Effective diffusivity of heterogeneous systems

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in Honor of John E. Morral

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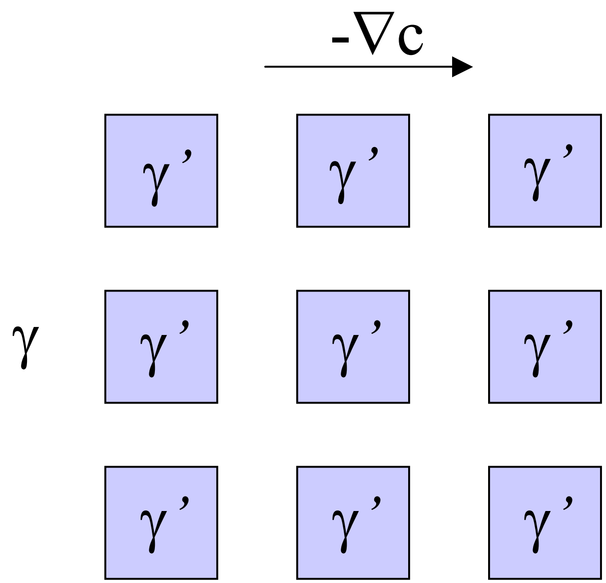
A problem that John might like (I guess…):

Effective diffusivity of a γ/γ’ alloy



How to find D^{eff} (D_γ, $D_{\gamma'}$)?

