Basics of diffuse interface modeling

1 Phase-field modeling

1.1 Introduction

In materials science and in general a number of physical phenomena involve motion of boundaries between entities which are homogeneous with respect to certain physical properties. These problems fall in the realm of what are known as free-boundary or moving boundary problems. Examples of such phenomena are solidification, precipitation, phase-separation, order-disorder transitions etc. A notable feature of such problems, involves, mass, heat or momentum transfer across *interfaces* which are the boundaries between physically homogeneous media (*phases*). Classically, such moving boundary problems were modeled using *sharp-interface methods* where the nodes which discretely represent the interface, are explicitly tracked and the appropriate boundary conditions at the interface are imposed at these boundary nodes, an example being the *boundary integral model*. This is however, time-consuming and memory intensive when one is intending to numerically compute using the sharp-interface descriptions of these free-boundary problems for large domain computations. In addition, the models are restrictive/limited in nature as complex geometric evolution involving multiple curvatures and catastrophic phase evolution are outside the scope of such models.

A second approach which enables a more elegant treatment of the problem are *diffuse-interface models*. Here, the dis-continuity in a physical property/quantity across the interface is allowed to vary over a finite width. The temporal evolution of any phase transformation is then implicitly tracked by following the evolution of this spatially continuous field as function of time. The boundary conditions are self-consistently accounted for in this description and the actual sharp-interface interface problem is retrieved when the length scale of the diffuse-interface region is much

smaller compared to the microscopic length scale of the morphological feature one is modeling.

The parameter for distinguishing between the phases can be chosen among the various extensive variables distinguishing the phases. Generally, the relevant parameter/s are the ones which are the more sensitive to the given processing conditions. So for example, for case of a pure material solidification, under constant pressure with equal molar volumes of the phases, the parameter could be either the order in the solid/liquid, the internal energy etc. This parameter which differentiates between the phases is termed as an *order parameter*. Another example for an order parameter is the *composition*.

Another perspective for diffuse-interface models, is to perceive order-parameters as *indicator-functions* in which an arbitrary set of spatially continuously varying functions are used to describe multiple-phases in the system. This set of parameters is then utilized to describe the variation of the intensive-extensive variables in the system through the use of implicit/explicit functions of the order parameter/s. This is the more elaborately used methodology as is usually termed the *Phase-field approach*.

It is important to note that, atomistically interfaces have finite thickness(over some angstroms). So, while this could be a physical motivation for phase-field/diffuse-interface formulations, the choice of the difference interface thickness in the mathematical model has no bearing on the physically realistic value. This is because in the model, the interface width is a physical construct utilized to elegantly reproduce the sharp-interface free-boundary problem. Since, the physical interface thickness is not present in the sharp-interface free-boundary problem, therefore it makes the reproduction in the phase-field/diffuse-interface model unnecessary. The choice of the length-scale of the diffuse interface is chosen as per the morphological length scale one is modeling. In the following sections, we will be presenting an overview of two models; one based on the choice of order-parameter as the composition (*Cahn-Hilliard*), and the other where the order parameter is non-conserved(*Allen-Cahn*). Essentially, the evolution equations which deterministically describe the evolution of the order-parameter functions ensure that the energy of the system is minimized. However, the two following descriptions, result in different evolution equations.

1.2 Cahn-Hilliard equation

Consider the diffusion equation for a single phase material with two components,

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} = \nabla \cdot (M\nabla\mu) = D\frac{\partial^2 c}{\partial x^2} \qquad (1.1)$$

which is a statement of mass-conservation, with the flux being written solely proportional to the gradient of the diffusion potential $\mu = \mu_A - \mu_B$ and M being the mobility of the atoms, $M = D/\dfrac{\partial \mu}{\partial c}$. At equilibrium, $\dfrac{\partial c}{\partial t} = 0$, the concentration profile can be solved for, to be linear between the values at the boundaries.

Now, consider a system of two phases in equilibrium with compositions c^α and c^β. Clearly, if we were to write a single thermodynamically consistent equation, for the entire system, $\dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial x^2}$ cannot remain valid, since this would imply, that in the event of no-flux (Neumann) boundary conditions (a closed system) a uniform composition field would be the equilibrium state of the system that clearly violates the thermodynamically derived equilibrium state of the system (equal chemical potentials of both components in each phase).

The problem lies in the last simplification that we have performed $M\nabla\mu = D\nabla c$, which is valid when $\mu = \dfrac{\partial f}{\partial c}$ as a function of composition is monotonically increasing, because, then it would be reasonable to derive that the flux due to the gradients in the diffusion potential are in the same direction as the gradient in the composition. This is however, not always true, i.e, when we exchange of material between two phases, with differing Gibbs-free energy, or the free energy of the material is non-convex $\dfrac{\partial^2 f}{\partial c^2} < 0$ for a certain region in the composition space.

Clearly, the generalized equation for the diffusion should be the one that is derived from the gradients of the diffusion potential, as flux of the atoms is in opposition to the gradients of the diffusion potential, thereby, with time, the gradients in the diffusion potential in the system diminish, with

the equilibrium state being achieved when the entire system is at the same diffusion potential.

