



Migration of inclusions in a matrix due to a spatially varying interface energy

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ABSTRACT

An interfacial energy can be a function of a bulk field such as temperature or electric field. We find that in a system with a gradient in temperature or electric potential, the resulting variation in interfacial energy can induce a particle to migrate by either surface or bulk diffusion. For a circular particle under a constant unidirectional gradient in the bulk field, the field dependence of the interfacial energy induces a circular particle to move as a circle at a constant velocity along the direction from higher to lower interfacial energy. A linear stability analysis of this steady state migration suggests that perturbations will damp out as time evolves, and thus under these conditions a migrating circular particle is morphologically stable. Other spatial distributions of interface energy can lead to the distortion of an initially circular shaped particle during migration. A phase field model is developed that captures these distortions and verifies the theoretical results mentioned above.

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For system consisting of a particle embedded in a matrix, a variation in temperature or electric field can change the bulk chemical potential along the particle-matrix interface such that the particle will move in the direction of the gradient [1–6]. Recent experiments suggest that Nickel (Ni)/Yttria-stabilized zirconia (YSZ) electrode and electrolyte during operation of solid oxide fuel cells; a variation in interfacial energy due to a non-homogeneous gas composition distribution in the pores [7] or an electric field distribution [8] in the electrode has been proposed to explain it. This inspires us to examine whether a variation in interface energy *alone* between an inclusion and matrix alone that is a result of a spatially varying bulk field can be a driving force for the migration of the particle. This is different from previous studies on migration of particles in electric field in which the particle has to be charged or directly responds to the electric field (known as electromigration) [4,5]. This is also different than the well studied marangoni effect in fluid dynamic where the variations of surface tension along the interface lead to shear stresses that act on the fluid through viscous forces, and thus induce a motion of the fluids in the direction of the temperature gradient [13].

We consider a particle phase with volume \mathbb{V}^α in matrix with volume \mathbb{V}^β (see Fig. 1) and interface energy σ that depends on a

quantity or a field (F) that varies with position \mathbf{x} . This field can be electric potential, temperature or species concentration distribution in the host. The Gibbs free energy in the system is

$$G = \int_{\Gamma(t)} \sigma[F(\mathbf{x}(s))] dS = \int_{\Gamma(t)} \sigma_F(\mathbf{x}(s)) dS \quad (1)$$

where $\Gamma(t)$ is the interface between the solid particle and its host material and $\sigma_F(\mathbf{x}) = \sigma[F(\mathbf{x})]$ captures the implicit spatial dependence of σ through the field F .

Denoting the interface by $\Gamma(t)$, mass conservation implies (detailed derivation can be found in Appendix A in [8]),

$$\partial_t \rho_i + \nabla \cdot \mathbf{J}_b^i = 0, \text{ in } \mathbb{V}^{\alpha,\beta} \quad (2)$$

$$(\rho_\alpha - \rho_\beta) u_n = [\mathbf{J}_b]_{\alpha,\beta} \cdot \mathbf{n} - \nabla_\tau \cdot \mathbf{J}_\tau, \text{ on } \Gamma(t) \quad (3)$$

for $i = \alpha, \beta$, where ρ_i is the atom number densities in \mathbb{V}^i , if there is no fluid flow or elastic deformation. \mathbf{n} is the unit outer normal direction on $\Gamma(t)$. u_n is the normal velocity on interface $\Gamma(t)$. \mathbf{J}_τ is the interface diffusion flux. \mathbf{J}_b^i is the mass diffusion flux in \mathbb{V}^i and $\mathbf{J}_b^i \cdot \mathbf{n}$ is the flux arriving at the interface from the bulk \mathbb{V}^i by diffusion. $\nabla_\tau = (I - \mathbf{n}^T \mathbf{n}) \cdot \nabla$ is the interface gradient operator.

