

Charged Particle Diffusion and Segregation in Solid and Liquid

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Solute particle transport in solid and liquid is of paramount important for people to understand its roles and tune the corresponding functions. In this work, we find a new mechanism for the transport, specifically, an internal electric field originating from solute atom concentration gradient based on *Yuheng Zhang equation*. This electric field is found to have a dramatic effect on transport of solute particles in solid and liquid. It either facilitates or prohibit solute particle diffusion, and may give birth to a threshold concentration above which segregation happens. Also because of this internal electric field, transport of one type of solute atom can be tuned by another type of particles. At last, segregation for solute particles at solid-liquid interface is investigated and it may arise from *Haiyan Zang potential*, an electric potential at interfaces once phase transformations happen. These findings may help people understand and tune related particle transport in solid and liquid.

Impurity and solute atom diffusion is very important for material performances, for instance, solute atom diffusion in alloys, impurity diffusion inducing breakdown of semiconductor devices, transport of sodium ions in human's cell fluid and so on. On the other hand, segregation in materials, an interesting phenomenon possessing both scientific and technical significance and attracting widespread attention, usually play a dominating role in their mechanical, electrical and kinetic behaviors. Segregation at grain boundaries can bring temper brittleness, creep embrittlement, intergranular corrosion, intergranular stress corrosion and cracking and intergranular brittleness of normally ductile metals, which are general phenomena and not restricted to one type of metal [1, 2]. For example, bismuth in copper, sulphur in nickel and many minor concentration of components in steel such as oxygen, phosphorus, tellurium, antimony and so on [3, 4, 5]. Moreover, segregation of typical dopant in silicon such as arsenic, boron, phosphorous and germanium is reported [6, 7, 8, 9] and seriously affect performance of metal-oxide-semiconductor field-effect transistor (MOSFET) [10].

To understand these problems, Fick's law is usually employed as a starting point [6], and nonlinear diffusion and new driving forces are usually taken into account to describe related diffusion, for example, considering anisotropic diffusion constant [11], concentration dependence of diffusion constant [11, 12], trapping of diffusible atoms [13, 14], effect of solute drag [15] and internal electric field inducing drift in nonmetals [16].

These impurity atoms and solute atoms usually carry net charges and bring strains in the matrix due to the distinct electronegativity and atomic sizes between them and

matrix atoms, resulting in a shift of Fermi surface energy (FSE). Based on *Yuheng Zhang equation* [17, 18], an internal electric field will emerge, inevitably causing an important driving force for transport of related charged particles. However, it is never considered in previous research. In this work, we explore its vital role in the transport processes and employ it to explain solute segregation.

According to Fick's law, the particle diffusion flux is

$$j_1 = -D\nabla n(x, t) \quad (1)$$

where $n(x, t)$ is position x and time t dependence of particle concentration percentage, D is diffusion constant. Based on Einstein diffusion relation, the diffusion constant equal to $D = uk_B T$, where k_B is Boltzmann constant, T is temperature, u stands for particle mobility in matrix. According to conservation of particle number, Fick's second law is

$$\begin{aligned} \frac{\partial n(x, t)}{\partial t} + \nabla \cdot j_1 &= 0 \\ \frac{\partial n(x, t)}{\partial t} &= D\nabla^2 n(x, t) \end{aligned} \quad (2)$$

As pointed out, electrically active impurities may alter electron FSE in rutilelike systems [19]. In analogy, for charged particles in solutions, they may also cause lift of FSE, i.e., electron chemical potential, resulting in an electric field in the solution. According to *Yuheng Zhang equation* [17, 18], the electric field is

$$\vec{E} = \frac{1}{q} \frac{\partial E_F}{\partial n} \nabla n(x, t) \quad (3)$$

where q is electron charge, E_F is particle concentration dependence of FSE. This electric field brings a term for Gibbs energy of system $-\frac{1}{2} \varepsilon_0 \varepsilon (\partial E_F / q \partial n)^2 (\nabla n)^2$, where ε_0 , ε

are vacuum permittivity and relative permittivity, respectively. This energy may be the gradient energy. Also the electric field inevitably induces a particle-drift term based on T. Teorell's theory [20]

$$j_2 = n(x,t)uQ\vec{E} \quad (4)$$

where Q denotes the particle charge. Actually, this is a linear theory. Here the orientation force, induction force and dispersion force are higher-order forces and may be much weaker than net charge force so that they are ignored. Also neglected are heat effects and convection in solution.

