Appendix A: Diffusivity of Vacancy
Mechanism of Diffusion in Solids

To analyze atomic diffusivity, we shall consider the vacancy mechanism of diffusion in a face-centered-cubic metal. We make the following assumptions in order to develop the analytical model.

1. It is a thermally activated unimolecular process. Unimolecular process means that we consider a single atom in the diffusion process and it is a near-equilibrium process. This is unlike chemical reactions that are bimolecular processes, such as rock salt formation, in which the collision of two atoms of Na and Cl is involved and the process is far from equilibrium.
2. It is a defect-mediated process. Here the defect is a vacancy.
3. The activated state obeys a Boltzmann’s equilibrium distribution from transition state theory. Hence, the Boltzmann distribution function is used.
4. It is assumed that the probability of reverse jumps is large due to small driving force, so we have to consider reverse processes. In other words, the process is not far from equilibrium.
5. Statistically, atomic diffusion obeys the principle of random walk.
6. A long-range diffusion requires a driving force.

At equilibrium, in a one-dimensional configuration, atoms are attempting to jump over the potential energy barrier with the attempt frequency, $\nu_0$, to exchange position with a neighboring vacancy, as depicted in Fig. A.1.
The successful or exchange jump frequency is given below on the basis of Boltzmann’s distribution:

\[ \nu = \nu_0 \exp \left( -\frac{\Delta G_m}{kT} \right), \]

where

\[ \nu_0 = \text{attempt frequency}, \]
\[ \nu = \text{exchange frequency}, \]
\[ \Delta G_m = \text{saddle point energy (activation energy of motion)}. \]

We note that there is a reverse jump at the same attempt frequency.

Now consider a driving force \( F \) (which equals the slope of the base line in Fig. A.2). The meaning of \( F \) will be discussed later. The forward jump is increased by

\[ v^+ = v \exp \left( \frac{\lambda F}{2kT} \right), \]

where \( \lambda \) is the jump distance. The reverse jump is decreased by

\[ v^- = v \exp \left( -\frac{\lambda F}{2kT} \right). \]

And the net frequency is

\[ v_n = v^+ - v^- = 2v \sinh \left( \frac{\lambda F}{2kT} \right). \]

Now, we take the “condition of linearization,”

\[ \frac{\lambda F}{kT} \ll 1. \]
Then the net frequency jump $v_n$ is “linearly” proportional to the driving force $F$:

$$v_n = v_n \frac{\lambda F}{kT}.$$ 

We can define a drift velocity

$$v = \lambda v_n = \frac{v\lambda^2}{kT} F.$$ 

Then, the atomic flux $J$, which has units of number of atoms per unit area per unit time, is

$$J = Cv = \frac{Cv\lambda^2}{kT} F,$$

where $M = v\lambda^2/kT$ is defined as the atomic mobility. The atomic flux $J$ is “linearly” proportional to the driving force $F$. The driving force is generally defined as a potential gradient,

$$F = -\frac{\partial \mu}{\partial x}.$$ 

In atomic diffusion, here $\mu$ is the chemical potential of an atom and is defined at constant temperature and pressure to be

$$\mu = \left( \frac{\partial G}{\partial C} \right)_{T,p},$$

where $G$ is Gibbs free energy and $C$ is concentration. For an ideal dilute solid solution,

$$\mu = kT \ln C,$$

$$F = -\frac{\partial \mu}{\partial C} \frac{\partial C}{\partial x} = -\frac{kT}{C} \frac{\partial C}{\partial x},$$

$$J = \frac{Cv\lambda^2}{kT} F = \frac{Cv\lambda^2}{kT} \left( -\frac{kT}{C} \frac{\partial C}{\partial x} \right) = -v\lambda^2 \left( \frac{\partial C}{\partial x} \right) = -D \left( \frac{\partial C}{\partial x} \right).$$

Hence, we have obtained Fick’s first law of diffusion:

$$\frac{J}{-(\frac{\partial C}{\partial x})} = D = \nu \lambda^2,$$

where $D$ is the diffusion coefficient (or diffusivity) in units of cm$^2$/sec. Then, $M = D/kT$. In the above derivation, as depicted in Fig. A.1, we have assumed
that the diffusing atom has a neighboring vacancy. For the majority of atoms in the lattice, this is not true, and we must define the probability of an atom having a neighboring vacancy in the solid as

\[ \frac{n_v}{n} = \exp \left( -\frac{\Delta G_{v}}{kT} \right) . \]

