

*The Kirkendall Effect and Diffusion in Solids***Introduction**

Diffusion is the governing mechanism in most physical systems, and is widely applicable to a variety of driving forces, including electric fields, temperature gradients, concentration gradients, and stresses, amongst others.⁴ Though biological systems also exhibit active transport mechanisms, including endo- and exocytosis, as well as the use of protein-based pumps and transporters, diffusion is similarly essential for acquisition of nutrients, flow of water between intra- and extracellular compartments, and maintenance of proper oxygen and carbon dioxide levels.⁸ In physical systems, such as those studied in materials science, diffusion governs innumerable processes, including phase transformations, motion of interfaces and dislocations, nucleation and growth of grains, and non-crystalline deformation mechanisms, such as shear transformation zones (STZs) exhibited in metallic glass systems.¹⁻³

In liquid and gaseous states, the underlying mechanism of diffusion is rather simple, in that atoms (or molecules) typically have enough local free volume to move down their respective gradients. In solids, however, the situation becomes more complicated, as room to move is not always available. Multiple mechanisms have been introduced to explain diffusion in crystalline solids, including the ring mechanism, vacancy mechanism, interstitial mechanism, and interstitialcy mechanism. The latter two rely on the formation of interstitial defects, in which the solute or host atom occupies sites between the normal sites of the crystal lattice. For small solute atoms, such as C, H, N, or O, the energy barrier for migration between these lattice sites is rather small, and thus the interstitial mechanism serves as the primary mechanism for these atoms. The interstitialcy mechanism is based on the cooperative exchange of atoms between interstitial and host lattice sites, and is exhibited in certain metals (e.g. AgBr) under certain conditions.³

Prior to the observations made by Ernest Kirkendall, the primary diffusion mechanism in materials that could not form interstitial defects was largely unknown. The proposed ring mechanism relies on a cooperative motion between host atom sites that permits local rearrangement. The vacancy mechanism, however, requires no cooperation, but rather the existence of thermally activated defects known as vacancies. At all temperatures above 0K, concentrations of vacancies will exist in the crystal, in which host lattice sites are unoccupied and the former resident atom is relocated to some form of sink, including dislocations, grain boundaries and other interfaces, or free surfaces. These vacancies may exchange with host atoms, thus inducing a local atomic flux that is of equal and opposite magnitude to the local vacancy flux. At elevated temperatures, vacancy concentrations become significant, as these point defects obey an Arrhenius relationship of the form $X_v = \exp(-\Delta G_f/kT)$, where X_v is the vacancy site concentration in the lattice, k is the Boltzmann constant, T is the absolute temperature, and ΔG_f is the vacancy formation energy, and can thus sustain significant atomic fluxes through the material.⁴

Ernest Kirkendall observed diffusion between a 70% Cu-30% Zn brass alloy and a pure Cu plate by embedding molybdenum wires in the brass. Mo is largely unreactive with these materials at elevated temperatures, and thus the wires were assumed to be maintained at a constant size. The width between the wires, however, was observed to change as the diffusion couple was held at an elevated temperature for extended periods of time. Specifically, the wires were observed to move closer together, indicating a net diffusive flux of material from the brass to the copper. As both materials were known to move down their concentration gradients, this indicates that the diffusion coefficient of zinc is larger than that of copper. Importantly, it also precludes the action of a ring mechanism, which cannot sustain net fluxes. From the similar atomic sizes and crystal structures of the materials, it was discovered that the vacancy mechanism is the dominant means of diffusion of substitutional atoms through a crystal lattice.⁴