According to Eq. (3), the normal velocity of the interface is proportional to the difference of bulk diffusion flux within bulk materials and/or interface gradient of interface diffusion flux along the interface. In some materials (such as for Ni), the diffusivity of Ni on

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the surface is in the order of $10^{-6}\text{cm}^2/\text{s}$ [11], whereas the diffusivity of Ni in the bulk is in the order of $10^{-12}\text{cm}^2/\text{s}$ at 1000C [12]. Under these conditions, Ni migration in the electrode of SOEC as mentioned in [7] can be taken as a surface diffusion dominant process. In some other scenarios, like some coarsening process within a certain temperature regime, bulk diffusion dominants. In order to understand particle migration by these two mass transport processes clearly, we study them separately in the following.

Surface diffusion: Considering mass transport along the interface, non-equilibrium thermodynamics implies

$$u_n = -\Omega_\alpha \nabla_\tau \cdot \mathbf{J}_\tau, \text{ on } \Gamma(t) \quad (4)$$

$$\mathbf{J}_\tau = -M_\tau \nabla_\tau (\nabla_n \sigma_F + \sigma_F \kappa), \quad (5)$$

where M_τ is the mobility of atoms along the interface and Ω_α is the atomic volume of the inclusion α , and $\nabla_n = \mathbf{n} \cdot \nabla$, see S.1, if the number density of atoms in \mathbb{V}^β can be neglected compared to that in \mathbb{V}^α . $\kappa = \nabla \cdot \mathbf{n}$. Here,

$$\nabla_n \sigma_F = \frac{\partial \sigma}{\partial F} \nabla F \cdot \mathbf{n}$$

evaluated along the interface. For example, in [7], the interfacial energy Ni/YSZ ($\sigma_{\text{Ni,YSZ}}$) depends on the electric potential (ε) distribution in the electrode, i.e.,

$$\sigma_{\text{Ni,YSZ}}(\varepsilon) = \sigma_{\text{Ni,YSZ}}^0 - \frac{1}{2} C_D (\varepsilon - \varepsilon_0)^2 \quad (6)$$

where C_D is the potential-independent double-layer capacitance and ε_0 is the potential of zero charge and $\sigma_{\text{Ni,YSZ}}^0$ is the interface energy at zero charge. In this case,

$$\nabla_n \sigma_{\text{Ni,YSZ}} = -C_D (\varepsilon - \varepsilon_0) \nabla_n \varepsilon.$$

To begin, an interface energy that depends on a field that also varies linearly along a single direction (x). We set the Cartesian coordinates at the centroid of the particle at $t = 0$ with an interface energy that decreases in the positive x -direction. For example, in Eq. (6), $(\varepsilon - \varepsilon_0)^2 \propto x$. Thus, since the the gradient is constant along x interface energy depends linearly on x , $\nabla \sigma_F = (\sigma_1, 0)$, where σ_1 is the magnitude of the gradient in σ_F . Scaling all quantities with units of length by R_0 , the interface energy by σ_0 , and velocity by $M_\tau \Omega_\alpha \sigma_0 / R_0^3$, the dimensionless forms resulting from the substitute of (4) into (5) are

$$V_n = \nabla_\tau^2 (\nabla_n \gamma + \gamma \kappa) \quad (7)$$

where V_n is the dimensionless normal velocity and $\nabla \gamma = (\eta, 0)$ is the dimensionless gradient in interface energy, where $\eta = \sigma_1 R_0 / \sigma_0$.

Steady state: Past work has shown that a circular particle can migrate at a constant velocity and shape when it is in a constant unidirectional temperature or electric potential gradient [3–5]. Thus, we examine the possibility of the steady state of circular particles subjected to an interface energy that varies with location due to a constant unidirectional gradient. Suppose there exists a steady state wherein a particle of arbitrary shape moves along the x -axis at a constant speed V . For simplicity, we only consider two dimensional cases. To describe the particle shape, we parameterize the interface at $t = 0$ by its arc length (s) starting from the point (at the right hand side) where the interface intersects the x -axis, $\alpha(s) = (x(s), y(s))$. Then the position vector on the interface is $\mathbf{X} = (X, Y) = (x(s) + Vt, y(s))$. $\varphi(s)$ is the angle between the outer normal direction on the interface and the positive x -direction (see Fig. 1). Since $\kappa(s) = d\varphi/ds$, $V_n = V \cos \varphi$ at steady state, Eq. (7) implies that

$$(V \frac{1}{\kappa} + 2\eta \kappa) \cos \varphi = (\eta X + 1) \frac{d}{d\varphi} (\kappa \frac{d\kappa}{d\varphi}) - 3\eta \sin \varphi \frac{d\kappa}{d\varphi}. \quad (8)$$