A. $D^{eff} = vD_{\gamma'} + (1-v)D_\gamma$

B. $\dfrac{1}{D^{eff}} = \dfrac{v}{D_{\gamma'}} + \dfrac{1-v}{D_\gamma}$

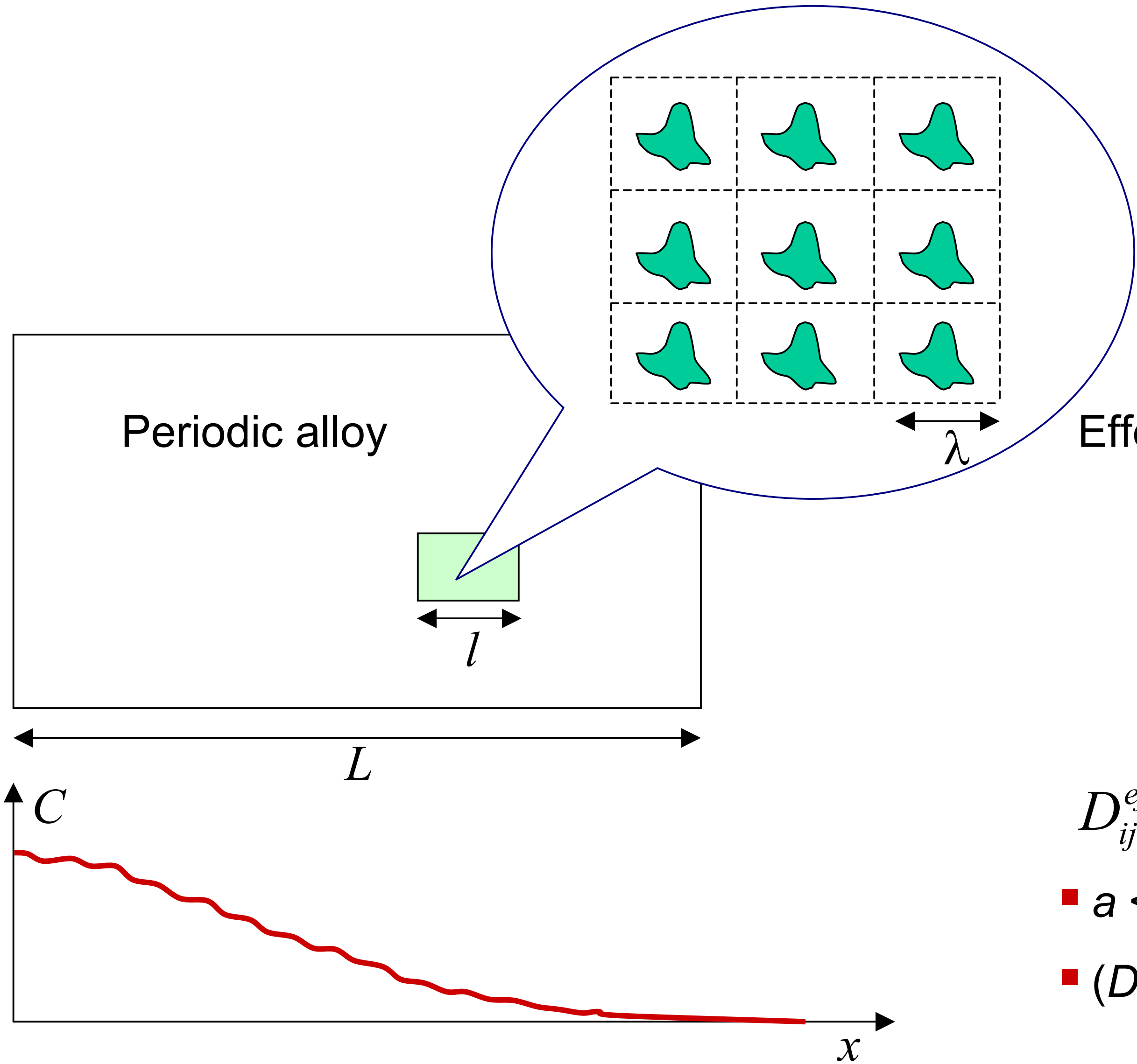
C. None of the above

When does D^{eff} exist?

Generalizations of the problem

- Diffusion in a general two-phase alloy with a periodic structure
- Diffusion in a continuum with periodic diffusivity $D_{ij}(\mathbf{x})$
- Include sink/source functions
- Include segregation in phases
- Include driving force
- Atomic diffusion on superlattices
  - Interstitial diffusion in crystals with multiple occupation sites
  - Grain boundary diffusion
  - Diffusion along a dislocation core

The problem of effective diffusivity



Exact diffusion equation:

$$\frac{\partial c}{\partial t} = \sum_{ij} \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial c}{\partial x_j}\right)$$

$D_{ij}(\mathbf{x})$ – periodic function

Effective diffusion equation:

$$\frac{\partial \bar{c}}{\partial t} = \sum_{ij} D_{ij}^{eff}\frac{\partial^2 \bar{c}}{\partial x_i \partial x_j}$$

D_{ij}^{eff} =const

D_{ij}^{eff} exists if:

- $a \ll \lambda \ll l \ll L$
- $(D_{ij})_{min} t \gg l^2$

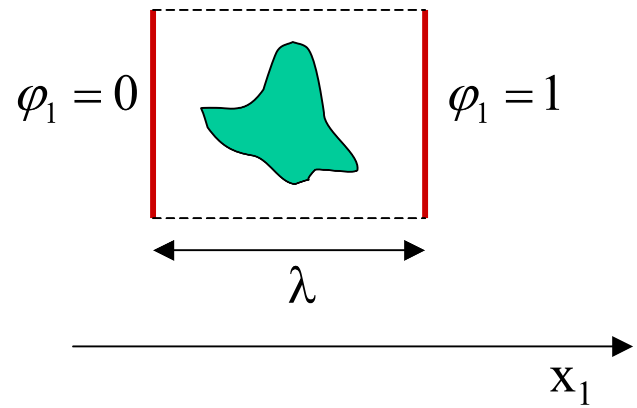
Existence of effective diffusivity

$$\frac{\partial \langle c \rangle}{\partial t} = \sum_{ij} D_{ij}^{eff} \frac{\partial^2 \langle c \rangle}{\partial x_i \partial x_j}$$

<…> - average over a repeat cell

Step 1: solve three steady-state problems on a repeat cell:

$$\sum_{ij} \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial \varphi_k}{\partial x_j} \right) = 0, \quad k = 1,2,3$$



with boundary conditions:

$$\varphi_k(\lambda, x_2, x_3) = \varphi_k(0, x_2, x_3) + \delta_{k1}$$
$$\varphi_k(x_1, \lambda, x_3) = \varphi_k(x_1, 0, x_3) + \delta_{k2}$$
$$\varphi_k(x_1, x_2, \lambda) = \varphi_k(x_1, x_2, 0) + \delta_{k3}$$

Step 2: find D_{ij}^{eff} as follows: $D_{ij}^{eff} = \lambda \sum_m \left\langle D_{im} \frac{\partial \varphi_j}{\partial x_m} \right\rangle$

NB: Even if the local diffusivity is isotropic, the effective diffusivity can still be a tensor, reflecting the **structural** anisotropy.