\( n_v \) is the total number of vacancies in the solid, \( n \) is the total number of lattice sites in the solid, and \( \Delta G_{v} \) is the Gibbs free energy of formation of a vacancy. Since in a face-centered-cubic metal, a lattice atom has 12 nearest neighbors, the probability of a particular atom having a vacancy as a neighbor is

\[ n_v \frac{n_v}{n} = n_v \exp \left( -\frac{\Delta G_{v}}{kT} \right) \quad n_v = 12. \]

Next, we have to consider the correlation factor in the face-centered-cubic lattice. The physical meaning of the factor is the probability of reverse jump; after the atom has exchanged position with a vacancy, it has a high probability of returning to its original position before the activated configuration is relaxed. The factor has a range between zero and unity. When \( f = 0 \), it means the probability of reverse jump is 100%, so the atom and the vacancy are exchanging position back and forth, which will not lead to any random walk but instead a correlated walk. When \( f = 1 \), it means that after the jump, the atom will not return to its original position, and it is a random walk because the next jump will depend on the random probability of a vacancy coming to the neighborhood of this atom. In fcc metals, \( f = 0.78 \), so about 80% of jumps are random walk, and about 20% are correlated walk. Finally, we have the diffusivity as

\[ D = f n_v a^2 \nu_0 \exp \left( -\frac{\Delta G_{m} + \Delta G_{v}}{kT} \right) , \]

\[ D = f n_v \lambda^2 \nu_0 \exp \left( \frac{\Delta S_{m} + \Delta S_{v}}{k} \right) \exp \left( -\frac{\Delta H_{m} + \Delta H_{v}}{kT} \right) = D_0 \exp \left[ -\frac{\Delta H}{kT} \right] . \]
Appendix B: Growth and Ripening Equations of Precipitates

The distribution function of a set of precipitates is obtained by solving the continuity equation in size space:

$$\frac{\partial f}{\partial t} = v \frac{\partial f}{\partial x},$$

where $f$ is the size distribution function of the precipitates and $v$ is the growth/dissolution velocity of the precipitates. To solve the continuity equation, the first step is to find the growth/dissolution velocity. In this appendix we shall derive the velocity of a spherical precipitate. When the diameter of the precipitates is in nanoscale, it is important to take into account the Gibbs–Thomson potential of curvature as in the LSW theory of ripening. In other words, the equilibrium concentration at the precipitate/matrix interface is a function of radius. When the precipitate diameter is large, we can assume the equilibrium concentration to be constant, independent of the radius.

**B.1 Kinetics of Precipitation**

We consider the growth or dissolution of a spherical particle or precipitate. Letting $R$ be the variable, the diffusion equation in spherical coordination, assuming a steady state, is

$$\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} = 0.$$  

The solution is

$$C = \frac{b}{R} + d.$$

(B.1)
The boundary conditions are

At $R = r_0$, $C = C_0$, we have $C_0 = \frac{b}{r_0} + d$. (B.2)

At $R = r$, $C = C_r$, we have $C_r = \frac{b}{r} + d$. (B.3)

Now, if we take the difference between the last two equations, we have

$$C_r - C_0 = b \left( \frac{1}{r} - \frac{1}{r_0} \right) = b \frac{r_0 - r}{rr_0} \approx \frac{b}{r} \quad \text{where } r_0 \gg r. \quad \text{(B.4)}$$

This is an important assumption. It means that precipitates are far apart. Note that if we take the volume fraction, $f$, the ratio of volume of the precipitate particles to the volume of the diffusion field, or the total volume of the precipitated phase to the total volume of the matrix, is

$$f = \frac{4\pi}{3} r^3 \frac{4\pi}{3} r_0^3 \approx \frac{r^3}{r_0^3} \to 0.$$  

It is a very small value: $f \to 0$. (This is a very important assumption in the LSW theory of ripening to be discussed later.)