This equation is satisfied for a circle with unit radius ($\kappa = 1$, i.e., $\varphi(s) = s$) moving at a constant velocity in the x -direction with $V = -2\eta$. The dimensional form of the migration velocity is,

$$U = -2 \frac{M_\tau \Omega_\alpha \sigma_1}{R_0^2}. \quad (9)$$

This shows that the velocity of the moving particle due to a field-dependent interface energy is proportional to the magnitude of the constant gradient of the interface energy, the value of the interface diffusion coefficient, and depends strongly on particle size as, $1/R_0^2$. The minus sign implies that the particle moves down the gradient in interfacial energy.

Since a morphological instability of a moving circular particle has been found in previous work [4,16,17], we also include the linear stability analysis of the steady state derived above in the supplementary material, see S.2. to determine if this steady state is stable, and thus observable experimentally, for the moving particle driven by gradient of surface energy. We find that the migrating particle is indeed morphologically stable, in contrast to previous mechanisms that lead to particle migration. When the particle motion is driven by a gradient of interfacial energy, the interfacial energy must be positive and we find the values of η that can make the perturbation to the steady state grow exponentially in time only occur when the interfacial energy is negative, which is not possible in experiment when there is surface or bulk diffusion.

Bulk diffusion: A phase field model is developed for the case of bulk diffusion. Applying the commonly used gradient and bulk free energy densities for two-phase systems, the free energy functional can be written as,

$$F(\phi) = \int_{\mathbb{V}} K(x) |\nabla \phi|^2 + A(x) f(\phi) dx \quad (10)$$

where ϕ is the order parameter and $K(x)$ and $A(x)$ are parameters related to the interface energy (see Fig. 1). $f(\phi)$ is the double well potential describing the free energy density of each bulk phase. Here, we take $f(\phi) = (1/2)(1 - \phi^2)^2$.

If take

$$\frac{K(x)}{K_0} = \frac{A(x)}{A_0} = \frac{\sigma_F(x)}{\sigma_0},$$

where K_0 and A_0 and σ_0 satisfying $\sigma_0 = (4\sqrt{2}/3)\sqrt{A_0 K_0}$ [see (S.3.10)] are the scaling constant of $K(x)$, $A(x)$ and $\sigma_F(x)$, respectively, and a characteristic length of R_0 and velocity V_0 , the dimensionless phase-field model can then be obtained in the usual way [10],

$$\frac{\partial \phi}{\partial t} = \mathcal{L} \nabla^2 \mu, \quad x \in \bar{\mathbb{V}} \quad (11)$$

$$\mu = -\epsilon \nabla \cdot [\gamma(x) \nabla \phi] + \gamma(x) \frac{1}{2\epsilon} \frac{\partial f}{\partial \phi} \quad (12)$$

where $\bar{\mathbb{V}}$ is the dimensionless domain of \mathbb{V} and

$$\epsilon = \frac{1}{R_0} \sqrt{\frac{K_0}{A_0}}, \quad \mathcal{L} = \frac{2M\sqrt{K_0 A_0}}{R_0^2 V_0} = \frac{3}{2\sqrt{2}} \frac{M \sigma_0}{R_0^2 V_0}, \quad \gamma(x) = \frac{\sigma_F(x)}{\sigma_0}.$$

Here M is the mobility coefficient, ϵ is the scaled interface thickness. Detailed derivation to the above model can be found in S. 3.

