Last time

Diffusion as a sequence of Random Jumps
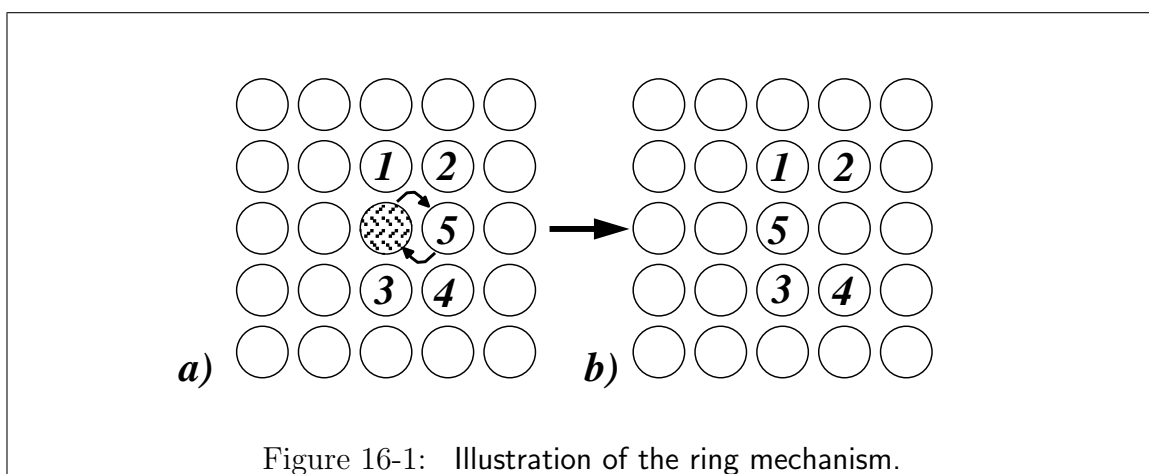
_____

_____

_____

_____

Diffusion as a time-dependent probabiltity distribution

_____

_____

_____

_____

Concentration as calcuated from Fick's law as a probability field
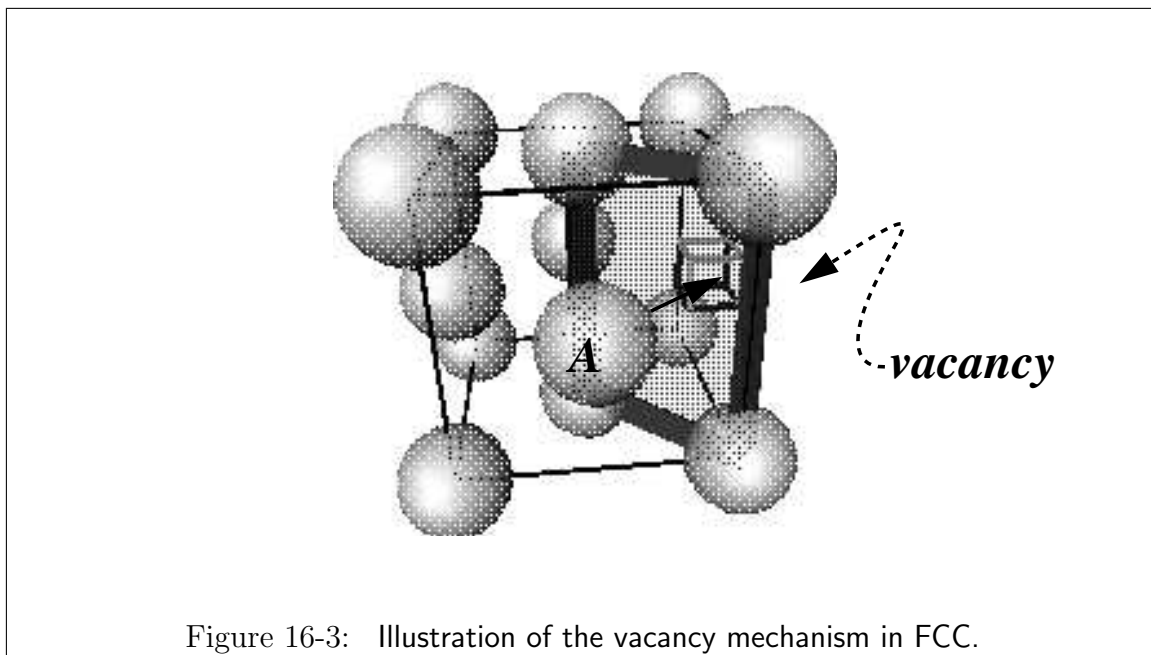
_____