However, the equilibrium state of the equation with compositions corresponding to two different phases, would correspond to a sharp transition from one composition c^α in one phase, to another composition c^β in another phase. The diffuse-interface methodology exists in mapping this sharp interface equilibrium over a finite interface region where the gradients in composition are finite, but are everywhere continuous.

In order to achieve this, we would need to make the diffusion potential gradients to be non-zero even in this particular sharp-interface state. To see, how we achieve this, for the sake of discussion, assume that we modify the diffusion equation as written before, by the addition of a term $-2\kappa\dfrac{\partial^2 c}{\partial x^2}$. With this modification, the evolution equation for the phase-field will read,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(M\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial c} - 2\kappa\frac{\partial^2 c}{\partial x^2}\right)\right) \qquad (1.2)$$

Clearly, the equilibrium state of this equation $\dfrac{\partial c}{\partial t} = 0$, would occur, when,

$$\frac{\partial}{\partial x}\left(M\left(\frac{\partial f}{\partial c} - 2\kappa\frac{\partial^2 c}{\partial x^2}\right)\right) = constant. \qquad (1.3)$$

Far away from the interface the composition is uniform on either side of the interface, and therefore, the constant of integration would be zero. Integrating again, we derive,

$$\left(\frac{\partial f}{\partial c} - 2\kappa\frac{\partial^2 c}{\partial x^2}\right) = constant. \qquad (1.4)$$

Again, far away from the interface, the gradients in composition are zero, and $\dfrac{\partial f}{\partial c}$ assumes the same value on either side of the interface which we will denote as μ_{eq}.

Therefore, the partial differential equation determining the equilibrium profile, is;

$$2\kappa \frac{\partial^2 c}{\partial x^2} = \frac{\partial f}{\partial c} - \mu_{eq}. \tag{1.5}$$

Multiplying, both sides with $\dfrac{\partial c}{\partial x}$, gives the following differential form, which can be integrated from one side of the interface $x = -\infty$ which is in one of the bulk phases to a point x,

$$d\left(\left(\kappa \frac{\partial c}{\partial x}\right)^2\right) = d\left(f - \mu_{eq}c\right) \tag{1.6}$$

$$\kappa \left(\frac{\partial c}{\partial x}\right)^2 = \left(f - \mu_{eq}c\right) - \left(f - \mu_{eq}c\right)_b, \tag{1.7}$$

where $\left(f - \mu_{eq}c\right)_b$ is *Legendre transform* of the free-energy. This is the chemical potential of one of the components in the system. Therefore, c represents the composition of the component A the intercept represents chemical potential of the component B. This is pictorially, described in the following schematic.

$$\mu_B = f\left(c\left(\mu\right)\right) - \mu c\left(\mu\right)$$
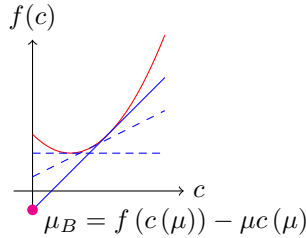
Clearly μ_A is equal in both phases at equilibrium and therefore $(f - \mu_{eq}c)_b$ assumes a unique value in both bulk phases. The above relation is true for every point in the domain. We see, that while far away from the interface $\dfrac{\partial c}{\partial x} = 0$, we still get the composition profiles which are uniform, and the diffusion potential corresponds to the equilibrium value μ_{eq}. However, now there exists a region in the domain where the gradients are finite and given by the equilibrium condition in Eqn. 1.7. Taking root, and integrating further we derive the composition profile that would be the equilibrium solution between the two phases,

$$\sqrt{\kappa}\frac{\partial c}{\partial x} = \sqrt{(f - \mu_{eq}c) - (f - \mu_{eq}c)_b}. \qquad (1.8)$$

Here, we choose the positive root, given that our boundary conditions for the profile are such that we go from a lower composition c^α to c^β. One can choose also the reverse, but we consistently transform our integration limits, which would result in an unique composition profile, independent of this choice. Integrating, the preceding equation once, we have

$$c\left(x\right) = c^\alpha + \frac{1}{\sqrt{\kappa}} \int_{x=-\infty}^{x} \sqrt{(f - \mu_{eq}c) - (f - \mu_{eq}c)_b}\, dx. \qquad (1.9)$$

As an example, choose $f\left(c\right) = c^2 \left(1 - c\right)^2$, with two phases, corresponding to the two minima in the curve at $c^\alpha = 0$ and $c^\beta = 1$. Clearly, $\mu_{eq} = 0$ and $(f - \mu_{eq}c)_b = 0$. Simplifying Eqn.1.8 using the above assumptions, we have

$$\frac{\partial c}{\partial x} = \frac{1}{\sqrt{\kappa}}c\left(1 - c\right). \qquad (1.10)$$