We compare the phase field results to the predictions of a sharp interface theory in the quasi-stationary approximation, Similar to the conclusions in [9], quasi-stationary assuming that the particle is nearly pure component 1 and the matrix is nearly pure component 2. μ_0 evolves by the following quasi-stationary diffusion equation and boundary conditions,

$$\nabla^2 \mu_0 = 0, \text{ in } \bar{\mathbb{V}}^\beta, \mathbb{V}^\alpha \setminus \bar{\Gamma}(t) \quad (13)$$

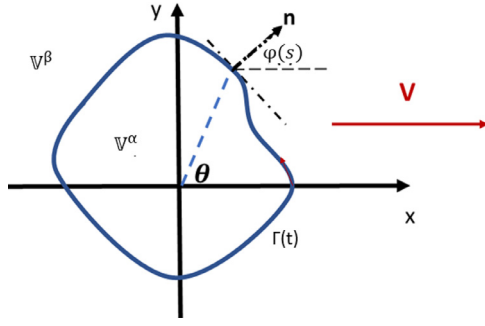


Fig. 1. Schematic showing a solid particle moving in a matrix.

$$\mu_0 = \omega(\nabla_n \gamma + \gamma \kappa), \text{ on } \bar{\Gamma}(t) \quad (14)$$

$$u_n = \frac{\mathcal{L}}{2} \left[\left[\frac{\partial \mu_0}{\partial n} \right] \right] \text{ on } \bar{\Gamma}(t) \quad (15)$$

where $\omega = \sqrt{2}/3$ and $[a] = a^\beta - a^\alpha$, for some quantity a . Here, in Eq. (15) and (11), for simplicity, the mobility is taken as a constant across the materials and their interfaces. In Eq. (2), at quasi-stationary state, the molar composition in each phase is constant. The bulk fluxes (J_b) in each phases under quasi-stationary assumptions is proportional to $\nabla \mu_0$ in Eq. (13).

As in the case of interface diffusion, we consider a circular particle with dimensionless radius 1 with an interface energy that varies due to a field with a constant gradient along the x-direction where $\nabla \gamma = (\eta, 0)$, solving the above equations, Eq. (13)-(15), in polar coordinates gives,

$$\mu_0(r, \theta) = 2\omega\eta r \cos \theta + \omega, \text{ for } r < 1 \quad (16)$$

$$\mu_0(r, \theta) = 2\omega\eta r^{-1} \cos \theta + \omega, \text{ for } r > 1 \quad (17)$$

$$u_n = -2\mathcal{L}\omega\eta \cos \theta, \text{ on } r = 1. \quad (18)$$

This implies that the circle will maintain its shape and move along the x-direction towards the region with lower interface energy with constant velocity

$$V = -2\mathcal{L}\omega\eta, \quad (19)$$

i.e., it is a steady state. While the existence of a steady state is also the case for surface diffusion, the dimensional form of the velocity is much different,

$$U = -\frac{M\sigma_1}{R_0}. \quad (20)$$

Most importantly the dependence of the velocity on particle size is weaker, $U \sim 1/R_0$.

Numerical simulations: We first verify our theoretical analysis given above using a phase field calculation. First, we consider a circle solid particle with a dimensionless radius 1 in a matrix subject to a linear distribution of interface energy along x-direction. Solving Eq. (11) in $\bar{\mathcal{V}} = [-2, 8] \times [0, 8]$ with periodic boundary conditions for ϕ and no flux boundary conditions for μ and $\mathcal{L} = 5e - 2$, $\epsilon = 0.02$ and $\nabla \gamma = (-0.1, 0)$.

Fig. 2(a) shows that the particle moves at a constant velocity in the direction of decreasing interface energy while maintaining a circular shape, following a short initial transient. The steady state particle velocity found in the numerical simulation is consistent with the theoretical prediction given by Eq. (19) to within 2.7% [see Fig. 2(c) and Fig. 3]. In addition, the influence of interface thickness (ϵ) in the phase field simulation is determined (see Fig. 3) showing that as the interface thickness is decreased the results are approach the theoretical or sharp interface result given in