_____

_____

_____

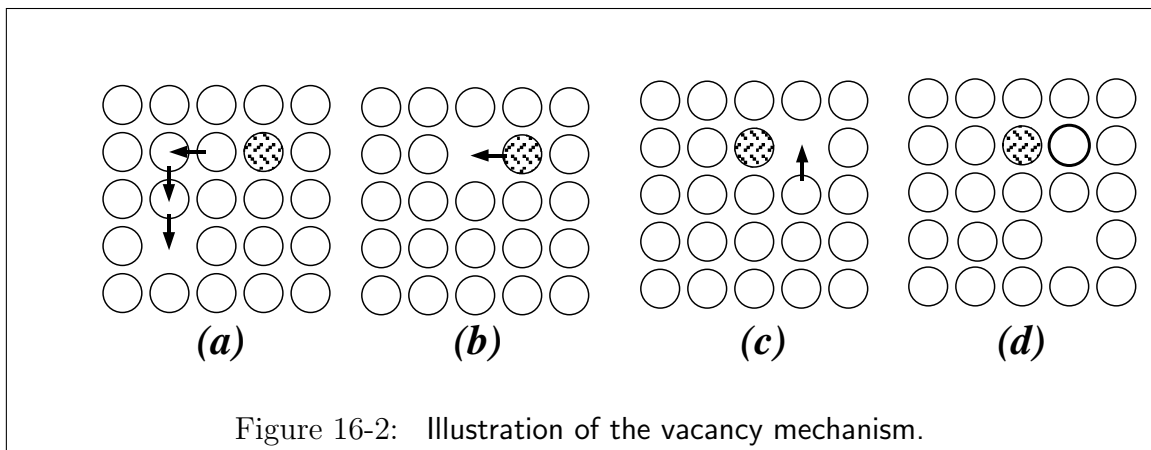# 3.21 Spring 2002: Lecture 16

Mechanisms of Diffusion in Crystals

Ring Mechanism

Figure 16-1:   Illustration of the ring mechanism.

Vacancy Mechanism

Figure 16-2:   Illustration of the vacancy mechanism.

Figure 16-3:   Illustration of the vacancy mechanism in FCC.

<u>Interstitialcy Mechanism</u>

Figure 16-4: Illustration of the intersticialcy mechanism.
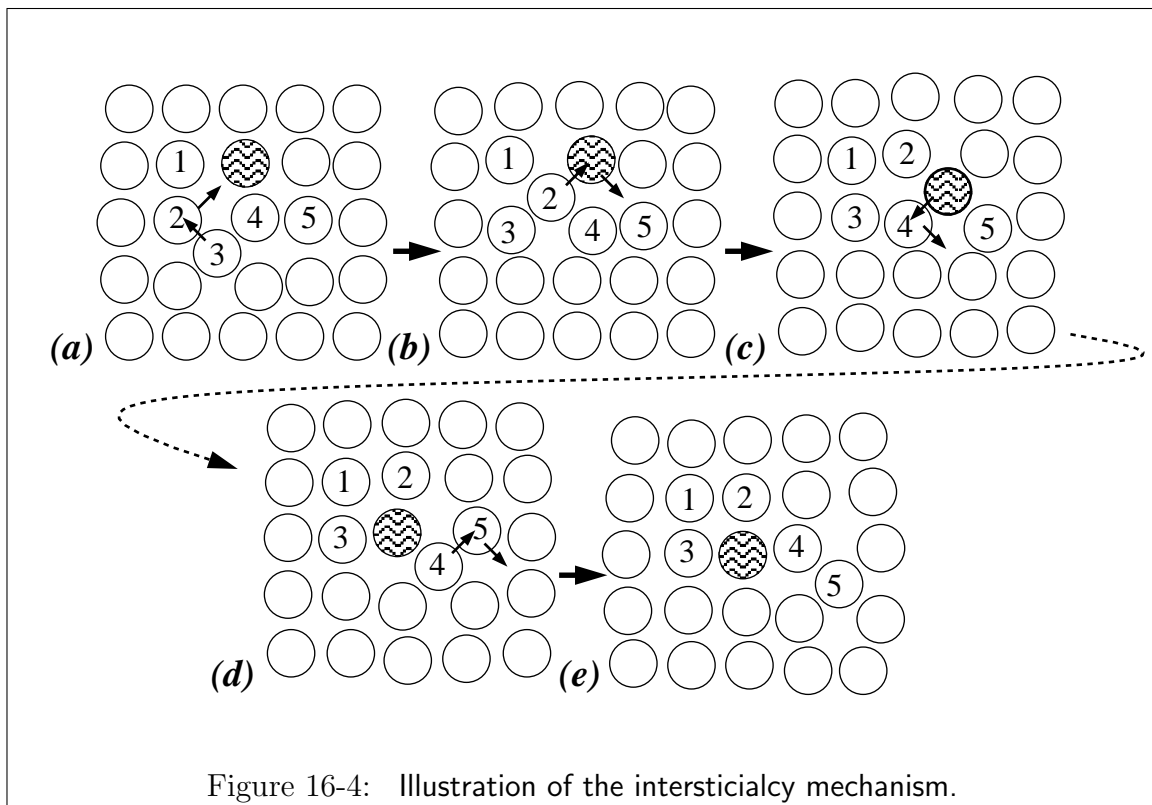
Interstitials
Types of Interstitials

