Discovery of A New Transport Mechanism and Physical Origin of Hume-Rothery Rules

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Transport of solute atoms in a solvent is of paramount importance for people to understand corresponding functions of alloys, doped-semiconductors and so on. In this work, utilizing *Yuheng Zhang equation*, a new transport mechanism was discovered and a simple analytical theory was constructed for the vital and widespread segregation phenomena in various areas. First, the theory successfully point out that solubility of solute atoms in a solvent exhibits temperature, electronegativity difference, atomic size and valence electron concentration dependence, clarifying physical origins of the famous *Hume-Rothery rules* for terminal solid solution in metallurgy. Second, this theory indicates that equilibrium partition coefficient upon solidification may arise from *Haiyan Zang potential* and may be determined by a basic principle that spatial gradient of electrochemical potential for any type of charged particles is always zero at equilibrium state. Third, the theory may uncover physical working principles of both precipitant and extractant. Fourth, the theory reveals that stress-induced segregation of solutes in a solvent may originate from the stress-induced electric potential which may further affect stress corrosion process, as agrees with experimental observations. Overall, these theoretical discoveries may help people gain more deep understanding of related segregation phenomena and find important applications in various areas.

keywords: transport; segregation; Hume-Rothery rules; equilibrium partition coefficient;

1. Introduction

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 such as arsenic, boron, phosphorous and germanium in semiconductors 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]. 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]. However, the theoretical efforts ever made were usually either very speculative or

rather empirical, and may not be able to give satisfactory explanations for the related complex segregation phenomena.

In this work, for the popular but puzzling segregation phenomena, we aimed to utilize *Yuheng Zhang equation* [17, 18] to explore the induced new transport mechanism of solute atoms in a solvent, and thereby attempted to build an analytical theory to clarify the relevant series of segregation phenomena, *e.g.*, physical origins of Hume-Rothery rules, equilibrium partition coefficient on solidification, stress-induced segregation and so on.

2. Results and Discussions

2.1 A New Transport Mechanism

According to Fick's law, the diffusion flux of solute atoms is

$$j_1 = -D\nabla n(\vec{r}, t) \tag{1}$$

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

$$
\frac{\partial n(\vec{r}, t)}{\partial t} + \nabla \cdot j_1 = 0
$$
$$
\frac{\partial n(\vec{r}, t)}{\partial t} = D\nabla^2 n(\vec{r}, t)
\tag{2}
$$

As pointed out, electrically active impurities may alter electron FSE in rutile-like systems [19]. In analogy, considering the distinctions in electronegativity, atomic sizes and valence state between solute atoms and solvent atoms, dissolution of solute atoms

in a solvent may usually cause lift of FSE, *i.e.*, electron chemical potential, resulting in an internal electric field in the solution. In terms of *Yuheng Zhang equation* [17, 18], the electric field is

$$\vec{E} = \frac{1}{q}\frac{dE_F}{dn}\nabla n(\vec{r},t) \tag{3}$$

where q is electron charge, E_F is solute atom concentration dependence of FSE. This electric field brings a term for Gibbs energy of system $-\varepsilon_0\varepsilon\left(dE_F/qdn\right)^2\left(\nabla n\right)^2/2$, where ε_0, ε are vacuum permittivity and relative permittivity, respectively. This energy may be the gradient energy in many cases. Also the electric field inevitably give rise to a new drift term based on T. Teorell's theory [20]

$$j_2 = n(\vec{r},t)u\frac{Q}{q}\frac{dE_F}{dn}\nabla n(\vec{r},t) \tag{4}$$

where Q denotes the charges carried by a solute atom because of the electronegativity differences between a solute atom and around solvent atoms.   This new drift term is the new transport mechanism mainly discussed in this work. Actually, this is a linear theory. Here the orientation force, induction force and dispersion force are ignored because they are higher-order forces and may be much weaker than net charge force. Also neglected are heat effects and convection in solution.

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

$$j_t = -D\cdot\left[1-\alpha n(\vec{r},t)\right]\nabla n(\vec{r},t) \tag{5}$$

where the parameter is $\alpha = Q(dE_F/dn)/qk_BT$. Generally speaking, FSE is a complex function of solute atom concentration $n(r, t)$ and it may be written as a polynomial series $E_F(n, T)= E_{F0}(T)+a_1(T)n+a_2(T)n^2+\cdots$. Thus, parameter dE_F/dn may be a function of

solute atom concentration $n(r, t)$. However, if the solute atom concentration is relatively small, it may be regarded as a constant, *i.e.*, only the linear term is considered, meaning that the electric field is a mean field and the interaction between solute atoms is ignored.

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

$$\frac{\partial n(\vec{r},t)}{\partial t} = D\nabla \cdot \left[\nabla n(\vec{r},t) - \alpha n(\vec{r},t)\nabla n(\vec{r},t)\right] \tag{6}$$

which is the governing equation describing transport of solute atoms in a solvent. It should be pointed out that the diffusion constant D of solute atoms may varies with their concentration because the related diffusive activation energy could be changed by the concentration. Sometimes it may be a minor effect and might be ignored. In this work, the concerned is main effects arising from internal electric field-induced new drift term given by Equation (4).