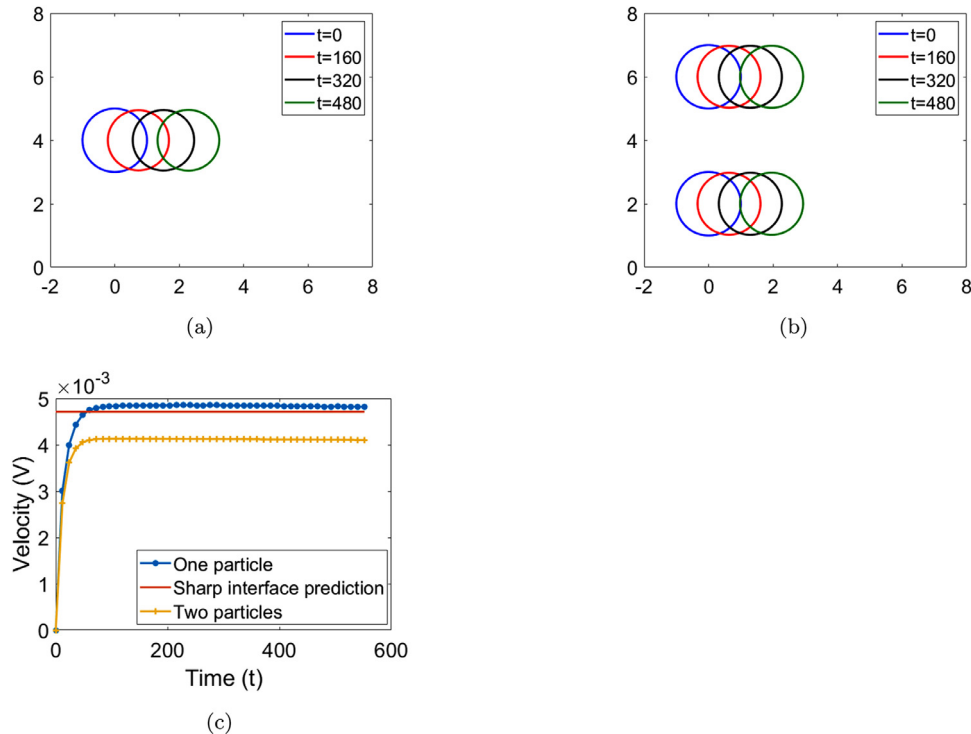


Fig. 2. (a) A particle and (b) two solid particles moving with constant velocity subject to a linear distribution of interface energy along x-direction [$\gamma(x) = -0.1x + 1$]. Here, we plot zero contour lines of the phase parameter as the interface between two phases. (c) The evolution of migration velocity with time. The red line is the predicted steady state in the sharp interface limit (Eq. (19)).

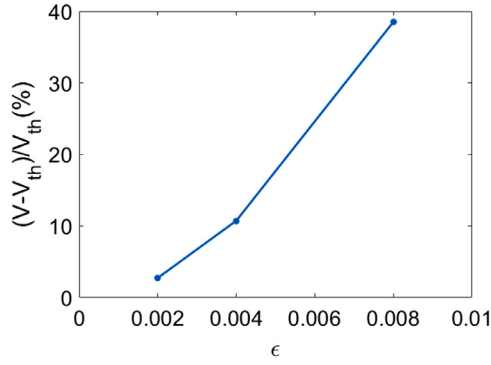


Fig. 3. Convergence of the migration velocity to its sharp interface theoretical prediction (V_{th}) as the interface thickness in the phase field simulation (ϵ) decreases

Eq. (18). Then, more than one particle are considered in the simulation for comparison to the single particle case. Since diffusional interactions between the particles are now possible, the particle migration rate is lower than that for a single particle. In addition, there is nearly no coarsening of the particles during migration [see Fig. 2(b)]. However, other calculations show that as the number density of the particles increases or particle separation decreases, the particles do coarsen while migrating.

Lastly, we investigate the migration of particle subject to non-linear distribution of interface energy along x-direction. Due to the spatially varying gradient in the field, an initially circular particle is distorted while moving in the direction of lower interfacial energy [see Fig. 4(a) and (c)]. The velocity of the particle is not constant,

see Fig. 4(b), as expected. Thus nonlinear spatial distributions of the bulk fields will give rise to complex shapes and major changes in the kinetics from that seen with a circular particle in fields with constant gradients.