Variational calculation of the effective diffusivity

Step 1: Minimize three functionals:

$$\Phi_k = \lambda^2 \left\langle \sum_{ij} D_{ij} \frac{\partial \varphi_k}{\partial x_i} \frac{\partial \varphi_k}{\partial x_j} \right\rangle, \quad k = 1,2,3$$

with boundary conditions:

$$\varphi_k(\lambda, x_2, x_3) = \varphi_k(0, x_2, x_3) + \delta_{k1}$$

$$\varphi_k(x_1, \lambda, x_3) = \varphi_k(x_1, 0, x_3) + \delta_{k2}$$

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Step 2: find D_{ij}^{eff} as follows: $D_{ij}^{eff} = \lambda \sum_m \left\langle D_{im} \frac{\partial \varphi_j}{\partial x_m} \right\rangle$

In the principal coordinate system the minimum values of Φ_k coincide with eigenvalues of D_{ij}^{eff}:

$$\left(\Phi_k\right)_{\min} = D_k^{eff}, \quad k = 1,2,3$$

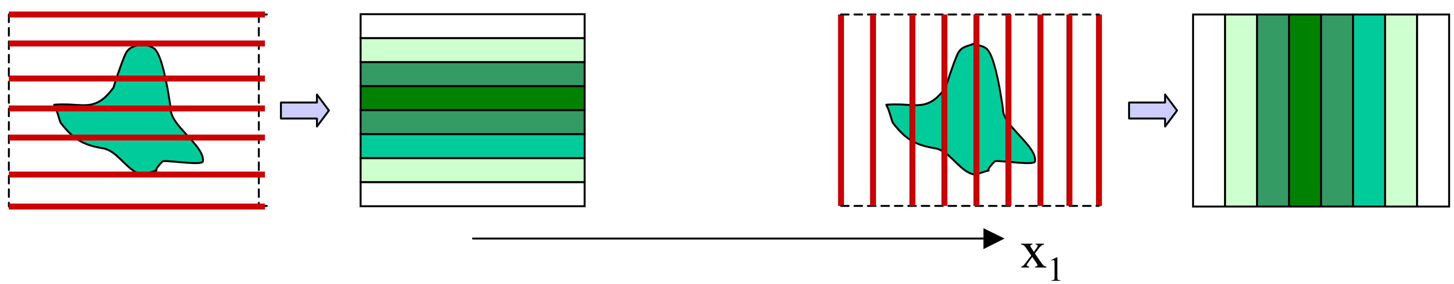
Upper and lower bounds from the variational approach

Suppose the local diffusivity is isotropic: $D_{ij} = \delta_{ij} D(\mathbf{x})$.

Bounds of D_1^{eff} :

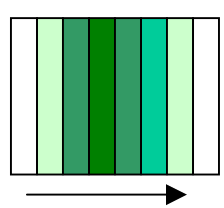
$$\boxed{D_1^- \le D_1^{eff} \le D_1^+}$$

$$D_1^- = \left\langle \frac{1}{\left\langle \frac{1}{D(\mathbf{x})} \right\rangle_{x_1}} \right\rangle_{x_2 x_3} \qquad D_1^+ = \frac{1}{\left\langle \frac{1}{\left\langle D(\mathbf{x}) \right\rangle_{x_2 x_3}} \right\rangle_{x_1}}$$

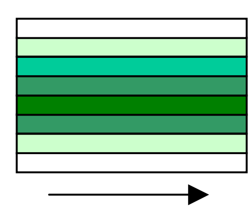


Using the relation $\langle D \rangle \langle D^{-1} \rangle \le 1$ we obtain the crude estimates:

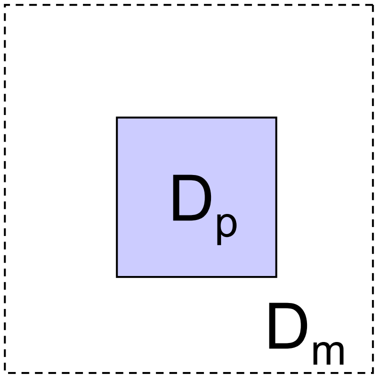
$$D_1^- = \frac{1}{\left\langle \frac{1}{\langle D \rangle} \right\rangle}$$



$$D_1^+ = \langle D \rangle$$



Example: diffusion in a γ/γ' - type structure



D^{eff} is isotropic

Upper bound:

$$D^{+} = D_m \frac{D_m + v^{2/3}(D_p - D_m)}{D_m + v^{2/3}(D_p - D_m) - v(D_p - D_m)}$$

Lower bound:

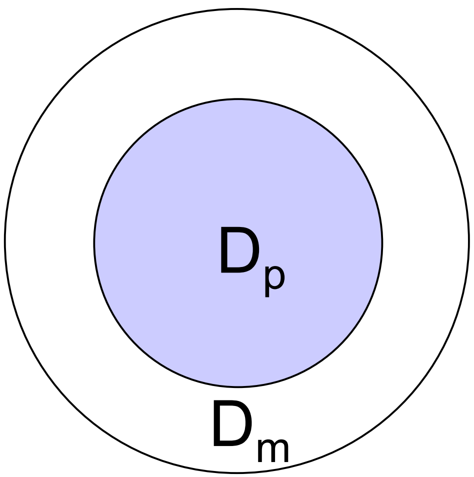
$$D^{-} = D_m \frac{D_p - v^{1/3}(D_p - D_m) + v(D_p - D_m)}{D_p - v^{1/3}(D_p - D_m)}$$

"Smart" guess: $D^{eff} \approx \dfrac{D^{+} + D^{-}}{2}$

Maxwell formula for the effective diffusivity*)

$$D^{eff} = D_m \left[1 + \frac{d(D_p - D_m)v}{D_p + (d-1)D_m - (D_p - D_m)v} \right]$$

d = dimensionality of space



$v = 0 \rightarrow D^{eff} = D_m$

$v = 1 \rightarrow D^{eff} = D_p$

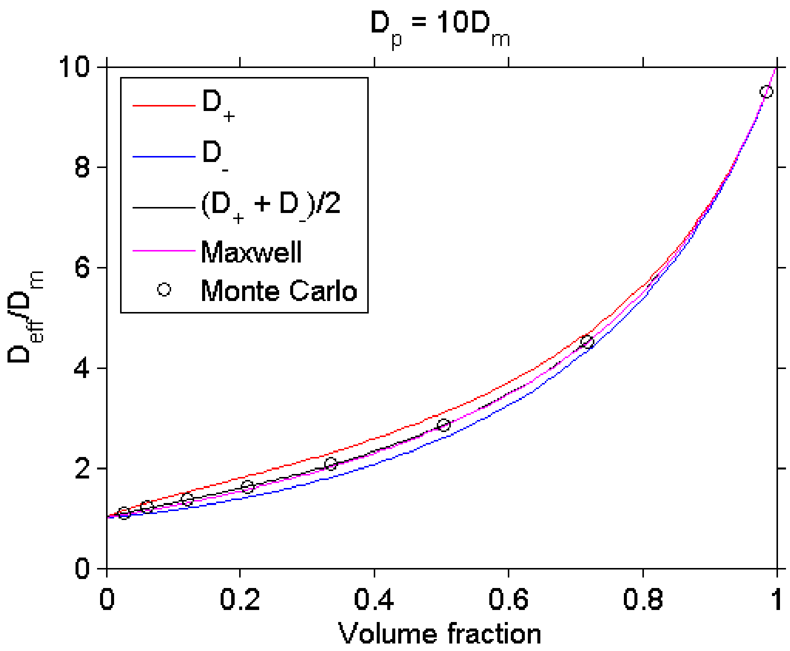
Expected to work well in isotropic structures

*) J.C. Maxwell, Treatise on Electricity and Magenetism, 3rd Edition (Clarendon Press, Oxford, 1904)