2.2 Physical Origin of Famous Hume-Rothery rules

As shown in Equation (5), if the charge amount Q carried by a solute atom is comparable with electron charge q, one percent of these charged solute atoms may induce a notable drift flux which can be comparable with the diffusion term at room temperature. The drift flux may result in several different situations for the transport of solute atoms. As is indicated by Equation (5), if the parameters satisfy $\alpha n(r,t) < 0$, the effective diffusion constant $D(1-\alpha n)$ may be enhanced apparently, causing a promoted directional transport of charged solute atoms. At equilibrium state, the solute atoms and solvent atoms are always mutually solvable at any temperature, achieving a complete homogeneous distribution in the solvent, as shown in Figure 1(a). If the parameter fulfills $0 < \alpha n(r,t) < 1$, the effective diffusion constant $D(1-\alpha n)$ may be reduced

remarkably and the related transport is hindered to some extent. When the equilibrium

state is reached, the solute atoms can also reach a homogeneous distribution in the

solvent, shown by α, β phases (light blue regions) in Figure 1(b). However, as

temperature decreases so that $\alpha n(r,t)>1$, interestingly, the sign of effective diffusion

constant $D(1-\alpha n)$ may be reversed, meaning that the drift flux determined by electric

field dominates the transport process and the solute atoms will transport from low-

concentration regions to high-concentration regions. Thereby aggregation regions and

sparse regions may be formed for the solute atoms, showing occurrence of solute

segregation, as is shown by the phase $\alpha+\beta$ (colored light orange) in Figure 1(b). It may

be an active segregation which is determined by the intrinsic physical and chemical

characteristics of solute atoms and solvent atoms rather than external factors such as

loading stress. Another type is passive segregation which may be yielded by outer

stimulus, $e.g.$, stress-induced segregation, and it will be discussed later.

A special case is $\alpha n(r,t)=1$, which may result in the important concept of solubility ,

$$n_c = k_B T \frac{q}{Q} \left(\frac{dE_F}{dn} \right)^{-1} \tag{7}$$

below which a uniform distribution of solute atoms in solvent is formed and above

which solute atom segregation happens at equilibrium state. Shown by this equation,

the solubility varies with temperature, which may give the solubility line shown by red

lines in Figure 1(b). For the solubility in a solvent, structure may be a very important

factor and it can influence FSE so heavily that solubility distinction may be quite

conspicuous in different phases of the solvent. Furthermore, considering both the local

volume strain and valence electron concentration alterations caused by solute atoms in

the solvent, FSE may be expressed as $E_F = E_F\left(\xi_V\left(n\right), n_e\left(n\right)\right)$. So Equation (7) may be rewritten as

$$n_c = k_B T \frac{q}{Q}\left(\frac{\partial E_F}{\partial \xi_V}\frac{\partial \xi_V}{\partial n} + \frac{\partial E_F}{\partial n_e}\frac{\partial n_e}{\partial n}\right)^{-1} \qquad (8)$$

where ξ_V is the local volume strain stemming from atomic size differences between a solute atom and a solvent atom, n_e denotes valence electron concentration. The sensitive FSE dependence of solubility shown by this equation may be in agreement with the report that solubility of imperfections strongly relies on shift of FSE [19].

Here physical origins of the famous *Hume-Rothery rules* in the area of metallurgy will be addressed on basis of Equation (8). Shown by this equation, a higher temperature usually leads to a larger solubility. A high temperature can eliminate segregation and make the solute distribute uniformly, but at low temperatures, the solute segregation occurs more easily. Surprisingly, the solubility line for terminal solid solution is found to always pass the original point in temperature-component eutectic phase diagrams in metallurgy, as is shown in Figure 1 (b). This conclusion may be very useful for checking and painting binary phase diagrams. Equation (8) also indicates that for any type of solute atoms, regardless of their physical and chemical properties, there always exists a portion of these solute atoms which can dissolve in the solvent. This conclusion completely agrees with that obtained using the method of Gibbs energy [43].

Equation (8) shows that a smaller amount of charges Q carried by a solute atom usually results in a larger solubility n_c, but a larger amount of charges Q brought by the solute atom leads to a smaller solubility n_c. As is known, the amount of charges may arise from the electronegativity difference between a solute atom and its surrounding

solvent atoms. A larger/smaller electronegativity difference may often cause a larger/smaller amount of charges taken by a solute atom, thereby creating a smaller/larger solubility, which is just an important *Hume-Rothery* rule [28].

Further, on basis of Equation (8), the solubility may be determined by mechanic-electric coupling $\partial E_F / \partial \xi_V$ of solvent and the local volume strain due to solute atoms, *i.e.*, the first term in the parenthesis. If mechanic-electric coupling $\partial E_F / \partial \xi_V$ of a solvent is relatively smaller, a larger atomic size difference between a solute atom and a solvent atom may be allowed, and it may be easy for various types of solute atoms to dissolve in it. On the contrary, if mechanic-electric coupling of a solvent is very large, it may be difficult for solute atoms to dissolve. Meanwhile, solubility of solute atoms strongly relies on the local volume strains ξ_V which is caused by the atom-size differences between a solute atom and a solvent atom. Generally speaking, a larger distinction in atom sizes usually leads to a smaller solubility. Reversely, a smaller atom-size difference may be anticipated to give rise to a larger solubility, as is another important *Hume-Rothery rule* [28].

Moreover, as pointed out by Equation (8), solubility of solute atoms in solvent may also be sensitively dependent on valence electron concentration (VEC) n_e. Analogous to *n*-type doping and *p*-type doping that can yield FSE lift for semiconductors in terms of VEC variations, dissolution of solute atoms in a solvent may also give birth to FSE lift by altering VEC. In general, FSE for most of metals varies dramatically with VEC, *i.e.*, a big amplitude of $\partial E_F / \partial n_e$, so that the solute atoms that alter the VEC noticeably may lead to a low solubility, but the solute atoms that change VEC of solvent subtly are

permitted to reach a high solubility, which is another vital Hume-Rothery rule [28]. It points out that in order to achieve a maximum solubility the solute atoms should typically have the same valence as solvent atoms.