The total particle flux is the summation of diffusion term and drift term,

$$j_t = -D \cdot \left[1 - \frac{Q}{q} \frac{n(x,t)}{k_B T} \frac{\partial E_F}{\partial n} \right] \nabla n(x,t) \quad (5)$$

Strictly speaking, the parameter $\partial E_F / \partial n$ is a function of solute concentration $n(x, t)$. However, if the particle concentration is relatively small, it may be regarded as a constant, meaning that the electric field is a mean field and the interaction between charged particles is ignored.

If the amount of particle charge Q is comparable with electron charge q , one percent of these charged particles may induce a drift flux which can be comparable with the diffusion term at room temperature. Let $\alpha = \frac{Q}{q} \frac{1}{k_B T} \frac{\partial E_F}{\partial n}$, there are several different situations for the transport of charged particles. As is shown in Figure 1, if $\alpha n(x,t) < 0$, the orientational transport of charged particles is promoted and a higher solute concentration will result in a larger and faster transport. If $\alpha n(x,t) > 0$ and $\alpha n(x,t) < 1$, the related transport is hindered to some extent. For the two situations, the solute particles

and solvent atoms are always miscible. However, in case that $\alpha n(x,t) > 1$, interestingly, the electric drift term dominates the transport and forms aggregation regions and sparse regions for the solute charged particles, indicating occurrence of solute segregation shown in Figure 1(c). Therefore, there exists a dynamical threshold concentration

$$n_c = k_B T \frac{q}{Q} \left(\frac{\partial E_F}{\partial n} \right)^{-1} \quad (6)$$

above which solute segregation happens and below which uniform distribution is formed for steady state. This may be analogous to the case that solubility of imperfections strongly relies on shift of FSE [19]. It very likes saturation concentration of a solution. Of noted is its temperature dependence, a higher temperature leading to a larger threshold concentration. At low temperatures, the solute segregation occurs more easily, and high temperature can eliminate segregation and make the solute distributed uniformly.

Based on the conservation of solute particle, it can be obtained that

$$\frac{\partial n(x,t)}{\partial t} = D \nabla \cdot [\nabla n(x,t) - \alpha n(x,t) \nabla n(x,t)] \quad (7)$$

which is the governing equation describing transport of charged particles. This theory is easily expanded to describe transport of two types and even more types of charged particles. Here transport of two different types of charges particles is given. The electric field is

$$\vec{E} = \frac{1}{q} \left(\frac{\partial E_F}{\partial n_1} \nabla n_1(x,t) + \frac{\partial E_F}{\partial n_2} \nabla n_2(x,t) \right) \quad (8)$$

Hence, the transport flux of the charged particles are easily obtained

$$j_{t1} = -D_1 \cdot [1 - \alpha_1 n_1(x, t)] \nabla n_1(x, t) + D_1 \frac{Q_1}{Q_2} \alpha_2 n_1(x, t) \nabla n_2(x, t) \quad (9)$$

$$j_{t2} = -D_2 \cdot [1 - \alpha_2 n_2(x, t)] \nabla n_2(x, t) + D_2 \frac{Q_2}{Q_1} \alpha_1 n_2(x, t) \nabla n_1(x, t) \quad (10)$$

where D_1 and D_2 are diffusion constants for the two types of charged particles, the parameters are $\alpha_1 = \frac{Q_1}{q} \frac{1}{k_B T} \frac{\partial E_F}{\partial n_1}$ and $\alpha_2 = \frac{Q_2}{q} \frac{1}{k_B T} \frac{\partial E_F}{\partial n_2}$. For steady state, there exist two cases, one is $1 - \alpha_1 n_1 - \alpha_2 n_2 > 0$ for arbitrary concentrations n_1 and n_2 , meaning that the two types of charged particles can reach uniform distribution at steady state; the other is $1 - \alpha_1 n_1 - \alpha_2 n_2 < 0$ for some group concentrations n_1 and n_2 , indicating that segregation happens for the steady state. These enlighten people that besides temperature, segregation state of a type of charged particles can be tuned and even eliminated by either applying an external electric field or adding another type of charged particles possessing negative parameter α in the matrix.