Model

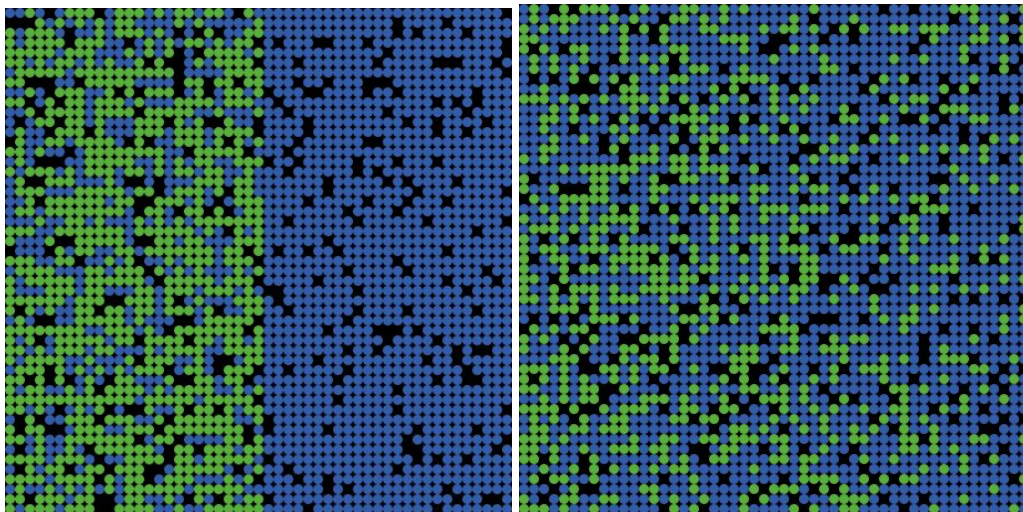
A solid diffusion model exists in the NetLogo environment, but is far from realistic, as is evident from numerous perspectives. The model assumes a single column of vacancies exists at the interface between two pure materials. Vacancies are randomly formed throughout a crystal, and thus a starting configuration such as that employed in the model is inaccurate. Similarly, the effects of temperature on the vacancy concentration are not considered, and the diffusion coefficients of the two atoms are assumed to be the same, which is, in general, unrealistic. The model was updated with more realistic conditions for each of these parameters. Additionally, one side of the diffusion couple was converted into an alloy to more accurately reproduce the Kirkendall dynamics. The initial configuration was created in the setup function. The “Concentration” input and “Temperature” slider are required for establishing the number of “blue” atoms in the alloy and the overall vacancy concentration in each side of the material, respectively. The Concentration input is the fraction of total lattice sites occupied by blue atoms on the left, and is thus a decimal. The Temperature slider ranges from 100K to 10000K in increments of 100K. The entire right side is assumed to consist of blue atoms, and the remaining spots that are not dedicated to vacancies are taken to be green atoms on the left side. The algorithm is constructed to ensure that no atoms (“turtles” in the NetLogo environment) overlap.

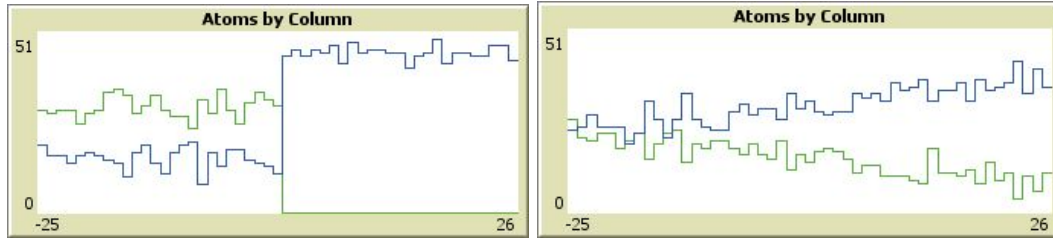
Though the vacancy formation in energy is, in general, not equal between two dissimilar metals (i.e. pure copper and brass), for simplicity, it was assumed that the formation energy was equal to the monovacancy formation energy in pure copper, 1.29 eV.¹¹ The code is structured with different variables representing vacancy formation energies in either phase, but the energies are simply set equal. Thus, one may easily change a single parameter in the code to examine the effects of different vacancy formation energies, which will only serve to change the initial concentration and distribution. It should be noted that the temperatures commonly used in determining diffusion coefficients are significantly lower than those necessary for appreciable diffusion in this model due to the small scale of the volume. A 51 x 51 grid is used to examine the dynamics, yielding a system of only 2601 atoms. The lattice parameter of copper is

approximately 3.60 Å, or 0.360 nm.⁶ As Cu crystallizes with a face-centered cubic structure, containing 4 atoms per unit cell, the 25 x 51 atom cell of the right-hand phase would only occupy $(.360)^3 * 1275/4 \sim 15 \text{ nm}^3$. Alternatively, to expect a single vacancy in 1275 atoms, a temperature of $-\Delta G/(k*\ln(1/1275)) \sim 2092 \text{ K}$. As the total number of atoms increases to values commonly used for diffusion coefficient experiments, the total number of vacancies increases significantly.