Upon integration, and applying the boundary conditions, we derive,

$$c\left(x\right) = \frac{\exp\left(\dfrac{x}{\sqrt{\kappa}}\right)}{1 + \dfrac{x}{\sqrt{\kappa}}}. \tag{1.11}$$

The following represents the equilibrium profile, in comparison, to the sharp-interface solution, which would be the result of the classical diffusion equation.
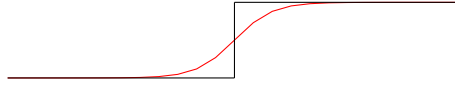
Clearly, we have achieved what we set out for namely, now the gradients at the interface are no longer infinite at equilibrium. To understand our modification let us look at out constructed term more carefully,

$$\mu = \frac{\partial f}{\partial c} - 2\kappa \frac{\partial^2 c}{\partial x^2}. \tag{1.12}$$

The chemical potential now is a function not only of the composition, but its gradients as well. This coupling is essential, in the introduction of a length scale that is related to the diffuseness of the interface. The reason the sharp interface solution is no longer the equilibrium solution with this modification, is clear, because, even in this state though while there is no gradient in the term $\dfrac{\partial f}{\partial c}$, huge gradients exist in the term $2\kappa\dfrac{\partial^2 c}{\partial x^2}$ on both sides of the discontinuity across the sharp-interface. Thus, in the sharp-interface state, material at higher composition will flow towards a material with the lower composition, because this is the direction of the gradient ($-2\kappa\dfrac{\partial^2 c}{\partial x^2}$), that is also the direction of mass transport. One can verify this using simple finite difference discretization. This flow will continue, until, force due to the gradients in $\dfrac{\partial f}{\partial c}$ become equal to that of the gradients of the divergence of the composition.

In order to formalize, this language of incorporation of gradients in the diffusion potential it is useful to start from the state of energy of the system. For this, we require the energy density at each point in space, such that on integration we can derive the entire, energy of the system. It is essential to note, that our energy density, needs to depend on the composition, its gradients and higher order spatial derivatives, which are by themselves functions of space. Therefore, our free energy density is a function with functions as arguments and therefore are *functionals*.

So what is the simplest energy density functional that we can write down? Well, we can start from the energy of a uniform composition state c_o and add energy contributions with respect to variations from this state. This construction, would write as,

$$f\left(c, \nabla c \nabla^2 c \ldots\right) = f_o\left(c\right) + \frac{\partial f}{\partial c'}\delta c' + \frac{\partial f}{\partial c''}\delta c'' + \frac{1}{2}\frac{\partial f}{\partial c'}\left(\delta c'\right)^2. \qquad (1.13)$$

There is one observation, that we can easily make, i.e, the energy state of the system cannot depend on the choice of the co-ordinate system, and therefore, should be rotationally invariant. This can only be guaranteed if $\frac{\partial f}{\partial c'}\delta c'$ makes zero contribution to the energy integral, which is true. Therefore, the simplest energy density that can be written is of the form,

$$f\left(c, \nabla c, \nabla^2 c\right) = f_o\left(c\right) + \kappa_1 \left(\frac{\partial c}{\partial x}\right)^2 + \kappa_2 \left(\frac{\partial^2 c}{\partial x^2}\right) \ldots \qquad (1.14)$$

where κ_1 and κ_2 can be calculated from the previous expressions. The energy of the system is a volume integral of the energy density, that can be formulated as,

$$\mathcal{F} = \int_{-\infty}^{\infty} f_o\left(c\right) + \kappa_1 \left(\frac{\partial c}{\partial x}\right)^2 + \kappa_2 \left(\frac{\partial^2 c}{\partial x^2}\right) \ldots dx. \qquad (1.15)$$

Partially integrating the last term in the integration, we have,

$$\int_{-\infty}^{\infty} \kappa_2 \left(\frac{\partial^2 c}{\partial x^2} \right) dx = - \int_{-\infty}^{\infty} \frac{\partial \kappa_2}{\partial x} \left(\frac{\partial c}{\partial x} \right) + \left[\kappa_2 \left(\frac{\partial c}{\partial x} \right) \right]_{\infty}^{\infty}. \qquad (1.16)$$

Since we are in the uniform state far from the interface, the constant in the integration vanishes, therefore we have,

$$\int_{-\infty}^{\infty} \kappa_2 \left(\frac{\partial^2 c}{\partial x^2} \right) dx = - \int_{-\infty}^{\infty} \frac{\partial \kappa_2}{\partial x} \left(\frac{\partial c}{\partial x} \right) dx = - \int_{-\infty}^{\infty} \frac{\partial \kappa_2}{\partial c} \left(\frac{\partial c}{\partial x} \right)^2 dx. \qquad (1.17)$$

Substituting, in the previous expression for energy density, we have,

$$\mathcal{F} = \int_{-\infty}^{\infty} f_o(c) + \kappa \left(\frac{\partial c}{\partial x} \right)^2 \dots dx. \qquad (1.18)$$

where $\kappa = \kappa_1 - \dfrac{\partial \kappa_2}{\partial c}$.