We have $b = r(C_r - C_0)$. Substituting $b$ into Eq. (B.3), we have

$$C_r = \frac{r(C_r - C_0)}{r} + d. \quad \text{(B.5)}$$

We have $d = C_0$, and Eq. (B.1) becomes

$$C(R) = \frac{(C_r - C_0)}{R} + C_0. \quad \text{(B.6)}$$

Therefore,

$$\frac{dC}{dR} = -\frac{(C_r - C_0)}{R^2}.$$  

At the particle/matrix interface for a particle of radius $r$, or $R = r$, we have

$$\frac{dC}{dR} = -\frac{C_r - C_0}{r}. \quad \text{(B.7)}$$

Then the flux of atoms arriving at the interface is

$$J = +D \frac{\partial C}{\partial R} = \frac{D(C_0 - C_r)}{r} \quad \text{at } R = r. \quad \text{(B.8)}$$

Note that when $C_r > C_0$, $J < 0$, the net flux is toward the particle, and thus
it grows. When $C_r < C_0$, $J > 0$, the flux leaves the particle so the particle dissolves.

**B.2 Growth Rate of a Spherical Particle Assuming $C_r$ Is Constant**

If $\Omega$ is atomic volume, in time $dt$, a volume is added to the spherical particle,

$$\Omega J Adt = \Omega J 4\pi r^2 dt = 4\pi r^2 dr,$$

where the last term is the increment of a spherical shell due to the growth. Hence,

$$\frac{dr}{dt} = \Omega J = \frac{\Omega D(C_0 - C_r)}{r}.$$  \hspace{1cm} (B.9)

**B.2.1 Case 1: The Growth of a Precipitate**

By integration and assuming when $t = 0$, $r = 0$,

$$r^2 = 2\Omega D(C_0 - C_r)t.$$  \hspace{1cm} (B.10)

Note here that if we follow Ham’s approach and take $C_r$ as a constant, it is not a function of $r$ as given by the Gibbs–Thomson equation. From the above equation, we see that $r \approx t^{1/2}$ and $r^3 \approx t^{3/2}$. Or we have

$$r^3 = [2\Omega D(C_0 - C_r)t]^{3/2}.$$  \hspace{1cm} (B.11)

**B.2.2 Case 2: The Depletion of Concentration in the Matrix (Mean-Field Consideration)**

On the other hand, we consider the loss of average concentration in the matrix, $\Delta C = C_0 - C$, due to the formation of the precipitate, where the average concentration in the matrix is $\bar{C}$, which can be regarded as the “mean-field” concentration (the conception of mean-field theory). In the beginning, the average concentration is $C_0$, and it changes to $\bar{C}$ when the precipitate grows.

Let $1/\Omega = C_p$ be the concentration in the solid precipitate. We have simply by mass balance,

$$\frac{4\pi}{3} r_0^3 (C_0 - \bar{C}) = \frac{4\pi}{3} r^3 \frac{1}{\Omega} = \frac{4\pi}{3\Omega} [2\Omega D(C_0 - C_r)t]^{3/2},$$  \hspace{1cm} (B.12)

$$\bar{C} = C_0 - \left[\frac{2D(C_0 - C_r)\Omega^{1/3}}{r_0^2} t\right]^{3/2} = C_0 - \left[\frac{2Bt}{3}\right]^{3/2},$$  \hspace{1cm} (B.13)
where

\[ B \equiv \frac{3D(C_0 - C_r)}{C_p^{1/3} r_0^2}. \]

We note that the above equation is the same as Eq. (1–36) in Chapter 1 in Shewmon.

**B.2.3 Case 3: Consider Growth of Precipitate and Depletion of the Matrix Together**

We can derive the last equation in a slightly different way. The growth of the precipitate reduces the concentration in the matrix. The amount of solute atoms diffusing to the precipitate in time \( \Delta t \) is

\[ J(r) 4\pi r^2 \Delta t = \text{number of atoms}. \]

It should be equal to the reduction of the average concentration in the volume of the sphere of diffusion of \( r_0 \). Hence, if take the average concentration in the matrix to be \( \bar{C} \),

\[ \frac{4\pi r_0^3}{3} \Delta \bar{C} = J(r) 4\pi r^2 \Delta t. \]

Or, we have

\[ \frac{\Delta \bar{C}}{\Delta t} = \frac{3}{4\pi r_0^3} 4\pi r^2 J(r) = \frac{3D}{r_0^3} (C_0 - C_r) r. \quad (B.14) \]

The conservation of mass requires that

\[ \frac{4\pi r_0^3}{3} (C_0 - \bar{C}) = \frac{4\pi}{3} r^3 C_p, \quad (B.15) \]

where \( C_p \) is the concentration of solute in the solid precipitate and \( C_p = 1/\Omega \). Hence,

\[ r = r_0 \left( \frac{C_0 - \bar{C}}{C_p} \right)^{1/3}. \quad (B.16) \]