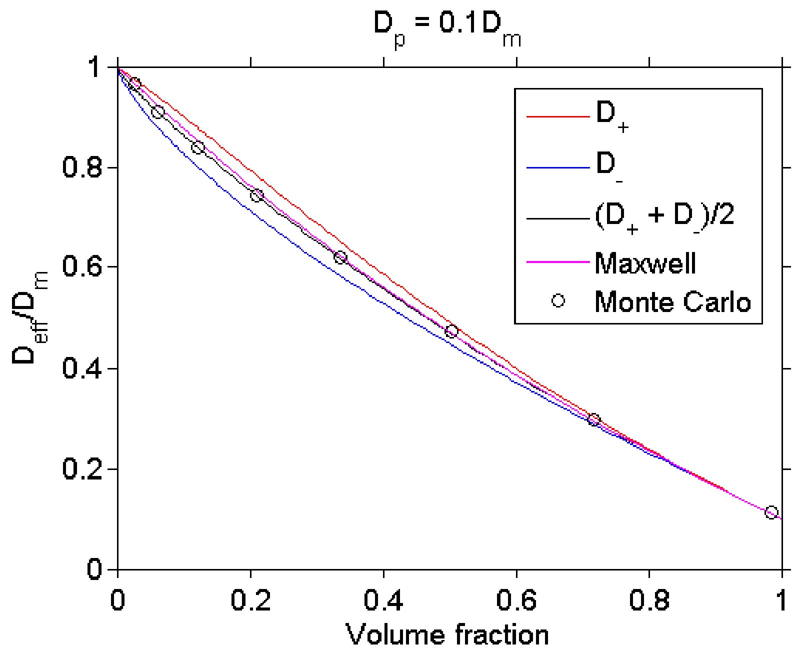
Comparison of different solutions

Cubic particles

Fast diffusion in particles



Slow diffusion in particles



- The gap between the bounds is relatively narrow
- The average between the bounds is an excellent approximation
- Maxwell is astonishingly good

How to include the segregation

Introduce a period potential $u(\mathbf{x})$ on diffusing atoms.

Equilibrium distribution of atoms: $c_{eq}(\mathbf{x}) = c_0 \exp\left(-\frac{u(\mathbf{x})}{kT}\right)$

Effective diffusion equation

$$\frac{\partial\langle c\rangle}{\partial t} = \sum_{ij} D_{ij}^{eff} \frac{\partial^2\langle c\rangle}{\partial x_i \partial x_j}$$

D^{eff} is obtained by replacing $D_{ij}(\mathbf{x})$ by

$$D_{ij}(\mathbf{x}) \frac{c_{eq}(\mathbf{x})}{\langle c_{eq}(\mathbf{x})\rangle}$$