In a word, the above analysis may convince people that Equation (8) uncovers the physical origin of famous *Hume-Rothery rules* in metallurgy, despite that a further quantitative comparison between Equation (8) and experimental results is still needed in the future.

2.3 Phase Transition-Induced Segregation

On basis of the new transport mechanism, let us switch to another case of active segregation, *e.g.*, solute atom segregation during solidification of matrix, a phenomena which usually happens in metallurgy. In binary alloy, due to electronegativity difference between solute atoms and solvent atoms, the solute atoms would carry either net positive charges or net negative charges. In the other respect, an electrical potential at the solid-liquid (SL) interface, *i.e.*, *Haiyang Zang potential*, was found to exist [18, 21, 22, 23, 24]. This potential may be written as

$$qV_Z(x) = \begin{cases} 0, \ x \le x_s; \\ qV_Z(x), \ x_s \le x \le x_l \\ qV_Z, \ x_l \le x \end{cases}$$

as is shown in Figure 2, where $x_l - x_s = d$ is width of SL interface which is usually in nanometer scale [25], x_s and x_l are positions of solid and liquid phase boundaries at SL interface, respectively, V_Z is *Haiyang Zang potential* at the interface. Thus position dependence of FSE could be written as the following,

$$E_F = E_F\left(n(x)\right) + qV_Z(x)$$

where $n(x)$ is position dependence of solute atom concentration. To a first approximation, here the solute concentration dependence of FSE for the solid and liquid phases of alloy is assumed to be the same as each other.

Due to the narrow width of SL interface, the transport processes of solute atoms at the SL interface may accomplish equilibrium state within a short time so that the diffusion term equals to the electric field-induced drift term.

$$(1-\alpha n(x))\nabla n(x) = \frac{Qn(x)}{k_B T}\nabla V_Z(x) \qquad (9)$$

where Q is the net charges carried by a solute atom because of the electronegativity difference between a solute atom and its surrounding solvent atoms. For simplicity, the possible convection and heat effects are not considered here. The analytical mathematical solution is

$$n(x) = -\frac{1}{\alpha}Pr\,oductLog\left[-\alpha n(x_s)exp\left(\frac{QV_Z(x)}{k_B T}-\alpha n(x_s)\right)\right] \qquad (10)$$

where the mathematical function is defined as $ProductLog(we^w)=w$, $n(x_s)$ is solute atom concentration at the solid phase boundary. In case of a dilute solution fulfilling $|\alpha n(x)|\ll 1$, the solute atom concentration at the interface could be simplified to be

$$n(x) \approx n(x_s)exp\left(\frac{QV_Z(x)}{k_B T}\right) \qquad (11)$$

This equation shows that the equilibrium partition coefficient $k_0 = n(x_s)/n(x_l) \approx exp(-QV_Z/k_B T)$ of solute atoms strongly depend on both its charge Q and *Haiyang Zang potential* at the SL interface. So, several conclusions may be obtained. First, in case that $QV_Z<0$, solute segregation happens at the SL interface and the equilibrium partition coefficient is $k_0>1$, meaning that the solute concentration

in solid phase would be higher than that in liquid phase. On the contrary, in case that $QV_Z > 0$ the equilibrium partition coefficient is $k_0 < 1$, demonstrating a higher solute concentration in liquid phase. Second, for a definite dilute solution fulfilling $|\alpha n(x_s)/k_0|$ $\ll 1$, the equilibrium partition coefficient is almost a constant and independent of solute concentration, as is the observed experimental results for boron (B) and gallium (Ga) in silicon when their concentration is very small [26]. Third, equilibrium partition coefficient is very sensitive to the net charge quantity Q which may originate from electronegativity difference between a solute atom and its surrounding solvent atoms. Therefore, a larger electronegativity difference usually generates a larger charge quantity Q, which is expected to cause more obvious segregation at the SL interface. Inversely, a smaller electronegativity difference may induce a smaller charge quantity Q, enabling a more uniform distribution at the SL interface, *i.e.*, the equilibrium partition coefficient close to one $k_0 \sim 1$. It may be verified by experimental investigations on correlation between electronegativity and partition coefficients of various solute atoms in semiconductors germanium and silicon [27]. Fourth, a larger *Haiyang Zang potential* may result in a much more serious segregation, and vice versa.

In some references, equilibrium partition coefficient k_0 of solute atoms at the SL interface was also given [28, 29] by

$$k_0 \propto exp\left(\frac{\mu_i^l - \mu_i^s}{k_B T} \right) \tag{12}$$

where $\mu_i{}^l$ and $\mu_i{}^s$ is equilibrium chemical potential for an individual solute atom in liquid and solid phases of the solvent, respectively. At first glance, this expression is different from Equation (11). Actually, they are the same as each other, where the

reasons will be provided in the following discussions.