By substituting \( r \) into the rate equation above, we have

\[ \frac{\Delta \bar{C}}{\Delta t} = -\frac{3D}{r_0^3} (C_0 - C_r) \frac{1}{C_p^{1/3}} \left( C_0 - \bar{C} \right)^{1/3}. \quad (B.17) \]
Let 

\[ B \equiv \frac{3D(C_0 - C_r)}{C_p^{1/3}r_0^2}. \]

We have 

\[ \frac{d\bar{C}}{dt} = -B(C_0 - \bar{C})^{1/3}. \]

By integration we obtain 

\[ \frac{3}{2}(C_0 - \bar{C})^{2/3} = -Bt + \beta. \]

At \( t = 0 \), \( C_0 = \bar{C} \), so \( \beta = 0 \).

Thus, we have the solution, 

\[ \bar{C} = C_0 - \left( \frac{2Bt}{3} \right)^{3/2}, \] 

which is the same as what we have obtained. Hence, we have 

\[ C_0 - \bar{C} \approx t^{3/2} \] for 3-dimensional growth.

Let \( \bar{C} = C_0 \left[ 1 - \left( \frac{2Bt}{3C_0^{2/3}} \right)^{3/2} \right] = C_0 \left[ 1 - \left( \frac{t}{\tau} \right)^{3/2} \right] = C_0 \exp \left[ -\left( \frac{t}{\tau} \right)^{3/2} \right] \]

if we assume \( t \ll \tau \), 

where 

\[ \tau = \frac{C_p^{1/3}r_0^2C_0^{2/3}}{2D(C_0 - C_r)} \approx \frac{r_0^2}{2D} \left( \frac{C_p}{C_0} \right)^{1/3}. \]

Usually \( D, C_p, C_0 \) are known, and we can design the experiment to control the growth of the precipitate.

**B.3 Gibbs–Thomson Potential: Effect of Surface Curvature**

Consider a sphere with radius \( r \) and surface energy per unit area \( \gamma \). The surface energy exerts a compressive pressure on the sphere because it tends
to shrink to reduce the surface energy. The pressure is

\[ p = \frac{F}{A} = -\frac{dE}{dr} = -\frac{d4\pi r^2 \gamma}{4\pi r^2} = -\frac{8\pi r \gamma}{4\pi r^2} = -\frac{2\gamma}{r}, \]  

(B.21)

If we multiply \( p \) by the atomic volume \( \Omega \), we have the chemical potential

\[ \mu_r = -\frac{2\gamma \Omega}{r}. \]  

(B.22)

This is called the Gibbs–Thomson potential due to the curvature of surface. We note that it is not just the potential of the surface atoms of the precipitate, it is the potential energy of all the atoms in the precipitate. We see that for a flat surface \( r = \infty \), \( \mu_\infty = 0 \) so we have

\[ u_r - \mu_\infty = \frac{2\gamma \Omega}{r}. \]  

(B.23)

In the following, we shall apply this potential to determine the effect of curvature on solubility. We consider an alloy of \( \alpha = A(B) \), where \( B \) is solute in solvent \( A \). At temperature \( T \), \( B \) will precipitate out. We consider two precipitates of \( B \), one larger than the other. The solubility of \( B \) surrounding the large one is less than that surrounding the smaller one. If we take \( X \) to be the solubility, we have

\[ X_\infty < X_{\text{large}} < X_{\text{small}}. \]

To relate the solubility to Gibbs–Thomson potential, we have the chemical potential of \( B \) as a function of its radius as

\[ \mu_{B,r} - \mu_{B,\infty} = \frac{2\gamma \Omega}{r}, \]  

(B.24)

where \( \gamma \) is the interfacial energy between the precipitate and the matrix. If we define the standard state of \( B \) as pure \( B \) with \( r = \infty \), we have

\[ \mu_{B,r} = \mu_{B,\infty} + RT \ln a_B, \]  

(B.25)

where \( a_B \) is the activity. According to Henry’s law,

\[ a_B = kX_B, r, \]

where \( X_{B,r} \) is the solubility of \( B \) surrounding a precipitate of radius \( r \). At \( r = \infty \),

\[ \mu_{B,\infty} = \mu_{B,\infty} + RT \ln a_B. \]
This implies that $RT \ln a_B = 0$, or $a_B = 1$. So $k = 1/X_{B,\infty}$. Therefore,

$$\mu_{B,r} = \mu_{B,\infty} + RT \ln \frac{X_{B,r}}{X_{B,\infty}}. \quad (B.26)$$