By means of Fick's second law, the time dependence of particle concentrations are given

$$\frac{\partial n_1(x, t)}{\partial t} = D_1 \nabla \cdot \{ [1 - \alpha_1 n_1(x, t)] \nabla n_1(x, t) \} - D_1 \frac{Q_1}{Q_2} \nabla \cdot [\alpha_2 n_1(x, t) \nabla n_2(x, t)]$$

$$\frac{\partial n_2(x, t)}{\partial t} = D_2 \nabla \cdot \{ [1 - \alpha_2 n_2(x, t)] \nabla n_2(x, t) \} - D_2 \frac{Q_2}{Q_1} \nabla \cdot [\alpha_1 n_2(x, t) \nabla n_1(x, t)]$$

Let us examine a special case, solute segregation during solidification of binary alloys, a phenomena which usually happens in metallurgy. In binary alloys, due to electronegativity difference for the two components, the solute particles would carry either net positive charges or net negative charges. In the other respect, at the solid-liquid (SL) interface, an electrical voltage, i.e., *Haiyang Zang potential*, was predicted

to exist [18, 21]. And it could be written as $qV_Z(x) = \begin{cases} 0, & x \leq x_s; \\ qV_Z(x), & x_s \leq x \leq x_l; \\ qV_Z, & x_l \leq x \end{cases}$ as is

shown in Figure 2, where $x_l - x_s = d$ is width of SL interface which is usually in nanometer scale [22], x_s and x_l are positions of solid and liquid phase boundaries at interface, respectively, V_Z is *Haiyang Zang potential* [21] at the interface. Thus position dependence of FSE could be written as the following,

$$E_F = E_F(n) + qV_Z(x)$$

Here the solute concentration dependence of FSE for the solid and liquid is assumed to be the same as each other.

Due to the narrow width of SL interface, the particle diffusion processes may reach equilibrium state within a quite short time so that the diffusion term equals to the electric field-induced drift term.

$$(1 - \alpha n(x)) \nabla n(x) = \frac{Qn(x)}{k_B T} \nabla V_Z(x) \quad (11)$$

where Q is the net charges carried by solute atoms, and the possible convection and heat effects are not considered. Its mathematical solution is $n(x) = -\text{ProductLog}\left(-\alpha e^{QV_Z(x)/k_B T - c}\right) / \alpha$, where the function is defined as $\text{ProductLog}(we^w) = w$. If $|\alpha n(x)| \ll 1$, the solute concentration at the interface could be simplified to be $n(x) \approx n(x_s) \exp(QV_Z(x)/k_B T)$, $x_s \leq x \leq x_l$. So, the solute segregation strongly depend on sign of its charge and *Haiyang Zang potential* at the SL interface of matrix. If $QV_Z < 0$, the solute concentration in solid would be higher than that in liquid, meaning that solute segregation happens at the SL interface and the segregation coefficient is $k = n(x_s)/n(x_l) \approx \exp(-QV_Z/k_B T) \geq 1$. On the contrary, in

case that $QV_z > 0$ the solute segregation coefficient is $k < 1$, showing that this coefficient is a constant and independent of solute concentration, as is the observed experimental results for boron (B) and gallium (Ga) in silicon [23] when their concentration is very small. If solute particle concentration is very large, nonlinear effects may emerge and should be investigated in the future.

In this work, we only consider the linear effects of an internal electric field which is induced by the solute particles in solid and liquid matrix, and not take into account of nonlinear effects and other sources, for example, electric field caused by dislocations in crystals, electric field arising from strain at interface due to lattice mismatch which usually occurs for thin films and so on. When one tries to understand the related transport phenomena, he/she must examine all the contributions.