For any type of charged particles in a system, there may exist a prevalent and fundamental principle that spatial gradient of electrochemical potential for these charged particles at equilibrium state is rigorously zero,

$$\nabla\left[\mu(\vec{r})+QV(\vec{r})\right]=0 \tag{13}$$

where $\mu(r)$, $V(r)$ is position dependence of chemical potential and electric potential of charged particles, respectively, Q is the net charges carried by an individual charged particle. This principle may be a natural result of the fact that the net flow of charged particles at equilibrium state is zero. Taking the simple approximation that the net charges Q is constant and does not vary with position, one may find

$$\nabla\mu(\vec{r})=Q\vec{E}(\vec{r}) \tag{14}$$

where the vector $\vec{E}(\vec{r})$ is position dependence of electric field. One may find that this equation is quite analogous to *Yuheng Zhang equation*. In reality, they are different from each other due to the following reasons. First, the time scale for electrons attaining equilibrium state is much shorter due to the much smaller electron mass than that of other charged particles. In many dynamical transport processes, *e.g.*, solute atom transport in a solvent, electron equilibrium state could be reached in so short time that it may accompany every micro-transport step of these charged particles. Hence, *Yuheng Zhang equation* may be employed to describe dynamical transport processes of charged particles, as was done in subsection 2.1. However, Equations (13) and (14) may not hold in these dynamical transport processes. Only when charged particles reach the equilibrium state, can Equations (13) and (14) be valid. Second, strictly speaking, the

net charges carried by a charged particle sometimes may vary to some extent with variations of the experienced chemical and physical environment, making a narrower application scope for Equation (14) than *Yuheng Zhang equation.*

Using *Yuheng Zhang equation* [17, 18], it may be obtained

$$\nabla\mu\left(\vec{r}\right)=\frac{Q}{q}\nabla E_{F}\left(\vec{r}\right) \tag{15}$$

Therefore, for charged particles at equilibrium state, the relation may be established,

$$\mu\left(\vec{r}_{2}\right)-\mu\left(\vec{r}_{1}\right)=\frac{Q}{q}\left[E_{F}\left(\vec{r}_{2}\right)-E_{F}\left(\vec{r}_{1}\right)\right] \tag{16}$$

On basis of this relation and *Haiyang Zang potential*, the correlation $\mu_i{}^{l}-\mu_i{}^{s}=QV_Z$ holds for solute atoms at SL interface of a dilute solution. As a result, for equilibrium partition coefficient k_0 of solute atoms at the SL interface, Equation (11) obtained in this work may be the same as Equation (12) given in references [38, 39].

In view of the analysis, a conclusion may be made that the equilibrium partition coefficient k_0 of solute atoms in a dilute solution may originate from electronegativity difference and *Haiyang Zang potential* at SL interface. Under actual industrial and experimental conditions, the solidification rate may be fast so that the solute atoms do not achieve equilibrium state. The corresponding actual partition coefficient may be much more close to 1. In some extreme situations, the solidification rate is so rapid that the electrons may not approach their equilibrium state across SL interface. There may be a net electrical current flowing through the SL interface. And the magnitude of actual electric potential at the SL interface may be smaller than that of *Haiyang Zang potential*, yielding the actual partition coefficient close to 1 as well. In addition, if electrical

conductivity of the SL interface is so small that electric equilibrium state may be far from reached, the actual partition coefficient may also be close to 1.

2.4 Working Principles for Precipitation and Extraction

In this subsection, the concerned is the precipitation and extraction that are another important example of active segregation.

Also using this new transport mechanism, the previous one-component transport theory may be easily expanded to describe transport of two and even more types of solute atoms that do not fabricate chemical species among them. Like previous theoretical treatment, inhomogeneous distribution of solute atoms may induce an electric field. According to *Yuheng Zhang equation* [17, 18], the electric field is

$$\vec{E} = \frac{1}{q}\left(\frac{dE_F}{dn_1}\nabla n_1\left(\vec{r},t\right) + \frac{dE_F}{dn_2}\nabla n_2\left(\vec{r},t\right) \right) \tag{17}$$

Hence, the total transport flux of the two types of solute atoms may be easily obtained

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

$$j_{t2} = -D_2 \cdot \left[1 - \alpha_2 n_2\left(\vec{r},t\right)\right]\nabla n_2\left(\vec{r},t\right) + D_2\frac{Q_2}{Q_1}\alpha_1 n_2\left(\vec{r},t\right)\nabla n_1\left(\vec{r},t\right) \tag{18}$$

where D_1 and D_2 are diffusion constants for the two types of solute atoms in the solvent, respectively, the parameters are $\alpha_1 = (dE_F/dn_1)Q_1/qk_BT$ and $\alpha_2 = (dE_F/dn_2)Q_2/qk_BT$, Q_1 denotes the charges carried by a solute atom, Q_2 is charges carries by a solute atom of another type. As is shown by the two equations, transport process for one type of solute atoms may be influenced obviously by another type of solute atoms. Upon achieving equilibrium state, there may exist two cases. One case is that the parameters fulfill the requirement $1 - \alpha_1 n_1 - \alpha_2 n_2 > 0$ for arbitrary concentrations n_1 and n_2, meaning that the two

types of charged atoms are homogeneously distributed in the solvent at equilibrium state. The other case is that this correlation may satisfy $1-\alpha_1 n_1-\alpha_2 n_2<0$ for some group concentrations n_1 and n_2, indicating that segregation happens for both the two types of solute atoms in the solvent.