Hence,

$$\ln \frac{X_{B,r}}{X_{B,\infty}} = \frac{\mu_{B,r} - \mu_{B,\infty}}{RT} = \frac{2\gamma \Omega}{rRT}.$$ 

Or if we consider $kT$ instead of $RT$, we have

$$X_{B,r} = X_{B,\infty} \exp \left(\frac{2\gamma \Omega}{r kT}\right). \quad (B.27)$$

### B.4 Effect of Curvature on Solubility (Ripening)

The solubility of $B$ around a spherical particle of $B$ of radius $r$ is given by

$$X_{B,r} = X_{B,\infty} \exp \left(\frac{2\gamma \Omega}{r kT}\right),$$

where $r = \infty$, the exponential equals unity. Thus, $X_{B,r}$ goes up when $r$ goes down. Now we replace $X_{B,r}$ by $C_r$ and $X_{B,\infty}$ by $C_\infty$, which is the equilibrium concentration on a flat surface. We have

$$C_r = C_\infty \exp \left(\frac{2\gamma \Omega}{r kT}\right). \quad (B.28)$$

If $2\gamma \Omega \ll r kT$, we have

$$C_r = C_\infty \left(1 + \frac{2\gamma \Omega}{r kT}\right),$$

$$C_r - C_\infty = \frac{2\gamma \Omega C_\infty}{r kT} = \frac{\alpha}{r}, \quad (B.29)$$

where $\alpha = \frac{2\gamma \Omega}{kT} C_\infty$,

$$C_r = C_\infty + \frac{\alpha}{r}. \quad (B.30)$$
Thus, $C_r$ is not a constant, but a function of $r$. Now we substitute $C_r$ into the growth equation of

$$\frac{dr}{dt} = \Omega J = \frac{\Omega D (C_0 - C_r)}{r}.$$ 

We have

$$\frac{dr}{dt} = \frac{\Omega D}{r} \left( C_0 - C_\infty - \frac{\alpha}{r} \right). \quad \text{(B.31)}$$

Note that $C_0 - C_\infty > 0$ always. We can define a critical radius $r^*$ such that

$$C_0 - C_\infty = \frac{\alpha}{r^*}.$$ 

Then we have

$$\frac{dr}{dt} = \frac{\alpha \Omega D}{r} \left( \frac{1}{r^*} - \frac{1}{r} \right). \quad \text{(B.32)}$$

The parameter $r^*$ is defined such that

- $r > r^*$, $\frac{dr}{dt} > 0$ The particle is growing.
- $r < r^*$, $\frac{dr}{dt} < 0$ The particle is dissolving.
- $r = r^*$, $\frac{dr}{dt} = 0$ The particle is in a state of metastable equilibrium. It has a concentration $C$ at the interface, or $C_r = C$.

In ripening, the larger particles grow at the expense of the smaller ones. It will approach a dynamic equilibrium distribution of size of the particles. The distribution function can be obtained by solving the continuity equation in size space. Knowing $dr/dt$, it is the beginning of the LSW theory of ripening.
Appendix C: Derivation of Huntington’s Electron Wind Force

In the following we present the assumptions and step-by-step derivation of Huntington’s model of electron wind force.

(1) Considerations are hemiclassical. Each electron is treated as a group of waves or Bloch waves with an average wave vector $k$ and group velocity of $V = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k}$, where the function $E(k)$ should be found from the electron band theory (dispersion law). For free electrons, $E(k) = \frac{\hbar^2 k^2}{2m^*}$, and for electrons at the bottom of the conduction band, $E(k) = E_{\text{min}} + \frac{\hbar^2 k^2}{2m_0}$, where $m^* = \frac{\hbar^2}{\partial E/\partial k}$ is the effective electron mass. We note that $\partial E/\partial k$ means gradient in $k$-space, e.g., a vector with components of $\partial E/\partial k_x$, $\partial E/\partial k_y$, $\partial E/\partial k_z$. For Bloch waves, according to the Bloch theorem, we recall that each quantum state of independent electron in the periodic potential $U(r + R) = U(r)$ and $R = n_1 a_1 + n_2 a_2 + n_3 a_3$ can be described by the product of a planar wave and periodic function $\Psi_{\bar{h}k}(r) = e^{i \bar{h}k \cdot r} W_{\bar{h}k}(r)$, where $W_{\bar{h}k}(r + R) = W_{\bar{h}k}(r)$ and $n$ is the band index.