Conclusion

In summary, we investigate transport of solute particles in solid and liquid. It is found that space gradient of charges particles would result in an internal electric field according to *Yuheng Zhang equation*, and this electric field can affect the transport processes of charged particles obviously. This field can facilitate particle transport for some solute particles, but for other particles it may impede related diffusion and indicate existence of a threshold concentration above which particle segregation will occur. Further, segregation for solute particles at solid-liquid interface is found to result from *Haiyan Zang potential*, an electric potential at interfaces once phase transformations happen. These results may open a door for people to interpret related phenomena and control them effectively.

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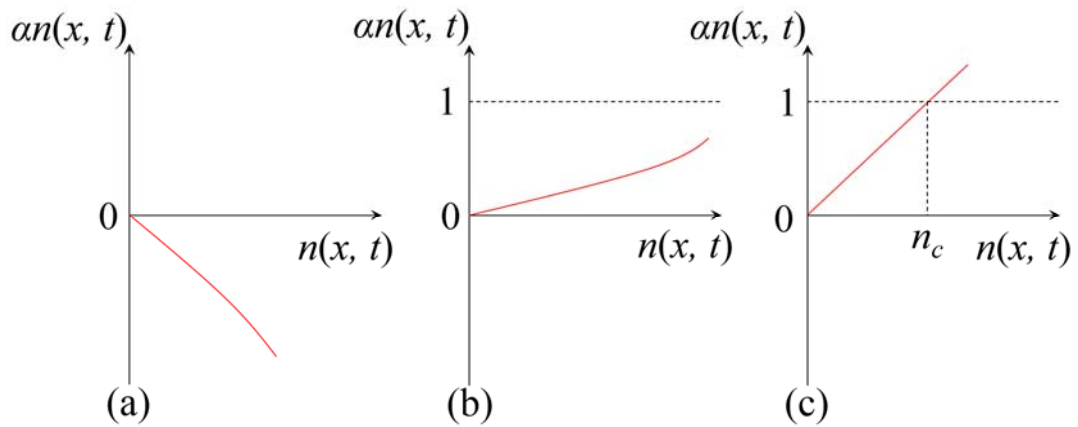


Figure 1. The solute concentration $n(x, t)$ dependence of product $\alpha n(x, t)$. (a) the parameter α is negative, resulting in a negative value of $\alpha n(x, t)$; (b) the parameter α is positive and the $\alpha n(x, t)$ value is always smaller than one regardless of solute concentration; (c) the parameter α is positive and the value $\alpha n(x, t)$ will exceed one at a threshold concentration n_c .

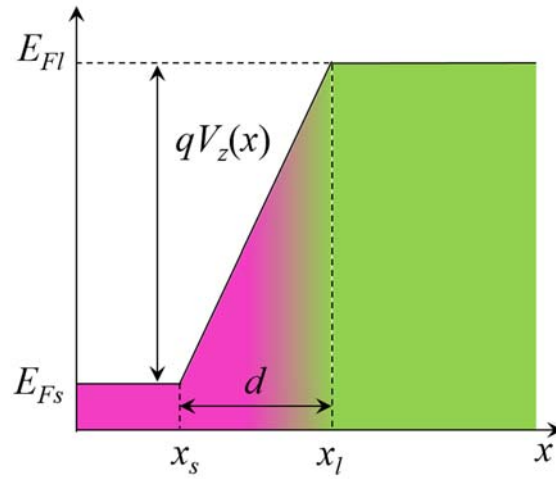


Figure 2. Schematic diagram for Fermi levels E_{Fs} , E_{Fl} of a solid nucleus (magenta) and its surround liquid (green) and the related electrical voltage $qV_z(x) = E_{Fs} - E_{Fl}$ at the interface (q denotes electron charge). The width of transition region (color gradient area) for Fermi levels is denoted by d which may be a constant for a definite material in its whole liquid-solid transition processes.