

1. (a) We are given the average square of the distance from the line of the fleas:

$$\langle x^2 \rangle = 36 \text{ in}^2$$

However the fleas are jumping in a two-dimensional plane, so the total average square distance traveled is:

$$\langle R^2 \rangle = 4Dt = \langle x^2 \rangle + \langle y^2 \rangle$$

From the symmetry of the problem we know that there is no difference in the jumping in the two directions, so  $\langle x^2 \rangle = \langle y^2 \rangle$ , and we have:

$$\langle R^2 \rangle = 2\langle x^2 \rangle$$

To relate this to the diffusivity, we recall that the mean square distance for a random walk of  $n$  jumps is given by:

$$\langle R_n^2 \rangle = na^2$$

Since  $n = \Gamma t$  we can write this as:

$$\langle R^2 \rangle = \Gamma a^2 t = 4Dt$$

where we have used the expression for diffusivity in two-dimensions given by:

$$D = \frac{1}{4}\Gamma a^2$$

Solving for  $D$  we find:

$$D = \frac{\langle R^2 \rangle}{4t} = \frac{\langle x^2 \rangle}{2t} = 1.5 \text{ in}^2/\text{hr}$$

- (b) The diffusivity and the mean jump frequency are related by:

$$D = \frac{1}{4}a^2\Gamma$$

So that the mean jump frequency is given by:

$$\Gamma = \frac{4D}{a^2} = 600 \text{ jumps/hr}$$

(c) With the wind the flux of the fleas is given by:

$$\mathbf{J} = -D\nabla c + c\mathbf{v}$$

Applying the conservation equation we have:

$$\begin{aligned}\frac{\partial c}{\partial t} &= -\nabla \cdot \mathbf{J} \\ &= D\nabla^2 c - \mathbf{v} \cdot \nabla c\end{aligned}$$

(d) We can find the average square distance traveled by considering each component of the displacement. For the  $x$  component of the  $i^{\text{th}}$  flea, we have:

$$x^i = x_0^i + vt$$

where  $x_0^i$  is the  $x$  displacement without the effect of the wind. Taking the average of the square of the  $x$  displacement we find:

$$\langle x^2 \rangle = \langle x_0^2 \rangle + 2vt\langle x_0 \rangle + (vt)^2$$

Since the average  $x$  displacement in the absence of the wind is zero, we have:

$$\langle x^2 \rangle = \langle x_0^2 \rangle + (vt)^2$$

The  $y$  motion is unaffected by the wind so we have:

$$\begin{aligned}\langle r^2 \rangle &= \langle x_0^2 \rangle + \langle y_0^2 \rangle + (vt)^2 \\ &= \langle r_0^2 \rangle + (vt)^2\end{aligned}$$

So the sum of the squares of the distances will be increased by the amount  $N(vt)^2$ .

(e) The physical situations of diffusion in solids where an analogous effect to the wind occur include; diffusion of electrons in the presence of a field. diffusion of a massive component in the presence of gravitational potential, and diffusion of a species with a different atomic volume in the presence of a stress gradient.

2. (a) For diffusion of an interstitial species in a BCC metal, there will be no correlation effects, so that  $f = 1$ . Since each impurity atom resides on an interstitial site, and the interstitial concentration is usually low, the probability factor is close to unity so  $p = 1 - n_I \approx 1$ , where here  $n_I$  is the number of interstitial atoms divided by the number of interstitial atom sites. The jump distance along the [001] direction is  $a_0/2$  so that  $s = 1/2$ . Considering the octahedral sites, there are four nearest neighbors for each site. For jumps along the [001] direction we consider the three equivalent sites along cube edges in three directions, which together have the 12 jumps shown in Fig. 2.1, two of which are along the [001] direction, so  $j = 1/6$  and  $z = 4$ . This gives for the diffusivity:

$$\begin{aligned}
 D &= f(sa_0)^2 \nu p j z \\
 &= \frac{a_0^2}{4} \nu \frac{1}{6} 4 \\
 &= \frac{a_0^2}{6} \nu_0 \exp\left(\frac{\Delta S_a}{k}\right) \exp\left(\frac{-\Delta H_a}{kT}\right)
 \end{aligned}$$