(2) $\frac{1}{\hbar} \left( \frac{\partial E}{\partial k} - \frac{\partial E}{\partial k'} \right) = \nabla' - \nabla$ is the change of electron’s group velocity as a result of scattering.

(3) $-m_0 \frac{\hbar}{\hbar} \left( \frac{\partial E}{\partial k_x} - \frac{\partial E}{\partial k'_x} \right) = -(p'_x - p_x)$ is momentum along the $x$-axis, transfer to defect during mentioned individual scattering.

(4) $f(k)$ is the probability that the quantum state $\bar{k}$ is occupied by some electron. The quantum cell in $k$-space with a “$k$-volume” is given by $\Omega = \frac{2\pi}{L_x} \cdot \frac{2\pi}{L_y} \cdot \frac{2\pi}{L_z} = \frac{8\pi^3}{V}$, where $V$ is the real total volume. At equilibrium, we have $f_0 = \frac{1}{e^{\frac{E_{\text{F}}}{kT}} + 1}$ (Fermi–Dirac distribution).

(5) $1 - f(k)$ is a probability that the quantum state $\bar{k}'$ was free or unoccupied before scattering, so that the Pauli exclusion principle does not forbid the $\bar{k} \rightarrow \bar{k}'$ transition.

(6) $W_d(\bar{k} \rightarrow \bar{k}')$ is a probability of this transition per unit time. It means that the product $W_d dt$ is a probability of transition during $dt$, if $dt \ll \tau_d$. 

(7) According to the Pauli principle, each quantum cell in $k$-space (with $\Omega = \frac{4\pi^3}{\lambda^3}$) may contain up to two electrons with opposite spins, so the $k$-volume per electron is $\frac{\Omega}{2} = \frac{2\pi^3}{\lambda^3}$.

(8) Now we consider unit volume $V = 1 \text{ m}^3$.

(9) The number of possible electron states in the “elementary” $k$-volume $dV_k = dk_x dk_y dk_z$ is $\frac{d^3 k}{\Omega} = \frac{d^3 k}{2\pi^3}$. The elementary $k$-volume is physically small.

(10) The momentum, $M_x$ along the $x$-axis, transferring from electrons to the defects in the unit volume $V = 1 \text{ m}^3$ per unit time is given as

$$-\int \int \frac{d^3 k}{4\pi^3} \left( p'_x - p_x \right) f(k)(1 - f(k'))W_d(k, k').$$

Or

$$\frac{dM_x}{dt} = -\left( \frac{1}{4\pi^3} \right)^2 \int \int \frac{m_0}{h} \left( \frac{\partial E}{\partial k_x} - \frac{\partial E}{\partial k'_x} \right) f(k)(1 - f(k'))W_d(k, k') \frac{d^3 k}{d^3 k'}.$$

(11) We shall represent the last equation by two integrals.

$$\frac{dM_x}{dt} = I_1 + I_2,$$

where

$$I_1 = -\left( \frac{1}{4\pi^3} \right)^2 \int \int \frac{m_0}{h} \left( \frac{\partial E}{\partial k_x} \right) f(k)(1 - f(k'))W_d(k, k') \frac{d^3 k}{d^3 k'},$$

$$I_2 = -\left( \frac{1}{4\pi^3} \right)^2 \int \int \frac{m_0}{h} \left( \frac{\partial E}{\partial k'_x} \right) f(k)(1 - f(k'))W_d(k, k') \frac{d^3 k}{d^3 k'}.$$

Since the integration is being made over all $k$ and all $k'$, we can interchange the variables in the first integral as

$$I_1 = -\left( \frac{1}{4\pi^3} \right)^2 \int \int \frac{m_0}{h} \left( \frac{\partial E}{\partial k'_x} \right) f(k')(1 - f(k))W_d(k', k) \frac{d^3 k}{d^3 k'}.$$