With this, we are now ready to define our generalized diffusion potential which depends also on the gradients. However, since we are dealing with functionals, the relevant operator for computing the variation of the total energy of the system corresponding to a local change in composition, needs to be derived from what is called as the *variational derivative* in the *calculus of variations*. This operator can be read as follows,

$$\frac{\delta \mathcal{F}}{\delta c} = \left(\frac{\partial}{\partial c} - \nabla \cdot \frac{\partial}{\partial \nabla} + \nabla^2 \cdot \frac{\partial}{\partial \nabla^2} \dots \right) f \qquad (1.19)$$

Using this operator on our constructed energy functional in Eqn.1.18, we compute our generalized diffusion potential as,

$$\mu = \frac{\partial f_o}{\partial c} - 2\kappa \nabla^2 c, \tag{1.20}$$

which is the modification, we included in our starting diffusion equation, to incorporate a diffuse interface as the equilibrium solution between two phases.

1.2.1 Properties of the equilibrium interface

In the previous sections we derived the solutions to the equilibrium profile of the composition between two phases. The profile at equilibrium has certain properties which being related to the properties of interface can be attributed to certain material properties. One of them is the *surface energy*. Recall, as a solution to the differential equation at equilibrium we derived an intermediate relation that is the Eqn. 1.7. This equation can be ra-arranged an written as following,

$$\kappa \left(\frac{\partial c}{\partial x} \right)^2 = f(c) - \left(f(c_b) + \mu_{eq} \left(c - c_b \right) \right). \tag{1.21}$$

where the subscript 'b' indicates the value on the left side of the interface $x = -\infty$. The second term in the preceding equation is nothing but the mixture energy between two phases of compositions c^α and c^β, where c_b corresponds to c^α. The R.H.S can then be interpreted as the excess to this mixture energy of the phases at equilibrium, and the solution to the partial differential is a statement of *equipartitioning* of energy between the gradient energy $\kappa \left(\frac{\partial c}{\partial x} \right)^2$ and the potential excess energy which is the R.H.S. This can be illustrated by assuming $f(c) = c^2 \left(1 - c^2 \right)$ and then with the following graph;
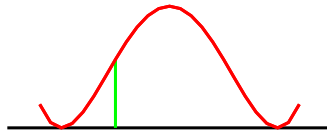
Physically, both of these energies represent the different energy penalties present in the free-energy density functional: the first penalizes the gradients, which is the reason, we now have a smooth continuous profile for the composition, the second contribution is the excess energy which the system has for values of the composition which are in between c^α and c^β. An equi-partitioning between these energy contributions in the functional gives the equilibrium composition profile that we derived in the previous section. Therefore, in this state the total energy of the system is the sum total of both energy contributions. Since, this energy is entirely, due to the presence of an interface in between the phases, this energy would the energy excess with respect to the bulk and therefore can be related to a material property which is the surface energy σ. The integral writes as

$$\sigma = 2 \int_{-\infty}^{\infty} \kappa \left(\frac{\partial c}{\partial x} \right)^2 dx. \tag{1.22}$$

Using equi-partitioning we have $\dfrac{\partial c}{\partial x} = \sqrt{(f(c) - (f(c_b) + \mu_{eq}\,(c - c_b)))/\kappa}$, (where we choose the positive root given the boundary conditions), we can derive,

$$\sigma = 2 \int_{c^\alpha}^{c^\beta} \sqrt{\kappa(f(c) - (f(c_b) + \mu_{eq}\,(c - c_b)))}dc \tag{1.23}$$

The second equilibrium property of the interface is of-course the length scale over which the system is diffuse. As is previously mentioned this is not a material property, although real interfaces are diffuse. This is a model parameter which can be chosen depending on the morphological length scale one is trying to model. So for example, if we are trying to model eutectic growth, this would chosen keeping in mind the length scale of the lamellar width, or in the case of a dendrite, it would be the length scale over which the dendrite tip is curved. The effective interface thickness "W" can be computed as follows,

$$\frac{\partial x}{\partial c} = \sqrt{\frac{\kappa}{f(c) - (f(c_b) + \mu_{eq}(c - c_b))}} \tag{1.24}$$

$$W = \int_0^W dx = \int_{c^\alpha}^{c^\beta} \sqrt{\frac{\kappa}{f(c) - (f(c_b) + \mu_{eq}(c - c_b))}} dc \tag{1.25}$$

1.3 Allen-Cahn equation

In the previous section of the Cahn-Hilliard equation, we formulated a generalized diffusion equation wherein, the mass-conservation equation is re-written using the gradient of a generalized diffusion potential which now also depends on the composition gradients. Such an equation naturally leads to a minimization of the total free-energy functional as can be appreciated from the following discussion. If we were, to compute the time-derivative of the change in the free-energy functional, it can written as,

$$\frac{\delta \mathcal{F}}{\delta t} = \int_{-\infty}^{\infty} \frac{\delta \mathcal{F}}{\delta c} \frac{\partial c}{\partial t} dx, \tag{1.26}$$

where f was our constructed free-energy functional $f(c, \nabla c) = f_o(c) + \kappa(\nabla c)^2$. Incorporating, $\frac{\partial c}{\partial t} = -\nabla \cdot J$, we have,

$$\frac{\delta \mathcal{F}}{\delta t} = -\int_{-\infty}^{\infty} \frac{\delta f}{\delta c} \nabla \cdot J dx. \tag{1.27}$$