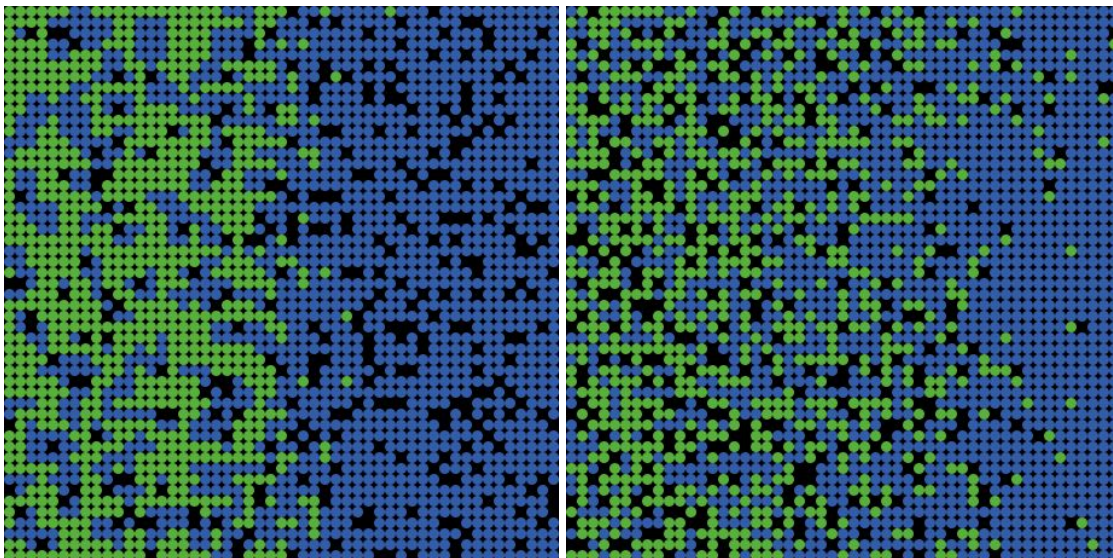
At each time point, a decision is made for each vacant site. In the initial form of the code, an equal probability is assumed for choosing any one of the non-empty neighboring sites for a vacancy. In order to account for differences in diffusion coefficients^{5,7,9} (i.e. the likelihood of an atom of a particular type switching with a vacancy), another user-input variable is introduced in the form of the diffusion ratio. This ratio is taken to be the probability of a blue atom exchanging with a vacancy divided by the probability of a green atom doing the same. An overall probability of a blue atom switching with a particular vacancy is calculated as the number of blue atoms surrounding the vacancy multiplied by this probability and divided by the total number of neighboring atoms. Due to the small system size and the mechanism by which the diffusion ratio is utilized, this ratio does not correspond directly to the ratio of the mass diffusivities, which instead reflect the average system properties rather than those exhibited by single atoms. Instead, this ratio more accurately reflects the ratio of the jump frequencies between the atom types. Checks are introduced to account for cases where a vacancy is surrounded by four other vacancies and where the neighboring sites have only one type of atom. A random probability is calculated in the range [0, 1) and is compared to this calculated probability. If the random value is larger or equal, then a neighboring green atom is chosen to switch with the vacancy, and if not, a blue atom is selected. This mechanism accounts for different likelihoods of diffusion based on atom type.

