eqn. 2.15 can be easily done. Consider the sum:

\[
\sum_{j=1}^{n-1} x^j
\]

if we multiply by \( x \) and add and subtract the necessary terms, we find the following equation:

\[
\sum_{j=1}^{n-1} x^j = x \sum_{j=1}^{n-1} x^j + x - x^n
\]

which can be solved for the original sum yielding:

\[
\sum_{j=1}^{n-1} x^j = \frac{x - x^n}{1 - x}
\]

If we differentiate this we find:

\[
\sum_{j=1}^{n-1} jx^j = x \frac{d}{dx} \sum_{j=1}^{n-1} x^j = x \frac{d}{dx} \left( \frac{x - x^n}{1 - x} \right) = \frac{x - nx^n + (n-1)x^{n+1}}{(x-1)^2}
\]

After some algebra we find:

\[
f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle}
\]
2.7. **CORRELATION COEFFICIENT**

The problem of finding $f$ is reduced to the calculation of $\langle \cos \theta \rangle$. In order to do so, we calculate the probability $p_k$ that the tracer will make its next jump to its $k^{th}$ nearest neighbor. Then $\langle \cos \theta \rangle$ will be given by:

$$\langle \cos \theta \rangle = \sum_{k=1}^{z} p_k \cos \theta_k$$

where $z$ is the number of nearest neighbors, and $\theta_k$ is the angle between the original jump and the jump to the $k^{th}$ nearest neighbor. In order to calculate $p_k$ we consider the various vacancy trajectories which will result in the vacancy jumping to the tracer atom position for the first time from the $k^{th}$ nearest neighbor. We imagine that the vacancy is jumping around in the vicinity of the tracer atom, exchanging positions with atoms in the region. The tracer atom jumps when the vacancy exchanges positions with the tracer atom for the first time. In order to know the direction of the tracer atom jump, we need to keep track the nearest neighbor position from which the vacancy jumps to the tracer atom position.

Consider a vacancy trajectory which has the vacancy jumping with the tracer atom from position $k$ after $i$ jumps. Since the vacancy will jump in random directions, for each jump it will jump to any of its $z$ nearest neighbors with equal probability of $1/z$. Thus the probability that the vacancy follows a given trajectory with $i$ jumps is $(1/z)^i$. Hence $p_k$, the probability that the vacancy will jump to the position of the tracer atom from the position $k$ is given by:

$$p_k = \sum_{i=1}^{m} n_i^k \left( \frac{1}{z} \right)^i$$

where $n_i^k$ is the number of distinguishable $i$ jump vacancy trajectories which result in the vacancy jumping from position $k$ to the position of the tracer atom. The number $n_i^k$ of ways for a given jump to occur can be counted on a case by case basis. The limit where $m \to \infty$ gives the exact result for $p_k$. For the purposes of illustration we consider $m = 4$, that is we consider vacancy trajectories with up to four jumps. The results for the two-dimensional close-packed array are in Table 2.1.

We are now in a position to calculate the probabilities of a tracer jump to a given nearest neighbor. We find:

$$p_6 = \frac{1}{6} + 5 \left( \frac{1}{6} \right)^3 + 8 \left( \frac{1}{6} \right)^4 = 0.196$$
<table>
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<th>i</th>
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<td></td>
<td>4</td>
<td>(1/z)^4</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2.1: Results of counting vacancy trajectories which result in the tracer jumping to the \( k^{th} \) nearest neighbor.
2.7. Correlation Coefficient

\[ p_{1,5} = \left( \frac{1}{6} \right)^2 + \left( \frac{1}{6} \right)^3 + 11 \left( \frac{1}{6} \right)^4 = 0.0409 \]
\[ p_{2,4} = \left( \frac{1}{6} \right)^3 + \left( \frac{1}{6} \right)^4 = 0.0062 \]
\[ p_3 = 2 \left( \frac{1}{6} \right)^4 = 0.0015 \]

We see immediately that the probability of going backward \( p_6 \) is over 100 times the probability of going forward \( p_3 \). By inserting our values for \( p_k \) into Eqn. 2.16, we find

\[ \langle \cos \theta \rangle = \sum_{k=1}^{z} p_k \cos \theta_k = -0.229 \]

so that:

\[ f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} = \frac{1 - 0.229}{1 + 0.229} = 0.627 \]

The value for \( f \) obtained by letting \( m \to \infty \) is \( f = 0.56 \), so that by considering only four jumps we have made a 12\% error. It is interesting to consider the fraction of possible trajectories which we have considered in our calculation. We know that the tracer eventually jumps from one of the nearest neighbors, so that:

\[ \sum_{k=1}^{z} p_k = 1 \]

By considering only four jumps we find:

\[ \sum_{k=1}^{z} p_k = 0.29 \]

so that we have ignored 70\% of the possible trajectories. It is clear from the size of our error in \( f \) that we have included the most important ones. In fact, it is interesting to consider what we get by considering only one jump. In this case we find:

\[ \langle \cos \theta \rangle = (-1)^{ \frac{1}{6} } = -0.167 \]

so \( f = 0.714 \) which is only off by about 28\%.

For this two-dimensional close-packed array, the correlation coefficient introduces a relatively small correction to the diffusivity. This is also true for three-dimensional structures as shown in Table 2.2. However, thus far we have only considered tracer diffusion, where the tracer is chemically identical.
to the host atom. We see soon that if there are chemical differences, there can be strong vacancy impurity interactions which lead to large correlation effects.

<table>
<thead>
<tr>
<th>Structure</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>0.655</td>
</tr>
<tr>
<td>Diamond</td>
<td>0.5</td>
</tr>
<tr>
<td>bcc</td>
<td>0.721</td>
</tr>
<tr>
<td>fcc</td>
<td>0.781</td>
</tr>
</tbody>
</table>

Table 2.2: Correlation coefficient for several common structures.

2.8 The Effect of Pressure

The way that the diffusion is affected by pressure can be revealing as to the diffusion mechanism. In order to examine this effect, we consider the Gibbs free energy:

\[ G = F + PV = U + PV - TS = H - TS \]

where \( F \) is the Helmholtz free energy, \( U \) is the internal energy, and \( H \) is the enthalpy. The increment \( dU \) is given by:

\[ dU = TdS - PdV \]

so that the increment of the Gibbs free energy is given by:

\[
\begin{align*}
\frac{dG}{dP} & = dU + d(PV - TS) \\
& = TdS - PdV + PdV + VdP - TdS - SdT \\
& = VdP - SdT
\end{align*}
\]

So we find for the rate of change of Gibbs free energy with pressure:

\[
\left. \frac{\partial G}{\partial P} \right|_T = V
\]

If we consider diffusion by a vacancy mechanism, we have for the diffusivity:

\[ D = f a_0^2 x_V \nu \]