Figure 16-5:   Intersticial sites in a BCC

Figure 16-6:   "Crowdion" sites in an FCC crystal

Figure 16-7:   Kick-out and dissociation mechanisms
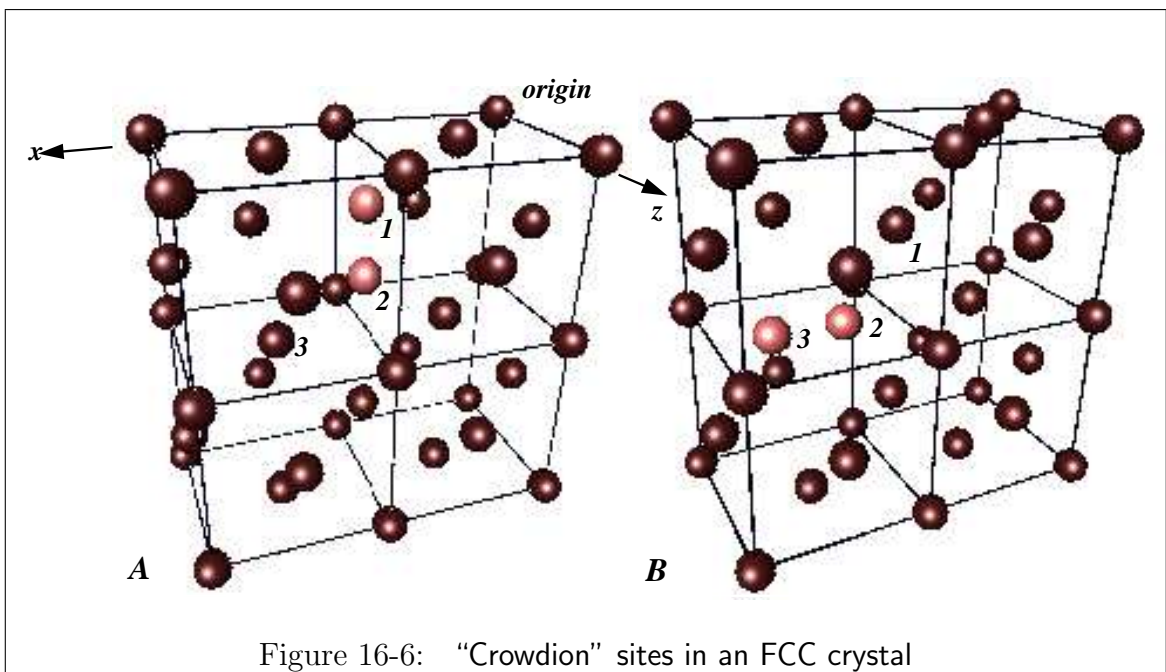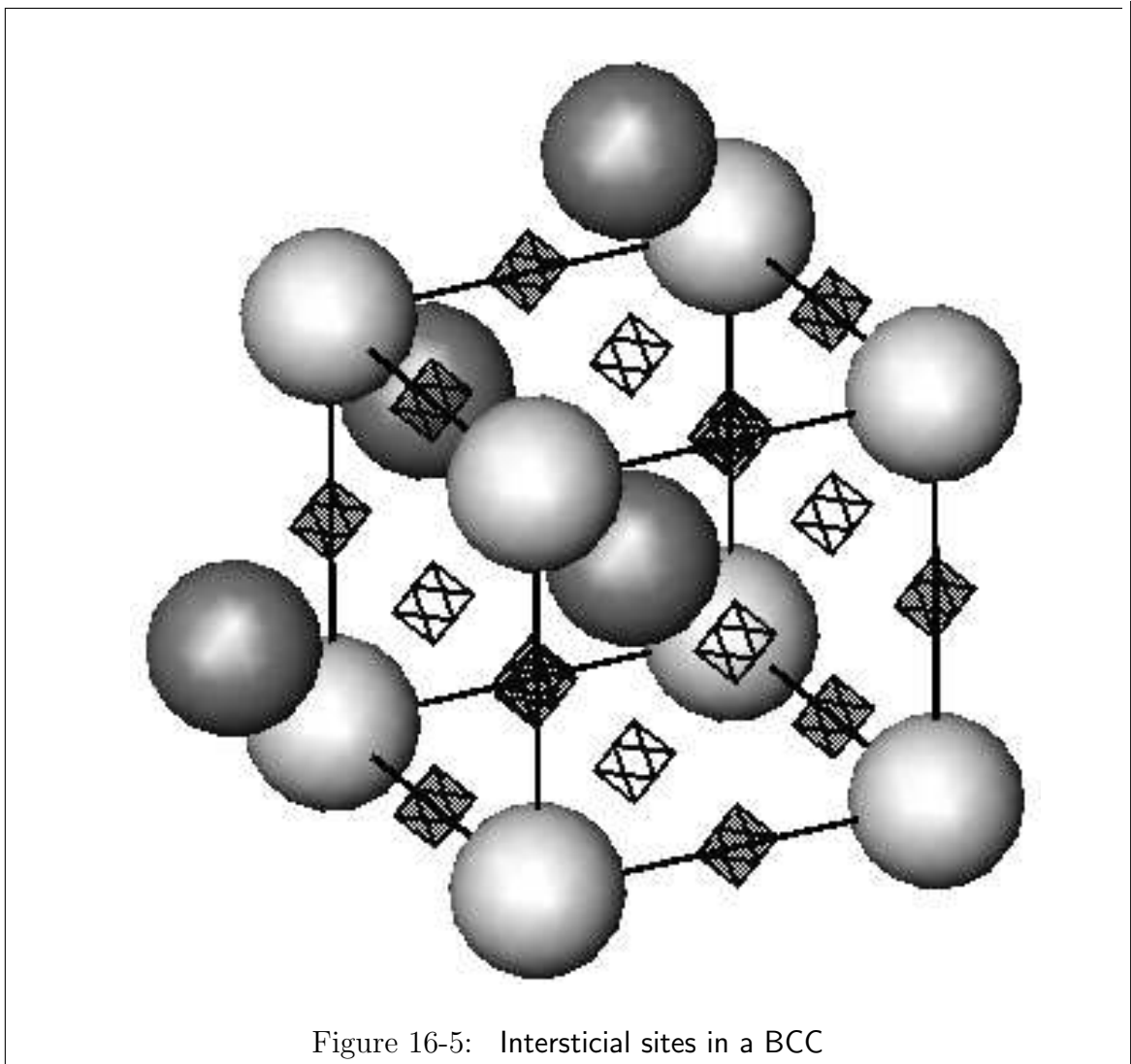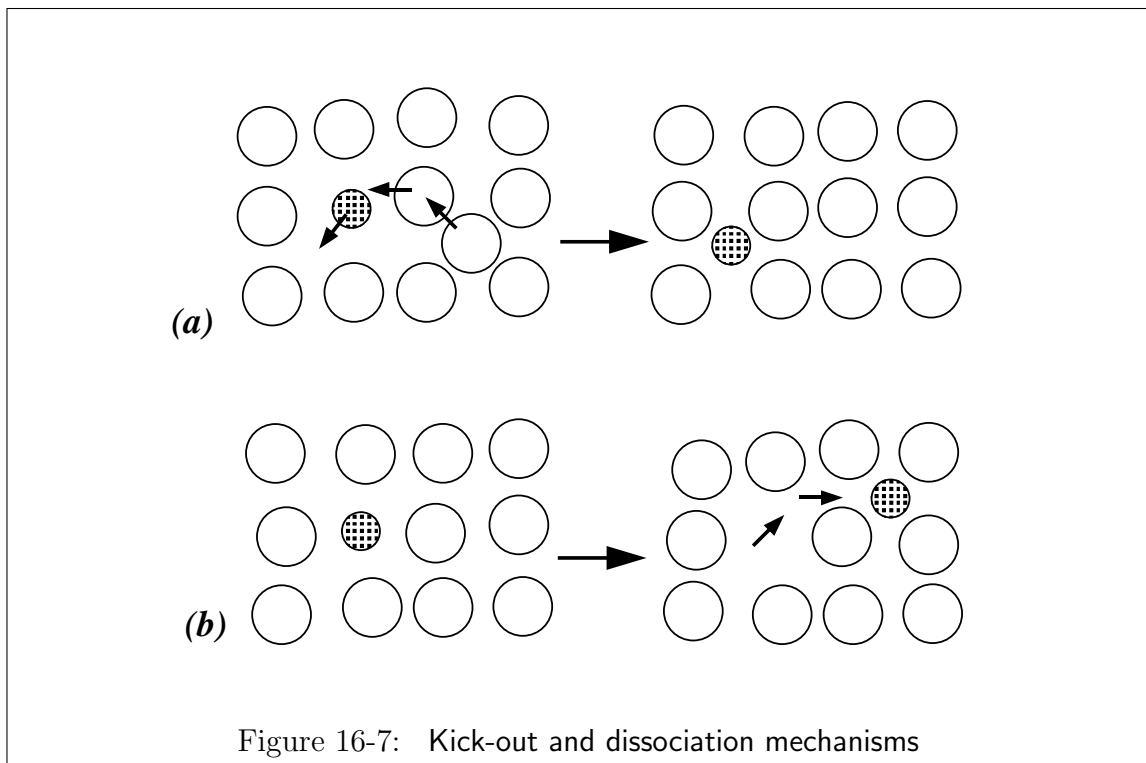
Simple Models for Interstitial Diffusivity