Behavior of the Model



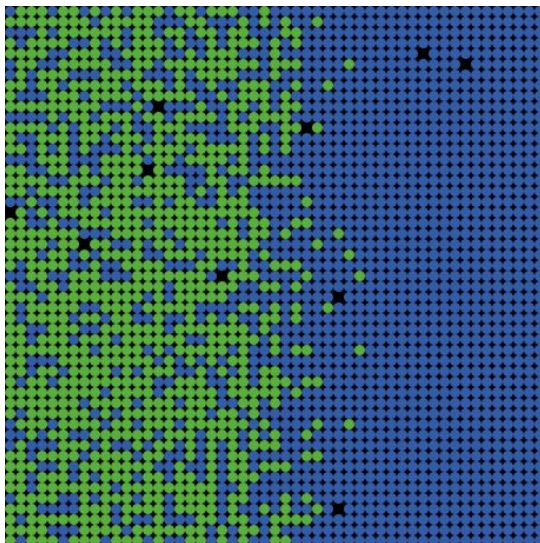


In examining the dynamics of the system, it is of interest to consider the limiting diffusion coefficient cases, as well as a case wherein the Kirkendall effect is reproduced. While the diffusion coefficient is commonly used to capture macroscopic diffusive behavior of the system, at the atomic scale, the commonly considered mathematical formulations are somewhat different. These mechanisms rely on the calculation of a jump frequency, which is a product of how often a given atom attempts to surmount the local energy barrier preventing it from diffusing into a neighboring vacant site and an Arrhenius-Boltzmann probability term for the success of a given jump in having a large enough energy based on thermal fluctuations.¹ An example scenario is presented above, with an initial concentration of blue of 0.30, a temperature of 7000 K, and a diffusion ratio of 0.90. The configuration on the right is obtained after ~15,000 ticks, and shows the system at a near-equilibrium state. Transient behavior in the initial system suggests a net vacancy flux toward the alloy phase due to the higher diffusion rate of the green atoms, but a lack of crystal defects prevents a long-term steady-state flux.



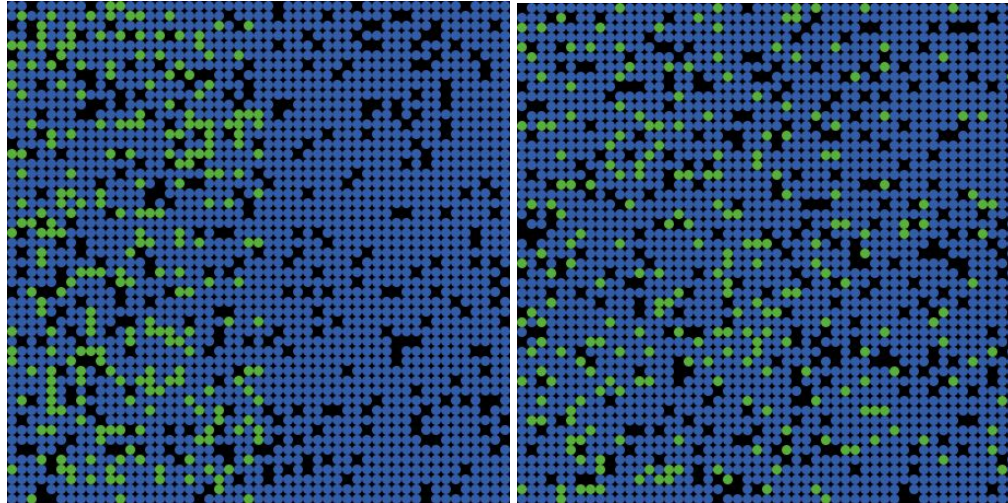
The limiting cases that may be considered occur when the diffusion ratio $\gg 1$, i.e. the blue atoms diffuse much faster than the green atoms, and when the ratio $\ll 1$, i.e. the green atoms diffuse much faster. These are depicted on the left (ratio = 15) and right (ratio = 1/15) above after 15,000 ticks. It is clear that the overall diffusion flux is decreased and the system has not reached an equilibrium state by this time point in either case, though due to differences in driving forces, the right-hand case has evolved more. In these cases, net vacancy fluxes can be identified on the

sides with high blue concentrations and green concentrations, respectively, due to the different diffusion coefficients.



The effects of temperature are considered above for a configuration identical to the first one except with the temperature set to 2700K after 15,000 ticks. This highlights the clear temperature dependence of the diffusion coefficient and vacancy concentration due to the Arrhenius forms.