The condition $1-\alpha_1 n_1-\alpha_2 n_2=0$ would give the solubility for the two types of solute atoms in the solvent, and it may enlighten people that besides temperature, solubility of solute atoms could be tuned by dissolution of another type of solute atoms. Usually, two situations may come for the parameter group α_1, α_2. One situation is that parameters are $\alpha_1>0$ and $\alpha_2<0$, for which the corresponding solubility is

$$n_{1c}{}' = n_{1c}\left(1-\alpha_2 n_2\right) \tag{19}$$

where n_{1c} represents the solubility of the solute atoms in a solvent at the absence of other type of solute atoms, n_{1c}' is the solubility at the presence of another type of solute atoms. As shown by this equation, the solubility line for one type of solute atoms relies on the concentration of another type of solute atoms, and the dissolution of solute atoms with negative parameter $\alpha_2<0$ may increase the solubility of other solute atoms.

Of emphasized is the other situation that the two parameters α_1, α_2 are both positive, resulting in two solubility lines for the two types of solute atoms at equilibrium state,

$$\begin{aligned} n_{1c}{}' &= n_{1c}\left(1-n_2/n_{2c}\right) \\ n_{2c}{}' &= n_{2c}\left(1-n_1/n_{1c}\right) \end{aligned} \tag{20}$$

where n_{2c} is the solubility at the absence of other types of solute atoms, n_{2c}' is the corrected solubility at the presence of another type of solute atoms. These solubility equations indicate that concurrent dissolution of different types of solute atoms in the

same solvent would mutually reduce respective solubility. Meanwhile, as suggested by Equations (18), the solute whose solubility is very tiny and do not form chemical species in the solvent may be used as either a precipitator producing precipitation or an extractant extracting other solutes. If the sign of charges Q_1 carried by a solute atom is opposite to that for a solute atom of another type in the same solvent, *i.e.*, $Q_1/Q_2<0$, the two types of solute may be able to draw away each other and either one can act as a precipitant, as shown in Figure 3(a)(b)(c). On the other hand, if the respective charges carried by the type of solute atoms and another type of solute atoms possess the same sign in the identical solvent, the two types of solute may appeal to each other and either one can be utilized as a potential extractant, as shown in Figure 3(d)(e)(f). Thus, from perspective of physics, one may conclude that *Yuheng Zhang equation*-induced dynamical transport Equations (18) may be the underlying working principles for the widely applied precipitants and extractants.

Moreover, by means of Equations (18) and Fick's second law, the time dependent distributions of the two types of solute atoms are given

$$\frac{\partial n_1(\vec{r},t)}{\partial t} = D_1 \nabla \cdot \left\{ \left[1 - \alpha_1 n_1(\vec{r},t) \right] \nabla n_1(\vec{r},t) \right\} - D_1 \frac{Q_1}{Q_2} \nabla \cdot \left[\alpha_2 n_1(\vec{r},t) \nabla n_2(\vec{r},t) \right]$$
$$\frac{\partial n_2(\vec{r},t)}{\partial t} = D_2 \nabla \cdot \left\{ \left[1 - \alpha_2 n_2(\vec{r},t) \right] \nabla n_2(\vec{r},t) \right\} - D_2 \frac{Q_2}{Q_1} \nabla \cdot \left[\alpha_1 n_2(\vec{r},t) \nabla n_1(\vec{r},t) \right]$$

$$(21)$$

To be noticed, in the analysis, the charge amount Q_1, Q_2 carried by different types of solute atoms in the solvent is assumed to be invariant with position and time. It may be a reasonable approximation in most cases. However, if the physical and chemical environment for the solute atoms changes very considerably, the charge amount may suffer some alterations and bring complexity, which needs further investigation in the

future.

2.5 Stress-Induced Segregation

In this subsection, stress-induced segregation, *i.e.*, an important example of passive segregation which is usually attributed to applied stimulus such as stresses here, will be touched on. It may be a very general and important phenomena usually encountered in various application areas, such as grain boundary stress-induced segregation of components in alloys [3, 4, 5], interface stress-induced dopant segregation in semiconductor films [6, 7, 8, 9, 10], interfacial strain driving segregation of doped cations in epitaxial multiferroic films [30] and so on. For these phenomena, the stresses usually give birth to inhomogeneous strains which enable FSE to lift for the matrix. As a response, an electric field will emerge according to *Yuheng Zhang equation*.

$$\vec{E} = \frac{1}{q} \frac{dE_F}{d\varepsilon_{ij}} \nabla \varepsilon_{ij} \tag{22}$$

where ε_{ij} is the strain component, $dE_F/d\varepsilon_{ij}$ could be regarded as the mechanic-electric coupling strength of matrix. The subscript indices obey Einstein summation rules. Like the previous treatment, the electric field would induce a drift flux for the dopant. Based on T. Teorell's theory [20] and Einstein diffusion relation, it is $j_2 = n(\vec{r},t) DQ(dE_F/d\varepsilon_{ij}) \nabla \varepsilon_{ij}/k_B Tq$, where Q is the net charge that an individual dopant carry in the matrix because of electronegativity difference between dopant atoms and matrix atoms. So the total transport flux for the dopant is

$$j_t = -D\nabla n(\vec{r},t) + n(\vec{r},t) \frac{D}{k_B T} \frac{Q}{q} \frac{dE_F}{d\varepsilon_{ij}} \nabla \varepsilon_{ij} \tag{23}$$

Upon reaching equilibrium state, the transport flux may become zero, resulting in the

spatial distribution of dopant

$$n\left(\vec{r}\right) = n\left(r_0\right)e^{Q\Delta E_F / qk_B T} \tag{24}$$

where $\Delta E_F = E_F(r) - E_F(r_0)$ is FSE difference. This distribution function indicates that the externally applied stimulus such as non-uniform stresses can indeed cause a passive segregation which differs from the active segregation aforementioned. Interestingly, this equation is quite similar with the well-known Boltzmann distribution function, and the value $n(r)exp(-QE_F(r)/qk_BT)$ may be a constant for dopants in a matrix, confirming that the electrochemical potential of charged atoms in a system is a constant at equilibrium state.