Recall that for a random walk in three-dimensions:

$$D = \frac{\Gamma r^2}{6} f \tag{16-1}$$

where Γ is the frequency of a succesful 'hop' and r is the average hop-distance.

The reaction rate theory was worked out for the case of activation over a *particular* barrier, i.e.,

$$\Gamma_{spec.} = \nu_{char.} \exp(\frac{-G^m}{kT}) \tag{16-2}$$

The relation of $\Gamma_{spec.}$ to the total succesful hop frequency is the sum of hop frequencies of all surrounding sites

$$\Gamma = \sum_{\text{nbr site}_i} \Gamma^i_{spec.} = \sum_{\text{similar sites}_j} \Omega_j \Gamma^j_{spec.} \tag{16-3}$$

where $\Gamma^i_{spec.}$ is the *particular* hop frequency into a site of type i and Ω_j is the degeneracy (i.e., count) of similar neighbors.

For example, consider the case of an interstitial atom in FCC-iron. There are four crystallographically similar nearest interstitial sites ($\Omega_{nn} = 4$); if the successful hop frequency into the next nearest neighbor, $\Gamma^{nnn}_{spec.}$, is negligible compared to the nearest neighbor hops ($\Gamma^{nnn}_{spec.} \ll \Gamma^{nn}_{spec.}$) then

$$\Gamma = \sum_{\text{similar sites}_j} \Omega_j \Gamma^j_{spec.} \approx 4\Gamma^{nn}_{spec.} \tag{16-4}$$

writing the hop distance r in terms of the lattice constant $r = a/2$, and combining with equations 16-1 and 16-4 for uncorrelated hops ($f = 1$), yields

$$D = \frac{a^2}{6}\nu_{char.}\exp(\frac{-G^m}{kT}) \tag{16-5}$$

as a good approximation that connects atomistic mechanisms to macroscopic diffusivity for interstitial diffusion in a hydrostatically stressed FCC crystal.

The Gibbs free energy of the activated state in the exponent results from the caveat of fixed stress. The Helmholtz free energy would appear for the case of fixed volume. Hydrostatic stress is results from the assumption that each neighboring interstitial site is the same—this would not be the case, for example, in tension ($\sigma_{yy} \gg \sigma_{xx}$ and $\sigma_{yy} \gg \sigma_{zz}$). Tension would break the symmetry of the interstitial sites by a tetrahedral distortion. This effect has been observed in steel.