In many physical systems, the stresses induced by introducing a solute atom as a result of straining of the lattice are partially relieved when the atom binds to a vacancy. This is indicated by a binding energy between a vacancy and solute atom. Here, we assume the atomic radii and crystal structures between the alloy and pure material are identical, so this term does not enter into the considered scenario. Thus, the only contributions to overall diffusion fluxes are the rates of exchange between individual particle types and vacancies. As a result, this simplifies to a simple kinetics problem. In the cases where the blue atoms exchange much faster, the limiting reaction is a vacancy exchanging with the green. Running the simulation with a small diffusion ratio results in rapid exchange with blue atoms and infrequent exchanges with green atoms. Thus, the green atoms serve as the limiting reaction and the overall diffusion rate is limited by the jump rate between green atoms and vacancies. In the opposite limiting case, green atoms exchange rapidly and diffusion is limited by exchange with blue. In either of these cases, it is apparent that diffusion is relatively slow, despite the overall exchange rate of each vacancy being 1 exchange per time point, highlighting the rate-limiting nature of the slower reaction in serial processes.¹⁰



In the case of the Kirkendall effect, the diffusion rates, while not identical, are rather similar, with the overall flux of zinc surpassing that of copper. As zinc is the green atom in this scenario, this corresponds to a diffusion ratio less than one. A value was taken as 0.9 in the above figure, which depicts the initial configuration and the configuration after 10,000 time points. The Kirkendall experiment was performed with a zinc concentration of 30% in the brass phase, which is used in reproducing the effect. To induce an appreciable vacancy concentration in a small volume, a high temperature of 7000K was utilized. The figure above shows an example initial configuration and the resulting final configuration.

Conclusion

Though this model makes the solid diffusion model from the NetLogo library significantly more accurate relative to physical systems, there are numerous assumptions that may still be relaxed in order to make the model even better at capturing the underlying mechanisms of diffusion. Included in these assumptions are: i) the diffusion mechanism, ii) the diffusion ratio and temperature, iii) crystal structure, iv) composition and v) defects.

As mentioned in the introduction, multiple different mechanisms are known to operate to accommodate diffusive fluxes, and are dependent largely on diffusion driving forces and structure of the material. It is difficult to incorporate mechanisms in the NetLogo environment that rely on the presence of interstitials due to the resulting strains induced in the lattice that prevent the crystal from assuming a completely uniform shape. In cases such as the Cu-Zn system or binary isomorphous systems like Cu-Ni, the vacancy mechanism dominates diffusion within the bulk crystal and this assumption is valid.

The jump frequency of a given atom type is a product of a vibrational frequency multiplied by an Arrhenius probability term, the latter of which is temperature-dependent.¹ If the activation energies for the jump differ between atoms, then the diffusion ratio term may also be temperature-dependent, altering which flux is faster. However, as temperature does not change throughout the simulation (which may be an added driving force as well in the form of a

thermal gradient), and the ratio is a user-input parameter, this only requires the user to put in the correct ratio for the given temperature.

Differences in crystal structure make the situation significantly more complicated and may cause the formation of incoherent interfaces or coherent interfaces with residual stresses that hinder atomic fluxes between the two sides of the sample. As brass is simply a solid solution of Zn in Cu, both will exhibit the FCC crystal structure of pure copper,⁶ and this complication need not be considered for the system above.

Composition, by itself, is not truly an added complication aside from any extra stresses that may develop from strains on the crystal lattice. Instead, it is the interaction of solute atoms with crystal defects that make the system far more complex. The presence of line defects (dislocations and ledges) often serve as sites where diffusion preferentially occurs due to the disordered structure of material in the core. These defects, as well as zero-dimensional (vacancies), two-dimensional (interfaces, grain boundaries, and free surfaces) and three-dimensional defects (e.g. precipitates) often serve as sites for segregation of solute to alleviate stresses, and 1D and 2D defects can support the annihilation and creation of vacancies to more accurately capture the steady-state net vacancy flux induced by differences in rates of diffusion between atoms.²

As is evident from the above discussion, the updated model still requires significant assumptions that are often not valid in physical systems. That being said, the underlying mechanisms accurately capture the fundamentals of one of the most significant processes in materials kinetics for small-scale closed systems without defects excluding the presence of a coherent interface without residual stresses. Additionally, the system can reproduce the basis of one of the principal experiments in understanding diffusion.