Indicated by Equation (24), for a matrix with a definite mechanic-electric coupling strength, a stronger stress may be easy to bring a larger FSE difference ΔE_F, thereby producing a more obvious segregation. By the contrast, such related passive segregation would weaken and even vanish by eliminating the external stimulus such as the non-uniform stresses. For a matrix with weak mechanic-electric coupling, the corresponding dopant segregation caused by stresses in the matrix may not be serious. Furthermore, shown by Equation (24), the segregation strongly depend on charge quantity Q that rises from the electronegativity distinction between an individual dopant and matrix. So, a larger electronegativity difference usually induce a more evident segregation, but a negligible electronegativity difference may respond to a more uniform distribution of dopant. Also of noted in Equation (24) is the visible temperature dependence. A high temperature will inevitably reduce the segregation whereas a low temperature makes the dopant segregation enhanced. Therefore, high temperature annealing may be an

efficient method for mitigating segregation, which has been widely applied in various realms, *e.g.*, high-temperature homogenization of alloys [31, 32, 33] and doped-semiconductors [8, 34].

To examine whether Equation (24) grasps the physics or not, comparison between this equation and experimental results should be performed. The key point is good estimations for charge quantity Q and mechanic-electric coupling strength $dE_F/d\varepsilon_{ij}$. The charge amount carried by a doped atom might be given by chemical valence difference between the doped atom and substituted atom. And a rational estimation for the mechanic-electric coupling strength could resort to *Yuheng Zhang equation* [17, 18] and flexoelectric field obtained by experiments. Take the Ca-doped important multiferroic BiFeO3 film as an example, the valence difference between Ca^{2+} ion and Bi^{3+} ion may be 1. Meanwhile, according to experimental results on flexoelectric field $\sim 10^6$ *V/m* and related strain gradient $\sim 10^5$ */m* [35], the mechanic-electric coupling strength may be approximated $dE_F/d\varepsilon_{ii} \sim 10$ *eV*. Therefore, for the doped $Bi_{0.98}Ca_{0.02}Fe_{0.95}Mn_{0.05}O_3$ epitaxial film with strain difference 3% at 700 ℃ [30], the segregation coefficient may be estimated by utilizing Equation (24) and it is *exp*(0.3/0.084)≈36, a value in satisfactory agreement with experimental segregation coefficient 60%/2%=30 [30]. For another case of carbon atoms in α-iron, an individual carbon atom may be expected to carry negative charges because of its much larger electronegativity than iron. Consequently, according to Equation (24), carbon atoms like to segregate at grain boundaries under tensile stresses due to the FSE uplift caused by the stress, which is in agreement with experimental observations [36] and may play a key role in stress

corrosion process of steel.

Of emphasized is that the FSE lift is dominated only by stresses in the above analysis. Albeit subordinate, sometimes a finite dopant concentration may still affect the FSE, thereby creating a corresponding drift term as pointed out by Equation (4). So, the total transport flux of dopant may be described by

$$j_t = -D\left[1 - \alpha n(\vec{r},t)\right]\nabla n(\vec{r},t) + n(\vec{r},t)\frac{D}{k_B T}\frac{Q}{q}\frac{dE_F}{d\varepsilon_{ij}}\nabla\varepsilon_{ij} \qquad (25)$$

Upon approaching equilibrium state, the transport flux becomes zero. The related analytical solution may be obtained easily

$$n(\vec{r}) = -\frac{1}{\alpha}ProductLog\left[-\alpha n(\vec{r}_0)exp\left(\frac{Q\Delta E_F}{qk_B T} - \alpha n(\vec{r}_0)\right)\right] \qquad (26)$$

where $\Delta E_F = E_F(r) - E_F(r_0)$ is FSE difference stemming from strains. If magnitude of the product is very small $|\alpha n(r)| \ll 1$, the solution could be simplified to be Equation (24).

2.6 Stress Corrosion

Stress corrosion is a widespread phenomenon in multi-realms such as pipelines [37, 38], body implants [39], compressor impeller [40], aerospace vehicles [38], nuclear power systems [38], boilers and cooling water systems [38] and so on. It usually gives rise to stress corrosion cracking which has been regarded as a pivotal failure mode in corrosive environments, causing a great many environmental disasters and a huge amount of economical loss over the world. It is widely accepted that stress corrosion is an electrochemical process and it often takes place under conditions of tensile stresses (residual or applied) and a specific chemical species unique to the type of alloy. Owing to great importance of stress corrosion, much research was devoted to the related

mechanisms, as was reviewed [40].

Here what are mainly concerned is the vital roles of tensile stress. For tensile stress exerting on an actual alloy, it may have several effects based on previous discussions. One is that the induced tensile strain may result in upturn of FSE, making tensile regions of this alloy more chemically reactive as dissolution anode. This effect may only be valid for the class of metals with positive mechanic-electric coupling $\partial E_F / \partial \xi_V \geq 0$. In general, the majority of metals like iron may belong to this class. This point was proved by experimental results that upon application of tensile stress, an immediate anodic change in potential occurs for iron-based alloy, making the tensile regions become anodic to other non-strained regions [36]. Another effect is that the tensile strain may lead to segregation of solute atoms, which may increase FSE further and make related tensile regions more susceptible to stress corrosion. By analyzing Equations (7), (24) and (26), the distinct cases and relevant conclusions are listed in Table 1.