- (b) For this case we are examining the diffusion of an impurity which normally resides on a lattice site, but which has some probability of residing on an interstitial site. Here the impurity jumps from an interstitial site to a lattice site, pushing the lattice atom off into an interstitial site. If the impurity has a different formation enthalpy for forming an interstitial than the host atoms, there may be some correlation, since the reverse jump may then be favored. The jump distance is again  $a_0/2$  so  $s = 1/2$ . The probability factor is  $n_I$  which is now just the number fraction of the impurity atoms which reside on interstitial sites, and is given by:

$$n_I = \exp\left(\frac{-\Delta G'_I}{kT}\right)$$

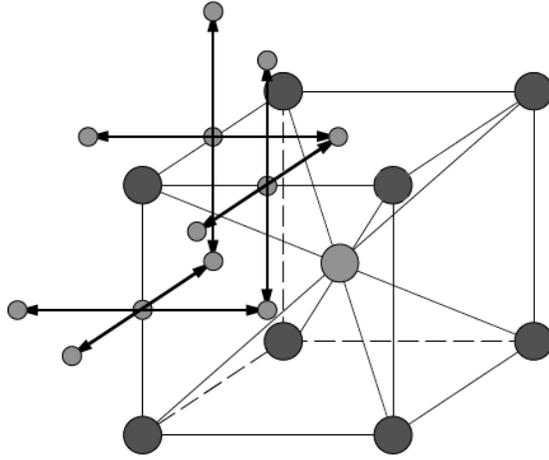


Figure 2.1: Schematic of interstitial jumps for an interstitial impurity which resides on the octahedral sites in a BCC lattice.

where  $\Delta G'_I$  is the formation free energy for an atom on an interstitial site. Each interstitial atom has two nearest neighbor lattice atoms, so  $z = 2$ , and if we again consider an interstitial on each of three equivalent edges, we find that  $1/6$  of the jumps are along the  $[001]$  direction, so that  $j = 1/6$ . Hence we have for the diffusivity:

$$\begin{aligned}
 D &= f(sa_0)^2 \nu p j z \\
 &= f \frac{a_0^2}{4} \nu n_I \frac{1}{6} 2 \\
 &= f \frac{a_0^2}{12} \nu_0 \exp\left(\frac{\Delta S_a + \Delta S_I}{k}\right) \exp\left(\frac{-\Delta H_a - \Delta H_I}{kT}\right)
 \end{aligned}$$

where  $\Delta S_I$  and  $\Delta H_I$  are the formation entropy and enthalpy for placing an atom on an interstitial site.

3. (a) The total number of atoms in the entire concentration is

$$\begin{aligned}
 N &= \int c(r,t) dV \\
 &= \int_0^\infty 4\pi r^2 c(r,t) dr \\
 &= \frac{4\pi\gamma}{(4\pi Dt)^{3/2}} \int_0^\infty r^2 e^{-r^2/4Dt} dr \\
 &= \gamma
 \end{aligned}$$

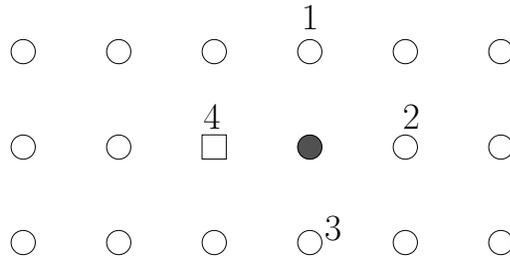


Figure 2.2: Two-dimensional square array with tracer and vacancy which have just jumped.

Hence probability that a given atom is in a spherical shell of radius  $R$  and thickness  $dR$  is

$$\mathcal{P}(R) dR = \frac{1}{\gamma} 4\pi R^2 c(R,t) dR$$

So the probability is

$$\mathcal{P}(R) = \frac{4\pi R^2}{(4\pi Dt)^{3/2}} e^{-R^2/4Dt}$$

(b) The mean square distance  $\langle R^2 \rangle$  can be found by

$$\langle R^2 \rangle = \int_0^\infty R^2 \mathcal{P}(R) dR = 6Dt$$

- (c) The random walk treatment in the text yielded the result for the mean square distance from the starting point after  $n$  jumps

$$\langle R^2 \rangle = na^2$$

where  $a$  is the jump distance. The number of jumps  $n$  is related to the jump rate  $\Gamma$  by  $n = \Gamma t$ . Hence equating our two expressions for  $\langle R^2 \rangle$  gives

$$na^2 = \Gamma ta^2 = 6Dt$$

Solving for  $D$  gives

$$D = \frac{1}{6}\Gamma a^2$$

4. An atom which has just exchanged with the vacancy will always jump back into the original site on its next jump no matter how many vacancy jumps it takes to do this. There is no way for the vacancy to get around to the other side of the atom without first causing a backward jump. Hence the average cosine of the atoms next jump is

$$\langle \cos \theta \rangle = (-1)$$

and the correlation factor is

$$f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} = 0$$

Diffusion on a string of atoms cannot occur by a vacancy mechanism.