References

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Source Code

```
globals [EnergyL EnergyR delGL delGR VacConcR VacConcL VacanciesR VacanciesL
num-green num-blue-left num-blue-right x y nblue ngreen pblue prob atom]
breed [atoms-green atom-green]
breed [atoms-blue atom-blue]
breed [atoms-right atom-right]

to setup
  clear-all
  set-default-shape turtles "circle"

  set delGL 1.29 * 1.6 * 10 ^ -19
  set delGR delGL
  set EnergyL (delGL / (1.38 * Temperature * 10 ^ -23))
  set EnergyR (delGR / (1.38 * Temperature * 10 ^ -23))
  set VacConcL exp(-1 * EnergyL)
```



```

set VacConcR exp(-1 * EnergyR)
set VacanciesL floor(VacConcL * (2 * max-pycor + 1)*(max-pxcor + 1))
set VacanciesR floor(VacConcR * (2 * max-pycor + 1)*(max-pxcor))

set num-blue-left floor(Concentration * (max-pxcor + 1)*(2 * max-pycor + 1))
Create-atoms-blue num-blue-left[
  setxy random (min-pxcor - 1) random-pycor
  loop[
    ifelse (any? other atoms-blue-here) = TRUE[
      setxy random(min-pxcor - 1) random-pycor
    ]
    [stop]
  ]
]

ask atoms-blue[
  set color blue
]

set num-green ((max-pxcor + 1) * (2 * max-pycor + 1) - num-blue-left - VacanciesL)
Create-atoms-green num-green[
  setxy random(min-pxcor - 1) random-pycor
  loop[
    ifelse (any? other atoms-green-here) or (any? atoms-blue-here) = TRUE[
      setxy random(min-pxcor - 1) random-pycor
    ]
    [stop]
  ]
]

ask atoms-green[
  set color green
]

set num-blue-right ((max-pxcor) * (2 * max-pycor + 1) - VacanciesR)
Create-atoms-right num-blue-right[
  setxy random max-pxcor + 1 random-pycor
  loop[
    ifelse (any? other atoms-right-here) = TRUE[

```

```

    setxy random max-pxcor + 1 random-pycor
  ]
  [stop]
]
]

ask atoms-right[
  set color blue
]

;; plot the initial state of the system
reset-ticks
end

to go
  ;; asks vacancies to ask a neighboring atom to
  ;; move into the vacancy
  ask patches with [not any? turtles-here]
    [ move-atom-to-here ]
  tick
end

;; chooses a neighboring atom to move onto a empty patch (vacancy)
to move-atom-to-here ;; patch procedure
  set nblue count (turtles-on neighbors4) with ([color = blue])
  set ngreen count (turtles-on neighbors4) with ([color = green])
  set pblue ifelse-value (nblue + ngreen = 0) [-1] [nblue * DiffusionRatio / (nblue + ngreen)]
  set prob random-float 1
  ifelse (pblue = -1)[stop][
    ifelse (ngreen = 0) [set atom one-of (turtles-on neighbors4) with ([color = blue])
      ask atom [move-to myself]
      stop
    ][
      set atom ifelse-value (prob >= pblue) [one-of (turtles-on neighbors4) with ([color = green])]
      [one-of (turtles-on neighbors4) with ([color = blue])]
      ask atom [ move-to myself ] ;; myself is the calling patch
    ]
  ]
]

```

end

;;; plotting procedures

to-report greens

 report turtles with [color = green]

end

to-report blues

 report turtles with [color = blue]

end

to plot-atoms [atoms]

 plot-pen-reset

 plot-pen-up

 let column min-pxcor

 repeat world-width [

 let n count atoms with [pxcor = column]

 plotxy column n

 plot-pen-down

 set column column + 1

 plotxy column n

]

end