Partially integrating, the R.H.S we derive,

$$\frac{\delta \mathcal{F}}{\delta t} = \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\frac{\delta f}{\delta c} \right) J dx - \left[J \frac{\delta f}{\delta c} \right]_{x=-\infty}^{x=\infty}. \tag{1.28}$$

Using, appropriate boundary conditions, such as those for a closed system, the second term in the integration will drop out. Additionally, recalling that $\mu = \dfrac{\delta f}{\delta c}$ and $J = -M\nabla\mu$, we derive the time derivative of the free-energy functional as,

$$\frac{\delta\mathcal{F}}{\delta t} = -\int_{-\infty}^{\infty} M\left(\nabla\mu\right)^2 dx. \qquad (1.29)$$

Clearly, the second term on the right hand side of the equation is negative for all dynamical states, rendering the time-derivative of the free-energy always negative, thus ensuring the minimization of the free-energy functional with time. Additionally, the rate of change in the energy is zero when the gradients in μ vanish.

In the particular, construction as described above, if we relax the constraint that our order-parameter is a conserved variable, it allows us to formulate other phenomenological laws which also ensure the minimization of the free-energy, albeit through a different evolution trajectory. So let us go back to our equation in Eqn.1.26. One of the simplest possibilities to ensure that the functional is minimized in time, would be,

$$\frac{\partial c}{\partial t} = -M\frac{\delta\mathcal{F}}{\delta c}, \qquad (1.30)$$

such that the time derivative of the free-energy functional now reads,

$$\frac{\delta\mathcal{F}}{\delta t} = -\int_{-\infty}^{\infty} M\left(\frac{\delta\mathcal{F}}{\delta c}\right)^2 dx. \qquad (1.31)$$

Clearly, here again, we minimize energy, however, the rate of change is zero, when the functional is an extremum given by $\dfrac{\delta\mathcal{F}}{\delta c} = 0$.

For clarity, in the subsequent discussion, we will assume that this set of evolution equations which are derived from a phenomenological ansatz,

is with respect to a different order-parameter which is η which is non-conserved. This is also the set-of equation describing Allen-Cahn dynamics. The particular set of equations, are applicable for materials phenomena describing evolution of grain-boundaries, order-disorder transitions etc,. Formally, the functional can be written in the same manner as before,

$$\mathcal{F} = \int_{-\infty}^{\infty} \left(f_o\left(\eta\right) + \kappa \left(\nabla \eta\right)^2 \right) dx. \tag{1.32}$$

The dynamical evolution equation is as described before,

$$\frac{\partial \eta}{\partial t} = -M \frac{\delta F}{\delta \eta}. \tag{1.33}$$

Applying, the operator for the variational derivative as given in Eqn.1.19, we derive,

$$\frac{\partial \eta}{\partial t} = -M \left(\frac{\partial f_o}{\partial \eta} - 2\kappa \nabla^2 \eta \right). \tag{1.34}$$

The equilibrium is achieved when the $\dfrac{\partial \eta}{\partial \eta}$ goes to zero. This is achieved when,

$$\frac{\partial f_o}{\partial \eta} = 2\kappa \nabla^2 \eta. \tag{1.35}$$

For a 1D-problem, the above equation has a solution. Multiplying, both sides of the previous equation with $\dfrac{\partial \eta}{\partial x}$, the above differential equation can be transformed into,

$$d\left(f_o\left(\eta\right)\right) = d\left(\kappa\left(\nabla\eta\right)^2\right). \tag{1.36}$$

The characteristics of the function $f_o\left(\eta\right)$ are the same as what we chose as an example in the Cahn-Hilliard equation, i.e. $f_o\left(\eta\right) = \eta^2\left(1 - \eta\right)^2$, having minima at $\eta = 0$ and $\eta = 1$. Therefore, integrating from left of an interface, between phases represented by $\eta = 0$ (on the left) and $\eta = 1$ (on the right), would give rise to,

$$f_o\left(\eta\right) = \kappa\left(\nabla\eta\right)^2, \tag{1.37}$$

considering, that the far-field gradients in η are zero. This is the relation of equipartitioning of energy between the potential $f_o\left(\eta\right)$ and the gradient energy denoted by $\kappa\left(\nabla\eta\right)^2$. Integrating, further, we would derive the equilibrium profile for the order-parameter η as,

$$\eta\left(x\right) = \frac{\exp\left(\dfrac{x}{\sqrt{\kappa}}\right)}{1 + \exp\left(\dfrac{x}{\sqrt{\kappa}}\right)} \tag{1.38}$$

This profile is the same as that we derived for the chosen form of $f_o\left(c\right)$ in the Cahn-Hilliard equation. Therefore, the properties related to the equilibrium profile, are also going to be similar.