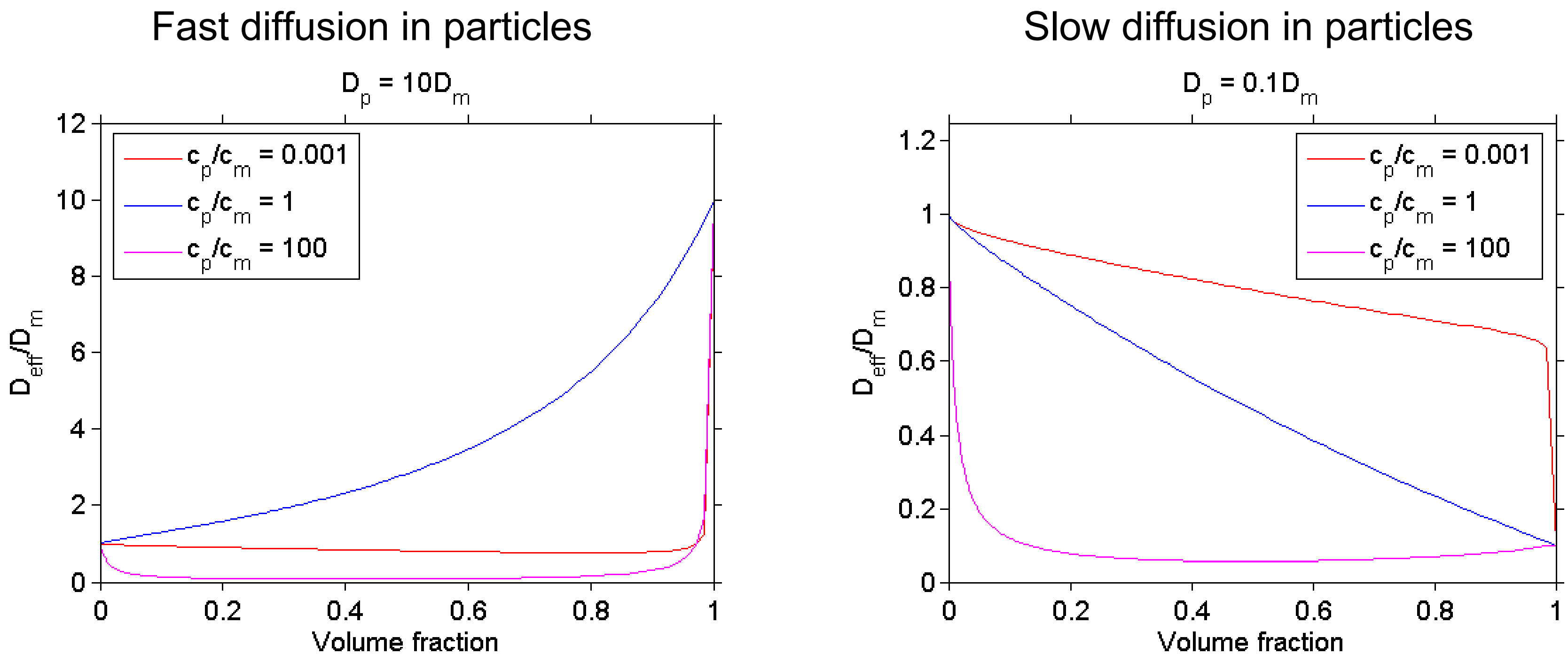
and applying the same procedure as before.

For a two-phase alloy we can reuse all previous solutions with the substitutions

$$D_m \quad \rightarrow \quad D_m \frac{c_m}{v c_p + (1-v) c_m} \qquad D_p \quad \rightarrow \quad D_p \frac{c_p}{v c_p + (1-v) c_m}$$

Effect of segregation on diffusion

Cubic particles



- Segregation in particles → trapping → low D^{eff}
- Segregation in matrix → lack of fast diffusion paths → low D^{eff}
- Segregation in particles → lack of fast diffusion paths + trapping → very low D^{eff}
- Segregation in matrix → axcess to fast diffusion paths → large D^{eff}

Effect of segregation on diffusion

Weakly inhomogeneous systems

$$D^{eff} = \langle D \rangle \left[1 - \frac{\langle (\Delta D)^2 \rangle}{3\langle D \rangle^2} - \frac{\langle (\Delta u)^2 \rangle}{3(kT)^2} + \frac{\langle \Delta D \Delta u \rangle}{3\langle D \rangle kT} \right]$$

$$\Delta D = D - \langle D \rangle$$

$$\Delta u = u - \langle u \rangle$$

Variation of diffusivity

Segregation

Diffusion-segregation correlation

Uncorrelated fluctuations always slow down the effective diffusivity

Further generalizations

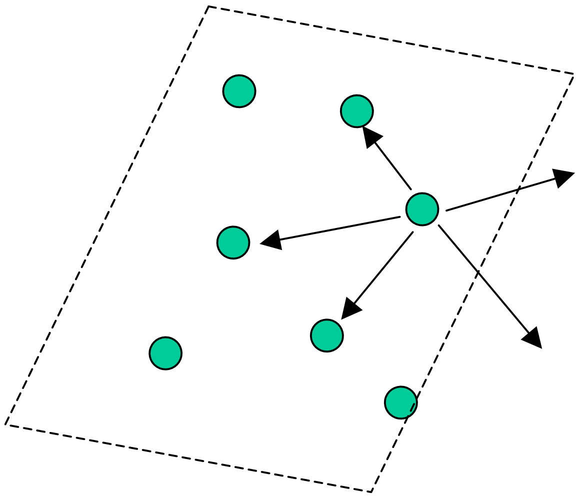
General form of the effective diffusion equation:

$$\frac{\partial\langle c\rangle}{\partial t} = \sum_{ij} D_{ij}^{eff} \frac{\partial^2\langle c\rangle}{\partial x_i \partial x_j} + \sum_{ij} \frac{D_{ij}^{eff}\langle c\rangle}{kT} \frac{\partial\langle U\rangle}{\partial x_i} + \langle f(\mathbf{x},t)\rangle$$