As is shown in Table 1, if a tensile stress increases FSE of a matrix metal, the negatively charged solute atoms may migrate to the tensile regions and consequently form a segregation. The segregation of solute atoms usually affects FSE reversely, wherein two cases exist. One case is that the solute atom agglomeration makes FSE increase further. To be opposite, the other case is that the solute atom agglomeration makes FSE decrease, which is of paramount importance for resisting stress corrosion on the tensile regions as an anode. On the other hand, for the same matrix metal, the positively charged solute atoms are prone to drift away from the tensile regions, also resulting in a segregation. Thus, there are also two situations for the segregation effect

on FSE. One situation is that the decrease of solute atom concentration generates an

ascent of FSE. The other situation is that the concentration decrease yields a descent of

FSE, which may aid the tensile regions in resisting the stress corrosion.

Table 1 Relations among different parameters of solute atoms in a matrix metal

whose Fermi surface energy (FSE) increases due to tensile stress (residual or applied).

Dopant charge Q	Segregation coefficient $k=n(r)/n(r_0)$	Parameter $\alpha=$ $(dE_F/dn)Q/qk_BT$	Parameter dE_F/dn	FSE
Positive	$k<1$	$\alpha<0$	Positive	Down
Positive	$k<1$	$\alpha>0$	Negative	Up
Negative	$k>1$	$\alpha<0$	Negative	Down
Negative	$k>1$	$\alpha>0$	Positive	Up

However, it could be found in Table 1 that segregation of solute atoms possessing a

positive value of parameter α may increase FSE of tensile regions, thereby promoting

susceptibility of these regions. And a larger positive value α sometimes brings much

more serious stress corrosion on tensile regions. Simultaneously, Equation (7) shows

that a large positive value α corresponds to a low solubility. So, segregation of solute

atoms that have a very low solubility is anticipated to dramatically increase

susceptibility to stress corrosion. For instance, the carbon atoms was experimentally

found to have a very low solubility in α-iron [41], and its segregation at grain

boundaries is expected to promote susceptibility according to the above discussions.

This point may be totally confirmed by experimental observations that agglomeration

of carbide was found to assuredly accentuate the anodic behavior of grain boundary [41]

and cementite at grain boundaries of mild steel was also found to enhance the susceptibility to stress corrosion [42].

In this work, only considered was the linear effects of an internal electric field which is induced by the solute atoms in solid and liquid solvent. But nonlinear effects and other sources of the electric field, for example, variations of the charge quantity carried by an individual solute atom, electric field caused by dislocations in crystals and so on, has not been taken into account. When one tries to understand the related transport phenomena, he/she must examine the related factors.

2. Conclusion

In summary, transport of solute atoms in a solvent was investigated. By using *Yuheng Zhang equation*, a new transport mechanism was discovered and consequently an analytical theory was built successfully for the popular segregation phenomena in multi-realms. The theory was able to give solubility of solute atoms in solvent. The solubility was found to exhibits temperature, electronegativity difference, atomic size and valence electron concentration dependence, which may clarify the physical origins of the famous *Hume-Rothery rules* for terminal solid solution in metallurgy. According to the theory, solute segregation at solid-liquid interface of solvent, *i.e*, equilibrium partition coefficient, was found to arise from *Haiyan Zang potential* and may be determined by a fundamental principle that spatial gradient of electrochemical potential for any type of charged particles is always zero at equilibrium state. The analytical theory further unraveled the working principles of both precipitant and extractant from the viewpoint of physics. Moreover, the theory indicated that stress-

induced passive segregation of solutes in a solvent may be caused by the stress-induced internal electric potential and it can further influence stress corrosion process seriously, which is in agreement with experimental results. In a word, the newly found transport mechanism and the consequently obtained theoretical discoveries may open a door for people to interpret the series of segregation phenomena and find important applications in various areas.