1.3.1 Properties of the equilibrium profile

In the preceding Allen-Cahn equation, we derived the profile of the diffuse-interface boundary between two phases, as a result of the equi-partitioning of energies between the gradient energy and the potential described by $f_o\left(\eta\right)$. Similar, to the composition profile as a result of the Cahn-Hilliard

equation, the profile $\eta(x)$ from the Allen-Cahn dynamics, has two important attributes. The first is of-course the surface energy, which can be written using the relation of equi-partition as the sum of the gradient and the potential terms as,

$$\sigma = 2 \int_{-\infty}^{\infty} \kappa \left(\nabla \eta\right)^2 dx \tag{1.39}$$

$$\sigma = 2 \int_{0}^{1} \kappa \frac{\partial \eta}{\partial x} d\eta, \tag{1.40}$$

where we have again assumed the boundary conditions, where at $x = -\infty$, $\eta = 0$ and $x = \infty$, $\eta = 1$. Using, Eqn. 1.37, we have,

$$\sigma = 2\sqrt{\kappa} \int_{0}^{1} \eta \left(1 - \eta\right) d\eta \tag{1.41}$$

$$= \sqrt{\kappa}/3. \tag{1.42}$$

Another of the properties, which is related to the length scale of the diffuse interface thickness, which can be found by integrating, the inverse of the gradient of the diffuse interface profile as,

$$W = \int_{0}^{1} \frac{\partial x}{\partial \eta} d\eta \tag{1.43}$$

Since, our potential is of the form $\eta^2 \left(1 - \eta\right)^2$, the preceding integral is singular in the bulk, therefore, it can be computed in a certain range of η, which we choose as $\eta = 0.1$ to $\eta = 0.9$ for the present integration, that results in,

$$W = \frac{1}{\sqrt{\kappa}} \ln\left(81\right). \tag{1.44}$$

In order to have a more useful control on the interface thickness, it sometimes becomes useful to introduce an additional parameter, which can be varied to adjust the height of the potential. Thus, the relations of the surface energy and the interface thickness can be written as, $\sigma = \sqrt{\kappa H}/3$, and the interface thickness $W = \sqrt{\dfrac{H}{\kappa}} \ln{(81)}$.

1.4 Modeling phase transformations

In the preceding sections, we have gone through the basic construction of the phase-field models. In this section, we will see how to model the problem of solidification using an Allen-Cahn type model coupled with a diffusion equation. For this, let us assume the example of pure material solidification, wherein due to heat diffusion, the melt gets cooled leading to solidification. So, in principle we are going to need two evolution equations, one for the field: order-parameter η whose evolution will indicate phase transformation from liquid ($\eta = 0$) to $\eta = 1$ that is the solid; the second, will be the evolution of the temperature field T. Lets see how we go about putting the things together. Firstly, the evolution equation for the temperature field can be derived from the conservation of the internal energy i.e,

$$\frac{\partial e}{\partial t} = -\nabla \cdot (\mathbf{J}), \qquad (1.45)$$

$$= \nabla \cdot (K\nabla T), \qquad (1.46)$$

where we have used Fourier's law, such that the flux of heat writes as $J = -K\nabla T$. The internal energy of the system e can be written as an interpolation of the internal energies of the solid e_s and the liquid e_l, using the order-parameter η. Near the melting-point, for small deviations in temperature, the internal energies of the respective phases can be approximated as,

$$e_s = C_v T \tag{1.47}$$

$$e_l = C_v T + L \tag{1.48}$$

where C_v is the specific heat and for a simplification, their values are taken the same and L is the latent heat. Using the interpolation function $h(\eta) = \eta^2 (3 - 2\eta)$, which has the properties $h(\eta) + h(1 - \eta) = 1$, one can write down the internal energy as,

$$e = e_s h(\eta) + e_l h(1 - \eta). \tag{1.49}$$

Inserting, the preceding equation in the evolution equation for the temperature Eqn.1.46, we can derive,

$$C_v \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) + L \frac{\partial h}{\partial t} \tag{1.50}$$

$$= \nabla \cdot (K \nabla T) + L \frac{\partial h}{\partial \eta} \frac{\partial \eta}{\partial t}. \tag{1.51}$$

