1. For the two-dimensional square lattice we can make a table analogous to Table 2.1 in the text. We label the sites as shown in Fig. 2.2 where the impurity and vacancy have just jumped. We find:

k	θ	i	p_i^k	n_i^k
4	π	1	$1/4$	1
		2	$(1/4)^2$	0
		3	$(1/4)^3$	3
1,3	$\pm\pi/2$	1	$1/4$	0
		2	$(1/4)^2$	0
		3	$(1/4)^3$	1

From this we find:

$$\begin{aligned} p_4 &= \frac{1}{4} + 3\left(\frac{1}{4}\right)^3 = \frac{19}{64} \\ p_1 = p_3 &= \left(\frac{1}{4}\right)^3 = \frac{1}{64} \end{aligned}$$

We then find for $\langle \cos\theta \rangle$:

$$\begin{aligned} \langle \cos\theta \rangle &= \sum_{k=1}^{z} p_k \cos\theta_k \\ &= p_4(-1) + p_1(0) + p_3(0) \\ &= -\frac{19}{64} \end{aligned}$$

Hence we find for f:

$$f = \frac{64 - 19}{64 + 19} = \frac{45}{83} \approx 0.524$$

2. (a) The probability that the vacancy will exchange with the impurity on the next jump is the ratio of the vacancy-impurity exchange rate ν_I to the sum of the exchange rates for all of the possible jumps. There are three other possible jumps for the vacancy, all of which break the vacancy-impurity pair. Hence the probability is:

$$p_{IV} = \frac{\nu_I}{3\nu_{HB} + \nu_I}$$

(b) To find the correlation coefficient we must find the average cos of the angle for adjacent jumps $\langle \cos\theta \rangle$. Considering only one jump trajectories, we have:

$$\begin{aligned} \langle \cos\theta \rangle &= \cos(180)\ p_{IV} \\ &= \frac{-\nu_I}{3\nu_{HB} + \nu_I} \end{aligned}$$

The correlation coefficient is then:

$$\begin{aligned} f &= \frac{1+\langle\cos\theta\rangle}{1-\langle\cos\theta\rangle} \\ &= \frac{3\nu_{HB}}{3\nu_{HB}+2\nu_I} \end{aligned}$$

(c) The probability that the vacancy will follow the five jump sequence is the product of the probabilities of each of the jumps. Hence we have:

$$\begin{aligned} p_{1-5} &= p_1 p_2 p_3 p_4 p_5 \\ &= \left(\frac{\nu_{HB}}{3\nu_{HB}+\nu_I}\right)\left(\frac{\nu_H}{3\nu_H+\nu_{HF}}\right)\left(\frac{1}{4}\right)\left(\frac{\nu_{HF}}{3\nu_H+\nu_{HF}}\right)\left(\frac{\nu_I}{3\nu_{HB}+\nu_I}\right) \end{aligned}$$

3. (a) The probability that a Cu atom will have a vacancy as one of its nearest neighbors will be just zx_V^0 where z is the number of nearest neighbors and x_V^0 is the equilibrium concentration of vacancies. Using the enthalpy of vacancy formation in the notes as an estimate of the free energy of formation for a Cu vacancy we find

$$\begin{aligned} x_V^0 &= \exp\left(\frac{-\Delta G_V'}{kT}\right) \\ &\approx \exp\left(\frac{-1.29eV}{kT}\right) \\ &= 3.22 \times 10^{-7} \end{aligned}$$

Hence the probability that a Cu atom will have a vacancy as one of its nearest neighbors is

$$\begin{aligned} p_{\mathrm{Cu-V}} &= zx_V^0 \\ &= 3.9 \times 10^{-6} \end{aligned}$$

(b) The number of vacancy impurity pairs is given by

$$x_{IV} = \frac{x_{It} z \exp\left[-(\Delta G_B' + \Delta G_V')/kT\right]}{1 + z \exp\left[-(\Delta G_B' + \Delta G_V')/kT\right]}$$

where $\Delta G_B'$ is the interaction energy between a vacancy and an impurity. From the handout on Point Defects by Wollenberger, we find that this quantity is given by

$$\Delta G_B' \approx -0.48 \text{ eV}$$

Inserting this into the above and again using the same approximation for $\Delta G_V'$ we find

$$\frac{x_{IV}}{x_{It}} = 1.0 \times 10^{-3}$$

(c) This probability that a Se atom will have a vacancy nearby is just the ratio x_{IV}/x_{It} plus the zx_V^0. Since the fraction of impurity atoms which are involved in vacancy-impurity pairs is so much higher than the free vacancy concentration the bound vacancies dominate this sum and we find for the probability just the ratio x_{IV}/x_{It}, which, as found above is about 10^{-3}. Hence a Se atom is about 260 times more likely than a Cu atom as one if its nearest neighbors.