Simple Models for Vacancy Diffusivity

The transition of an atom into a vacant site has the same treatment as the above case for interstitials, except that two additional factors must be considered:

Vacancy Population The probability of an atom passing through its activated state and into a vacant site is the product of two probabilities: 1) the activation probability, $\exp(-G^m/kT)$, and 2) the probability that the neighboring site will be vacant, X_V, the site fraction of vacant sites.

The activation barrier, G^m, depends on the presence of a neighboring vacancy. The terms in the probabilities are not necessarily independent, but it is a good approximation to treat the probabilities as independent terms so that they multiply.

Correlations Because an atom that has just hopped into a vacant site will always have a vacancy as a neighbor (i.e., the site that it had previously occupied), there is a strong correlation between steps and thus $f \neq 1$ as in an uncorrelated random walk.

With the physically justifiable assumption that vacant site occupation is small (thus neglecting the probability of two neighboring vacancies[26], the successful hop frequency Γ_V can be related to the sum of particular vacancy hops as in equation 16-3.

For self-diffusion on a hydrostatically stressed FCC lattice, there are 12 crystallographically similar nearest neighbor sites, $\Omega_{nn} = 12$. Therefore the successful hop frequency of an FCC-vacancy is:

$$\Gamma_V = 12\nu_{char.}\exp(-\frac{G_V^m}{kT}) \tag{16-6}$$

where G_V^m is the Gibbs free energy of a the vacancy in its activated transition state.

Disregarding all other mechanisms of diffusion (i.e., interstiticialcy) The successful hop frequency, Γ_A of *an atom chosen at random* is the product of two probabilities:

$$\Gamma_A = \Gamma_V X_V = 12\nu_{char.}\exp(-\frac{G_V^m}{kT})X_V \tag{16-7}$$

---

[26]This probability is larger than the product X_V^2. Why? Think about it.

If the vacancies are in equilibrium, X_V^{eq} can be related to the Gibbs free energy difference between an occupied and unoccupied site, G_V^f, and[27]

$$\Gamma_A = 12\nu_{char.} \exp(-\frac{G_V^m + G_V^f}{kT}) \tag{16-8}$$

Collecting terms and relating the jump distance, r, to the lattice constant $r = a/\sqrt{2}$,

$$D_A = \frac{\Gamma_A r^2}{6} f = \nu_{char.} \exp(-\frac{G_V^m + G_V^f}{kT})f \tag{16-9}$$

The correlation factor, f, can be estimated with the following model. A specific atom A is likely hop back into its original site $1/\Omega_{nn}$ times—therefore a vacancy will typically have nonzero net displacement after about $\Omega_{nn} + 1$ attempts, where two of the attempts (the back-and-forth steps) will have been ineffective. Therefore only fraction, $(\Omega_{nn} - 1)/(\Omega_{nn} + 1)$, of all hops should be considered succesful. For an FCC lattice, $f \approx 11/13$. This approximation is not very different those obtained from more accurate models.

Lattice Diffusion in Ionic Crystals

Just as in substitutional diffusion via the vacancy mechanism in which the diffusivity has an Arrhenius factor associated with the population of defects, a similar defect population appears in ionic crystals where the defects are more complicated.