The above equation can be interpreted as follows, the first term on the right represents the diffusive current due to the gradients in the temperature field, while the second term $L \dfrac{\partial h}{\partial \eta} \dfrac{\partial \eta}{\partial t}$, is the source term representing the release of latent-heat due to solidification represented by the advance/receding of the solidification interface given by $\dfrac{\partial \eta}{\partial t}$. Additionally, note that the source of heat is concentrated at the interface ($0 < \eta < 1$), which is precisely the region where phase-transformation occurs. Clearly, we now have an equation, which truly couples the rate of change of the temperature with all the physical details related to the process of the phase transformation, and that is applicable for the entire domain, i.e. the bulk solid, the bulk liquid and the interface. What remains is however the question as to how we can describe the evolution equation for $\dfrac{\partial \eta}{\partial t}$. For this, we make use of

the Allen-Cahn equation. What we have seen in the previous sections is
that when the two minima lie at the same energy level, the equilibrium
solution in 1D, gives rise to an interface with defined width. Of-course,
if we were to add a term to the energy such that it tilts one of the
energy levels with respect to the other, the phenomenological equations of
motion, are so constructed that the evolution of the η will be in a direction
such that one of the phases with the higher energy will be consumed in
favour of the phases with lower energy. Clearly, this is then a suitable
recipe for modeling phase-transformation. Formally, this departure from
equilibrium will induce a driving force in the system that can be expressed
as a difference of energies of the two phases. This "driving force" can be
derived from a simple Taylor series expansion of the energies of the phases
at equilibrium.

$$g_s\left(T\right) = g_s\left(T_m\right) + \frac{\partial g_s}{\partial T}\left(T - T_m\right) \qquad (1.52)$$

$$g_l\left(T\right) = g_l\left(T_m\right) + \frac{\partial g_l}{\partial T}\left(T - T_m\right), \qquad (1.53)$$

where G_s and g_l denote the free-energy densities of the solid and the liquid
respectively. By using the definition of entropy we have $s_s = -\dfrac{\partial g_s}{\partial T}$ and
$s_l = -\dfrac{\partial g_l}{\partial T}$. The difference g_s and g_l would be the departure from the
equilibrium, which we are going to refer to as the driving force which
writes as,

$$g_l\left(T\right) - g_s\left(T\right) = \left(s_s - s_l\right)\left(T - T_m\right). \qquad (1.54)$$

Recall, in the present discussion, we had assumed that the specific heats
of the the solid and the liquid phases are equal, thus $\Delta s = s_s - s_l$ can be
simply written as, L/T_m. Therefore, the driving force reads,

$$g_l\left(T\right) - g_s\left(T\right) = L\frac{\left(T - T_m\right)}{T_m}. \qquad (1.55)$$

Incorporating this as the driving force, the evolution equation for the variable η writes as,

$$\frac{\partial \eta}{\partial t} = -M \left(\frac{\partial f_o}{\partial \eta} - 2\kappa \nabla^2 \eta \right) - M \underbrace{L \frac{(T - T_m)}{T_m} \frac{\partial h(\eta)}{\partial \eta}}_{driving force} . \qquad (1.56)$$

In the preceding equation it is clear from the term "driving force" that when the temperature is below T_m, there is positive evolution of the variable η implying solidification. Similarly, one can have the reverse(melting) for $T > T_m$.

1.4.1 Modeling alloy solidification
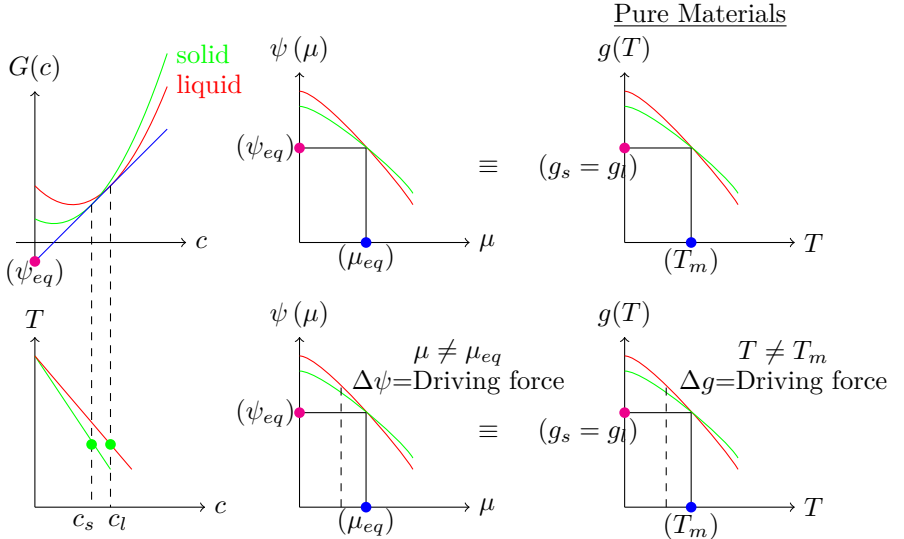
The formulation of a driving force for the case of say a binary alloy solidification can be derived analogically as for pure materials. Assuming conditions of local thermodynamic equilibrium(LTE) (which in the case