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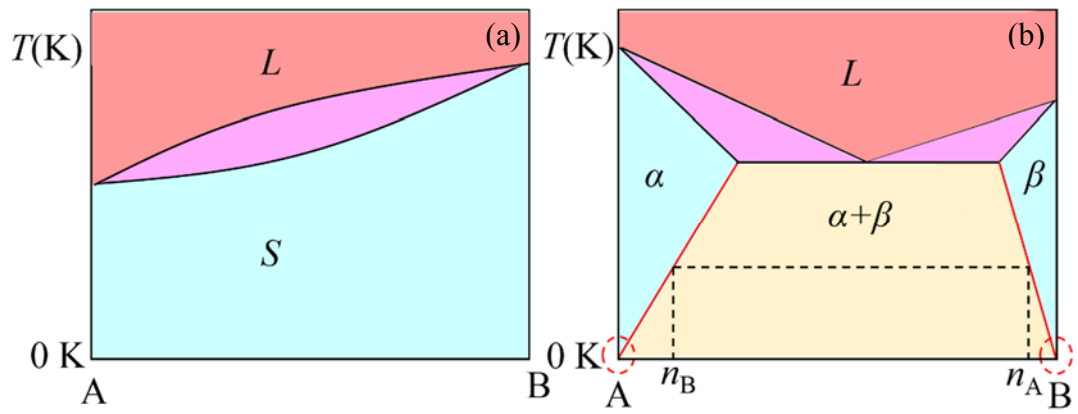
Figure 1. Schematic binary phase diagrams. (a) a typical binary phase diagram for the mutually soluble components A and B; (b) a typical eutectic binary phase diagram for the two components A and B. The solubility lines (red lines) pass the original point (red dashed circles) of binary phase diagram.
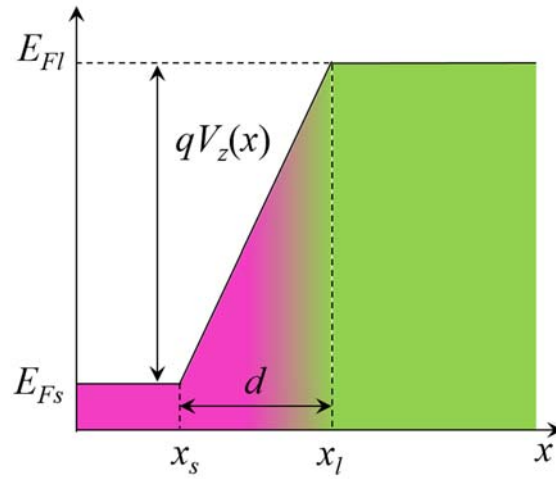
Figure 2. Schematic diagram for Fermi levels E_{Fs}, E_{Fl} of a solid nucleus (magenta) and its surround liquid (green) and the related electrical voltage $qV_z(x)= E_{Fs}-E_{Fl}$ at the interface (q denotes electron charge). The width of transition region (color gradient area) for Fermi levels is denoted by d which may be a constant for a definite material in its whole liquid-solid transition processes.
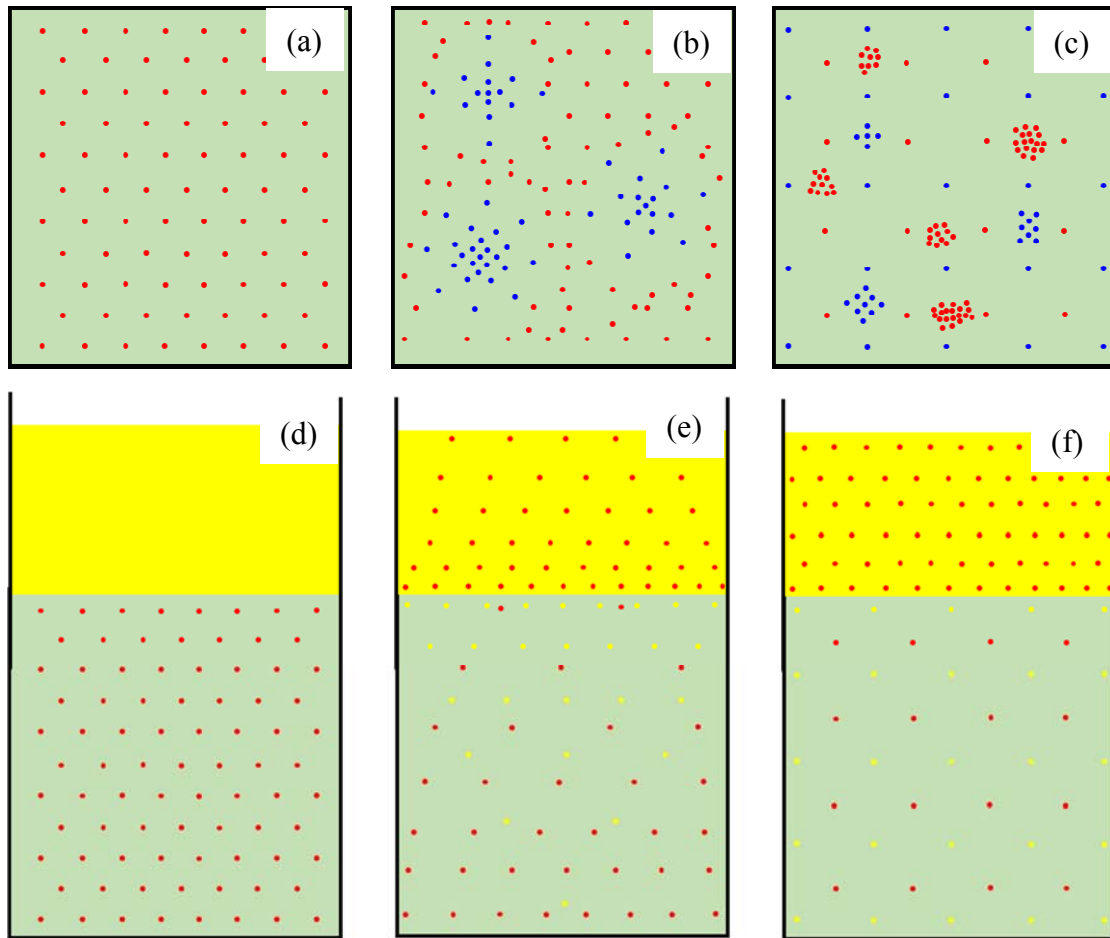
Figure 3. Schematic diagrams of precipitation processes and extraction processes. (a) uniformly distributed solute atoms (red circled) in a solvent (light green); (b) solvation of a precipitator (blue circled) and the induced initial precipitation process of solute atoms; (c) completed precipitation process of solute atoms and the formed precipitate particles (red clusters); (d) initial distribution of extractant (yellow) and uniformly distributed solute atoms (red circled) in a solvent (light green); (e) intermediate extraction process and the transport for both solute atoms and extractant atoms (yellow circled) in the solvent; (f) competed extraction process and the homogeneous distribution of solute atoms and extractant atoms in the solvent.