---

[27]The gibbs free energy of an occupied site is a reference energy taken to be zero in the calculation for both G_V^m anf G_V^f.
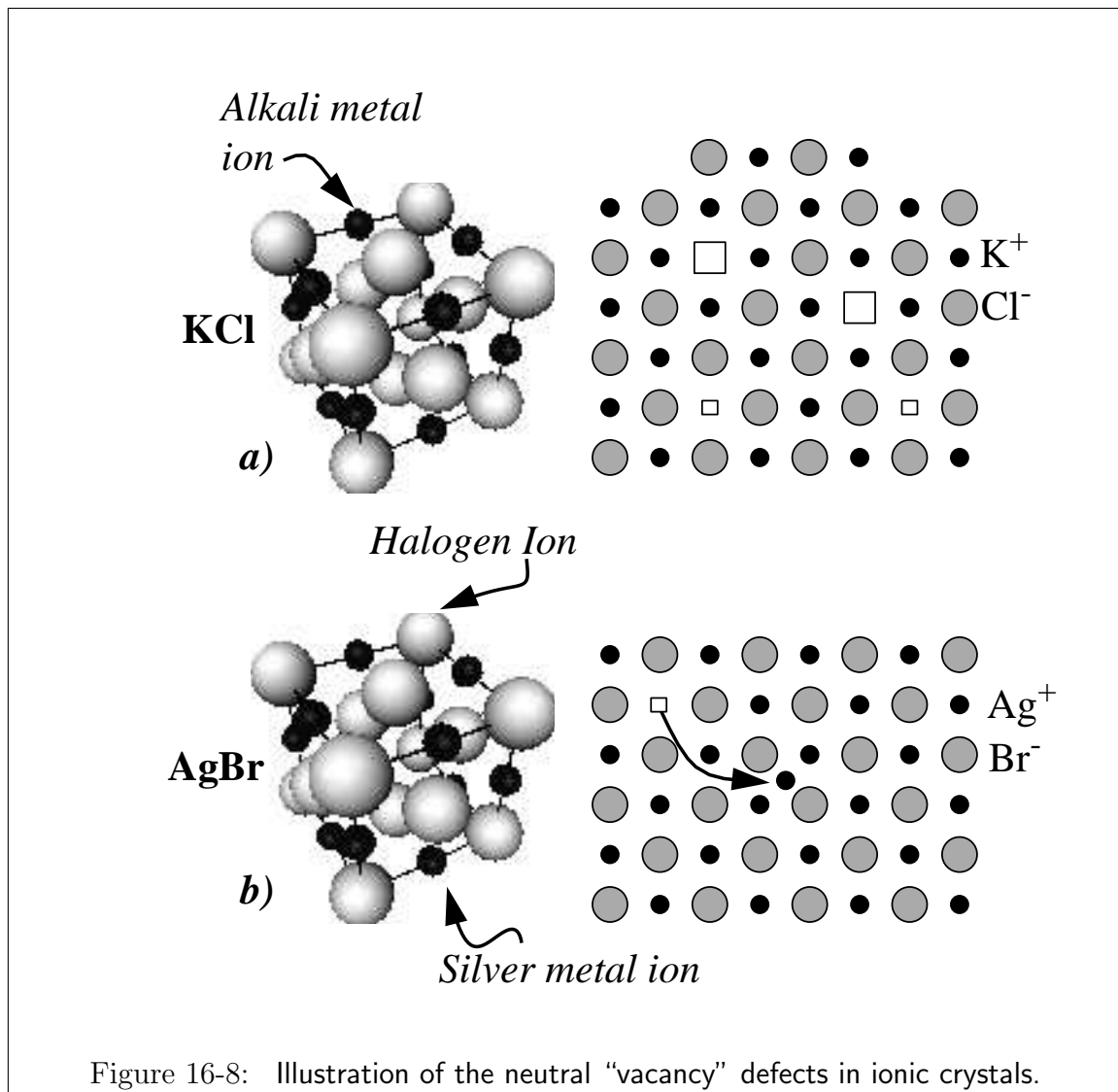
Figure 16-8:   Illustration of the neutral "vacancy" defects in ionic crystals.

In an ionic crystal, a vacancy at a cation (positive ion) or an anion site would leave a charge of the opposite sign unless that vacancy is compensated by another charged defect. The two common types of defects is a Schottky defect, where a pair of vacancies of opposite signs appear on each sublattice—and a Frenckel defect where a vacancy is compensated by an interstitial. If the cations and anions have differing magnitudes of ionic charge, then the defects must involve more sites to satisfy charge neutrality.

In ionic crystals, the notation for defect concentration identifies the chemical species, where the species is located relative to a perfect lattice, and the charge on the species. The commonly employed notation for charged defects is Kroger-Vink:

$$\Xi_S^C \text{ where } \begin{cases} \Xi \text{ is the chemical species of vacancy } V \\ S \text{ is type of lattice site the defect occupies (}i\text{ for interstitial)} \\ C \text{ is the effective charge on the defect} \end{cases} \quad (16\text{-}10)$$

where,

$$C = \begin{cases} \times \text{ if the defect is neutral} \\ \cdot \text{ if the defect has positive charge (one dot for each positive charge)} \\ '\text{if the defect has a negative charge (one prime for each negative charge)} \end{cases} \quad (16\text{-}11)$$

For example consider, putting calcia into a zirconia lattice:

$$CaO \xrightarrow{ZrO_2} Ca''_{Zr} + O^\times_O + V^{..}_O \tag{16-12}$$

The Schottky formation reaction is given by:

The equilibrium for Shottkey formation involves two unknowns:

Charge neutrality provides an additional constraint:

This forms a set of equations that can be solved for the defect concentration that affects the diffusivity.