of pure materials implies that the temperature of the solid and liquid are equal at the interface), the driving force for phase transformation in alloys is the difference of the grand-potentials of the solid and the liquid phases (or the difference of the chemical potentials of any of the chemical entitities depending on whether we start from a Helmholtz free-energy density or a Gibbs-free energy density in the functional). In the present description, we adopt a Helmholtz free energy density which then results in the driving force for solidification being described as $\Psi_l - \Psi_s$ in the same manner as $g_l - g_s$ for the case of pure materials solidification. The difference is, while the state-variable in the case of the pure material solidification is the temperature T, it becomes the diffusion-potential μ in the case of binary alloy solidification. This analogy can be well appreciated from the diagramm in Fig 1.4.1. At equilibrium, the common-tangent construction gives the equilibrium compositions of the solid and liquid, which can be read from the equilibrium phase diagram. This same equilibrium can also be represented as the intersection of the grand-potential densitities $\Psi(\mu)$ expressed as a function of the diffusion-potentials μ, where $\Psi_s(\mu_{eq}) = \Psi_l(\mu_{eq})$, in the same manner as $g_s(T_m) = g_l(T_m)$ for the case of pure materials. Away from equilibrium $\mu \neq \mu_{eq}$, $\Psi_l \neq \Psi_s$, and we have a driving force for phase transition given by the difference of the grand-potential densities.

Therefore, using this above analogy we can write down the driving force for phase transition for alloys purely in terms of the diffusion potential μ by performing a Taylor series expansion around equilibrium, until first order as follows,

$$\Psi_s(\mu) = \Psi_s(\mu_{eq}) + \frac{\partial \Psi_s}{\partial \mu}(\mu - \mu_{eq}) \tag{1.57}$$

$$\Psi_l(\mu) = \Psi_l(\mu_{eq}) + \frac{\partial \Psi_l}{\partial \mu}(\mu - \mu_{eq}). \tag{1.58}$$

From the fig. 1.4.1 it is clear that we can express the grand-potential as $\Psi(\mu) = g(c(\mu)) - \mu c(\mu)$, which is the essentially the *Legendre transform* of g. Therefore, we can derive,

$$\frac{\partial \Psi}{\partial \mu} = \frac{\partial g}{\partial c}\frac{\partial c}{\partial \mu} - \mu\frac{\partial c}{\partial \mu} - c \tag{1.59}$$

$$= -c, \tag{1.60}$$

where we have used $\frac{\partial g}{\partial c} = \mu$. Clearly, then we can write the driving force for solidification $\Psi_l - \Psi_s$ as,

$$\Psi_l - \Psi_s = (c_s^{eq} - c_l^{eq})(\mu - \mu_{eq}), \tag{1.61}$$

where we have used $\Psi_l(\mu_{eq}) = \Psi_s\mu_{eq}$ and $\left.\frac{\partial \Psi_l}{\partial \mu}\right|_{\mu_{eq}} = -c_l^{eq}$ and $\left.\frac{\partial \Psi_s}{\partial \mu}\right|_{\mu_{eq}} = -c_s^{eq}$. This relation can be transmitted in the evolution equation for the phase-field variable η as,

$$\frac{\partial \eta}{\partial t} = -M\left(\frac{\partial f_o}{\partial \eta} - 2\kappa\nabla^2\eta\right) - \underbrace{M(c_l^{eq} - c_s^{eq})(\mu - \mu_{eq})\frac{\partial h(\eta)}{\partial \eta}}_{driving\,force}. \tag{1.62}$$

The time-update of the coupled variable μ can be achieved in the same manner as we derived the evolution equation for the temperature from the conservation of the internal energy. The local composition writes as,

$$c = c_s h(\eta) + c_l(1 - h(\eta)), \tag{1.63}$$

analogically as the internally energy before. More rigourously the above relation derives from the interpolation of the grand-potential densities $\Psi(\mu) = \Psi_s(\mu)h(\eta) + \Psi_l(\mu)(1 - h(\eta))$, and taking the derivative with respect to the diffusion potential lets us to the relation, $\frac{\partial \Psi}{\partial \mu} = \frac{\partial \Psi_s}{\partial \mu}h(\eta) + \frac{\partial \Psi_l}{\partial \mu}(1 - h(\eta))$.

Substituting the above relation between the compsition and the diffusion-potential into the mass-conservation equation we have,

$$\frac{\partial c}{\partial t} = \nabla \cdot (M \nabla \mu) \tag{1.64}$$

$$\left(\frac{\partial c_s}{\partial \mu} h(\eta) + \frac{\partial c_l}{\partial \mu} (1 - h(\eta)) \right) \frac{\partial \mu}{\partial t} = \nabla \cdot (M \nabla \mu) - (c_s(\mu) - c_l(\mu)) \frac{\partial h(\eta)}{\partial t}. \tag{1.65}$$

Clearly, we can can compare the evolution equations obtained in Eqn. 1.51 and Eqns. 1.65. The first term on the right-hand side of both equations represent the diffusive fluxes, while the second-term on R.H.S of both equations represent the source-terms from phase transformation. While in the case of pure material solidification this represents the latent heat of phase transformation, for the case of isothermal alloy solidification, it is the amount of mass -transfer occurring as a result of solute re-distribution during phase transformation. Thus, we are able to derive the evolution equations for phase transformation of pure materials and alloys with a similar starting point of first deriving the driving forces in terms of the relevant state variables and then coupling it with the appropriate conservation equations.