Then in $I_1$ and $I_2$, we have the same $\frac{\partial E}{\partial k_x}$, and thus we have

$$\frac{dM_x}{dt} = (-I_2) - (-I_1)$$

$$= \left( \frac{1}{4\pi^3} \right)^2 \int \int \frac{m_0}{h} \left[ f(k')(1 - f(k))W_d(k, k) - f(k')(1 - f(k))W_d(k', k) \right] \frac{d^3 k'}{d^3 k}. $$
(12) Huntington showed that to simplify the expression of the last equation, he used the concept of relaxation time $\tau_d$. This notion was first introduced for the analysis of the kinetic Boltzmann equation for gases. With certain approximation, the rate of change of the distribution function can be represented as

$$\frac{\partial f(t,k)}{\partial t} = \frac{1}{4\pi^3} \int \{ f(\vec{k})(1 - f(\vec{k}'))W_d(\vec{k},\vec{k'}) - f(\vec{k'})(1 - f(\vec{k}))W_d(\vec{k'},\vec{k}) \} \, d^3k' - \frac{f(t,\vec{k}) - f(\vec{k})}{\tau_d}$$

for the equilibrium distribution. For the stationary case, $\frac{\partial f}{\partial t} = 0$, so that

$$\frac{1}{4\pi^3} \int \{ f(\vec{k})(1 - f(\vec{k}'))W_d(\vec{k},\vec{k'}) - f(\vec{k'})(1 - f(\vec{k}))W_d(\vec{k'},\vec{k}) \} \, d^3k' = \frac{f(t,\vec{k}) - f(\vec{k})}{\tau_d}.$$  \tag{C.2}

In the above equation, $f(\vec{k})(1 - f(\vec{k}'))W_d(\vec{k},\vec{k'})$ is the probability per unit time of $\vec{k} \to \vec{k}'$ transition, provided that the state $\vec{k}$ before transition was filled and the state $\vec{k}'$ was empty. The function $f(\vec{k'})(1 - f(\vec{k}))W_d(\vec{k'},\vec{k})$ is the probability per unit time of the inverse transition.

(13) By substituting Eq. (C.2) into Eq. (C.1), we have

$$\frac{dM_x}{dt} = \frac{m_0}{\hbar} \frac{\partial E(\vec{k})}{\partial k_x} f(\vec{k}) - \frac{m_0}{\hbar} \frac{\partial E(\vec{k})}{\partial k_x} f_0(\vec{k}).$$

(14) Let the relaxation time be independent of $\vec{k}$ and $\tau_d = \text{constant}$. Then

$$\frac{dM_x}{dt} = \frac{m_0}{\hbar \tau_d} \frac{1}{4\pi^3} \int d^3k \frac{\partial E(\vec{k})}{\partial k_x} f(\vec{k}) - \frac{m_0}{\hbar \tau_d} \frac{1}{4\pi^3} \int d^3k \frac{\partial E(\vec{k})}{\partial k_x} f_0(\vec{k}).$$

(15) Evidently, the average vector velocity of electrons in equilibrium is zero:

$$V_x = \left. \frac{1}{\hbar} \frac{\partial E}{\partial k_x} \right|_{\text{eq}} = \left. \frac{1}{\hbar} \frac{\partial E}{\partial k_y} \right|_{\text{eq}} = \left. \frac{1}{\hbar} \frac{\partial E}{\partial k_z} \right|_{\text{eq}} = 0.$$

Therefore,

$$\int \frac{\partial E}{\partial k_x} f_0(\vec{k}) d^3k = 0.$$
Thus,

$$\frac{dM_x}{dt} = \frac{m_0}{\hbar \tau_d} \frac{1}{4\pi^3} \int \frac{\partial E}{\partial k_x} f(\mathbf{k}) d^3k.$$  \hfill (C.3)

(16) To relate the momentum change to force, we have the current density given as

$$j_x = (-e)n \mathbf{v}_x = (-e) \int \frac{d^3k}{4\pi^3} f(k) \cdot \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial k_x},$$  \hfill (C.4)

where $n = \frac{d^3k}{4\pi^3} f(k)$ is the number of electrons per unit volume with $k$ belonging to $d^3k$. Indeed, $\frac{d^3k}{4\pi^3}$ is the number of “single electron cells” in the “volume” of $d^3k$ of $k$-space, and $f(k)$ is the “inhabitance” of cell.

(17) Combining Eqs. (C.3) and (C.4), we obtain

$$\frac{dM_x}{dt} = -\frac{j_x m_0}{e \tau_d}. \hfill (C.5)$$

This is a momentum change along the $x$-direction, transferred to defects (the diffusing atoms) per unit time per unit volume.