In conclusion, we show that a variation of the interfacial energy due to a gradient in a bulk field can lead to particle migration. If a particle is circular and is subject to a field with a constant gradient it will remain circular and migrate at a constant rate. If there are diffusional interactions between particles or a non-constant bulk gradient then the migration velocity will change from that of an isolated circular particle and the migrating particle will no longer have a circular morphology.

There have been a number of recent experimental observations of Ni particle migration away from the YSZ/Ni-YSZ interface during operation of solid oxide electrolysis cells [7,14,15], and it has been suggested that this is driven by a gradient in surface energy, due either to the electrical overpotential gradient [7] or a variation in the H₂/H₂O vapor composition in the Ni-YSZ pores [14]. The present results verify and quantify this idea, providing a means for predicting the rate of such migration that can be useful for predicting electrolysis cell degradation. Moreover, as it is suggested in [11,12], the bulk diffusivity of Ni is much smaller than the surface diffusivity of Ni, the process of Ni migration should be dominated by surface diffusion. Another interesting point worth noting is, for both surface diffusion and bulk diffusion cases, the migration velocity of spherical particles is inversely proportional to the particle size (R_0). Thus, the size scale of the Ni particles in the YSZ is extremely important in setting the migration rate, as has been verified in our recent three-dimensional phase field simulations of Ni evolution in YSZ (see our upcoming manuscripts on this topic).

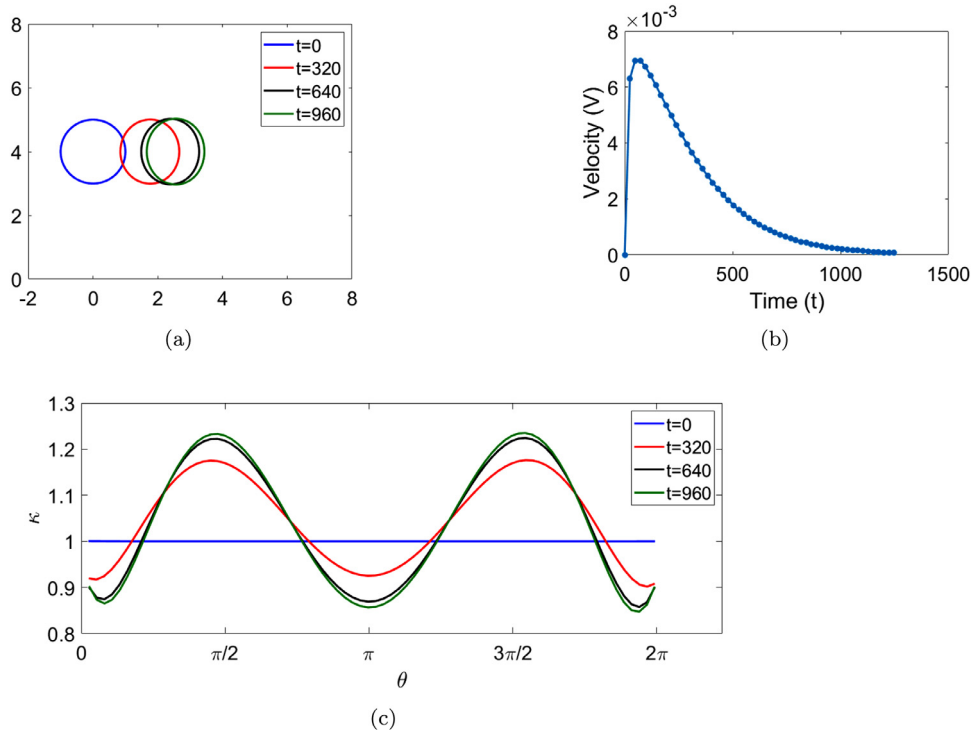


Fig. 4. (a) A particle moving when subjected to a non-linear distribution of the interfacial energy along x-direction [$\gamma = 0.005(x+2)^3 - 0.05(x+2)^2 + 1$]. (b) The evolution of the migration velocity with time. (c) Curvature of the interface with respect to θ , which is the angle between the line connecting the point on the interface drawn from the particle centroid and the positive x-axis as shown in Fig. 1, showing that the particles are not spherical.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.scriptamat.2021.114235](https://doi.org/10.1016/j.scriptamat.2021.114235)

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