4. (a) For this case we have $s = 1$, $p = x_V$, and $jz = 1$, since the jump distance is the lattice parameter, all interstitial atoms reside on interstitial sites and the probability that a given site is vacant is the vacancy number fraction, and there is one site in which to jump along a given direction. The exchange frequency ν is the rate at which an interstitial atom and an interstitial vacancy exchange.

   (b) The site corresponding to a backward jump has a vacancy there for sure since it just exchanged with the atom, so the probability that the atom jumps there is just $1/z$ where z is the number of nearest neighbors, which in this case is 6. The probability that each of the other sites is vacant is just x_V so the probability that the atom will jump to any one of them is x_V/z. So with the

exception of the backward jump, the atom could jump to any one of its nearest neighbors with equal probability. We note that if the atom could jump to any site with equal probability, corresponding to the random walk, the average of the cosine between subsequent jumps will be zero. Hence the average of the cosine of all the non-backward jumps is $0 - (-1) = 1$. The average of the cosine including the backward jump is

$$\langle \cos\theta \rangle = \frac{1}{z}(-1) + \frac{x_V}{z}(1) = \frac{1}{z}\,(x_V - 1)$$

giving for the correlation factor

$$f = \frac{z - (1 - x_V)}{z + (1 - x_V)} = \frac{z - x_A}{z + x_A}$$

Note that, within the given assumptions of jump probabilities, this is valid for any structure, not just the simple cubic structure considered in this problem. When $x_V \to 1$, corresponding to a very low interstitial atom concentration, the correlation factor becomes $f = 1$, which is the result we found for diffusion of interstitial species when the interstitial concentration low. When $x_V \to 0$, corresponding to very high interstitial concentration we find $f = (z-1)/(z+1)$ which is the same result as we found for the vacancy diffusion mechanism in the one-vaccancy-jump approximation. So in the simple cubic structure we find that the correlation factor is in the range 0.71 to 1, and so is only a weak function of vacancy concentration. This is shown in Figure 3.1.

The diffusion coefficient is then

$$D = \frac{z - (1 - x_V)}{z + (1 - x_V)}\; a_0^2\; \nu\; x_V$$

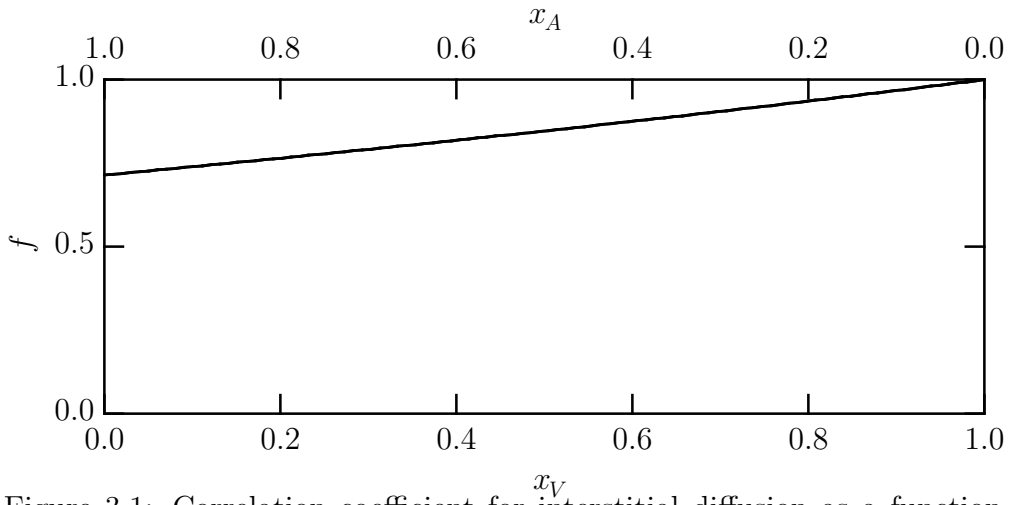

Figure 3.1: Correlation coefficient for interstitial diffusion as a function of vacancy and atom concentration.