(18) Let $N_d$ be the density of defects (number of defects per unit volume). Then, according to Newton’s second law, the force at one defect, caused by electron wind, is

$$F_x = \frac{1}{N_d} \frac{dM_x}{dt} = -\frac{j_x m_0}{e \tau_d N_d}.$$  \hfill (C.6)

This force has a clear physical meaning assuming the condition that during atomic jump the defect feels much more than one collision. Characteristic time of one successful jump is of the order of Debye time, $\tau_{\text{Debye}} \sim 10^{-13}$ sec. So for Eq. (C.6) to be reasonable, it is necessary that the product of scattering frequency, $\nu_{\text{scatter}}$, and Debye time be much less than unity:

$$\nu_{\text{scatter}} \approx \frac{kT V_F}{l},$$

where $l$ is the mean free path length of electron around defect, $V_F/l$ is the frequency of “possible” collisions, and $kT/\epsilon_p$ is the fraction of electrons which are able to be scattered according to the Pauli principle.

$l \approx \frac{1}{\sigma n}$ where $\sigma$ is the cross section and is about $10^{-19}$ m$^2$ (according to Huntington’s estimate).

$$n \sim 10^{29} \text{ m}^{-3} (n_{\text{ex}} \approx \frac{kT}{\epsilon_p} n \approx 10^{27} \text{ m}^{-3}), \frac{kT}{\epsilon_p} \approx 10^{-2}, V_F = \frac{\hbar k_F}{m_0} \approx 10^6 \text{ m/ sec}.$$
Thus, \( \nu_{\text{scatter}} \approx 10^{-1}10^n \sigma \approx 10^{-2}10^610^{59}10^{19} \approx 10^{14} \text{sec}^{-1} \).
So \( \nu_{\text{scatter}} \tau_{\text{Debye}} \approx 10 \gg 1 \).

(19) Let us now transform Eq. (C.6) in terms of electric field: \( j_x = \frac{\varepsilon_x}{\rho} \), where \( \rho \) is an average resistance of metal. According to the Drude–Lorentz–Sommerfeld model, the resistance \( \rho \) of a metal can be written as

\[
\rho = \frac{|m^*|}{ne^2\tau},
\]

where \( m^* = \frac{\hbar^2}{\partial^2} \) is the effective electron mass.

Huntington used the same expression for the resistance of defects,

\[
\rho_d = \frac{|m^*|}{ne^2\tau_d},
\]

so that we have \( \tau_d = \frac{|m^*|}{ne^2\rho_d} \).

Thus, from Eq. (C.6), we obtain

\[
F_x = -\frac{\varepsilon_x}{\rho} \frac{m_0 ne^2 \rho_d}{eN_d |m^*|} = - \left( \frac{m_0 ZN}{|m| N_d} \right) \varepsilon_x,
\]

(19.7)

where \( N \) is the density of ions and \( Z \) is the valence number; \( n = ZN \).

Thus, we have the effective charge

\[
Q^* = -Z^* e, \text{ where } Z^* = \frac{m_0 ZN}{|m^*| N_d} = Z \frac{m_0 \rho_d}{|m^*| N_d}.
\]

(20) Now, let us take into account the fact that \( \tau_d, \rho_d, \) and \( F_x \) change from position to position. Obviously, they shall reach a maximum at the saddle point of diffusion.

Assume that \( F(y) = F_m \sin^2 \left( \frac{\pi y}{a} \right) \), where \( y \) is not the \( y \)-axis. Rather it is a coordinate along the jumping path, which usually does not coincide with the \( x \)-axis. Work or change of potential barrier is

\[
U_j = \int_0^{a_j/2} F(y)dy = F_m \cos \theta_j \int_0^{a_j/2} \sin \frac{\pi y}{a} dy = \frac{a_j F_m}{4} \cos \theta_j.
\]

After averaging in all possible jump directions, we have

\[
J_x = C \frac{D}{kT} \frac{1}{2} F_m.
\]
The factor of $1/2$ is due to the integral of

$$\int_0^{a/2} \sin^2 \frac{\pi y}{a} \, dy = \frac{1}{2} \left( \frac{a}{2} \right).$$

(21) Thus, we have finally the effective charge number:

$$Z_{\text{eff}} = \frac{1}{2} Z_{\text{max}}^* - Z = Z \left( \frac{1}{2} \frac{m_0}{|m^*|} \frac{\rho_{\text{max}}}{N} - 1 \right).$$
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