- U – “slow” field: $|\nabla U|\lambda \ll U$
- The “fast” component of field, $u(\mathbf{x})$, is incorporated into D^{eff}
- $f(\mathbf{x},t)$ – sink/source function

$\boxed{\text{This generalization does not affect the calculation of } D^{eff}\text{ !}}$

Discrete model



- N sites per repeat cell
- Site energies $u(\mathbf{x})$
- Jump rates $\Gamma(\mathbf{x},\mathbf{x}')$

How to find D^{eff} ?

Examples of applications:

- Interstitial diffusion in crystals with multiple occupation sites. For example, T and O sites in BCC and HCP crystals
- Grain boundary diffusion
- Diffusion in dislocation cores
- Diffusion in polymers

Exact solution of the model

$$D_{ij}^{eff} = \sum_{\{\mathbf{x},\mathbf{x}'\}} c(\mathbf{x})\Gamma(\mathbf{x},\mathbf{x}')(x'_i - x_i)\left[(x'_j - x_j) + S_j(\mathbf{x}') - S_j(\mathbf{x})\right]$$

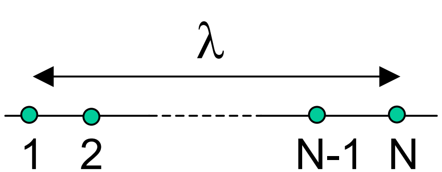
$$c(\mathbf{x}) = \frac{\exp\left(-\frac{u(\mathbf{x})}{kT}\right)}{\sum_{\mathbf{x}'}\exp\left(-\frac{u(\mathbf{x}')}{kT}\right)}$$ - equilibrium occupation probabilities

S(**x**) – displacement vectors (Huntington and Ghate, 1962)

They must be determined by solving the 3Nx3N linear system:

$$\sum_{\mathbf{x}'}\Gamma(\mathbf{x},\mathbf{x}')\left[\mathbf{S}(\mathbf{x}') - \mathbf{S}(\mathbf{x}) + (\mathbf{x} - \mathbf{x}')\right] = 0$$

Example:



$$D^{eff} = \lambda^2\left(\frac{1}{c_1\Gamma_{12}} + \frac{1}{c_2\Gamma_{23}} + \ldots + \frac{1}{c_N\Gamma_{N1}}\right)^{-1}$$

Variational formulation and bounds

The displacement vectors can be found by minimizing the functions

$$\Phi_i = \sum_{\{\mathbf{x},\mathbf{x}'\}} c(\mathbf{x})\Gamma\left(\mathbf{x},\mathbf{x}'\right)\left[\left(x'_i - x_i\right) + S_i(\mathbf{x}') - S_i(\mathbf{x})\right]^2, \quad i = 1,2,3$$

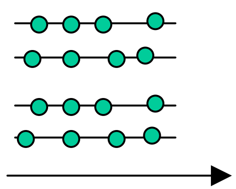
In the principal coordinate system the minimum values of Φ_i coincide with eigenvalues of D_{ij}^{eff} :

$$\left(\Phi_k\right)_{\min} = D_i^{eff}, \quad i = 1,2,3$$

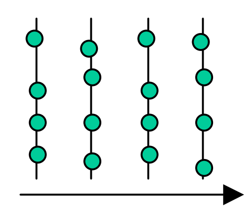
This allows calculations of bounds of D_1^{eff}

$$\boxed{D_1^- \le D_1^{eff} \le D_1^+}$$

Parallel atomic rows



Sequential atomic layers



Summary

- Effective diffusivity in any periodic system, atomic or continuum, can be calculated exactly or approximated by bounds
- The discrete model can be used for numerical solution of the continuum problem
- Segregation, driving forces, sinks and sources can be readily included
- The discrete model does not include the defect-induced (Bardeen-Herring) correlations