



# Generalized transport model for phase transition with memory



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## ABSTRACT

A general model for phenomenological transport in phase transition is derived, which extends Jäckle and Frisch model of phase transition with memory and the Cahn–Hilliard model. In addition to including interfacial energy to account for the presence of interfaces, we introduce viscosity and relaxation contributions, which result from incorporating memory effect into the driving potential. Our simulation results show that even without interfacial energy term, the viscous term can lead to transient diffuse interfaces. From the phase transition induced hysteresis, we discover different energy dissipation mechanism for the interfacial energy and the viscosity effect. In addition, by combining viscosity and interfacial energy, we find that if the former dominates, then the concentration difference across the phase boundary is reduced; conversely, if the interfacial energy is greater then this difference is enlarged.

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## 1. Introduction

Phase transitions in materials have long been observed, yet general models which describe the interfaces evolution in both time and space during transition are still developing. Currently, two main modelling approaches can be found in literature. The first, based on the sharp interface approach, is called the Stefan model [1] and it tracks the evolution of interface explicitly by solving a coupled multi-physics problem, which usually encompasses both energy and mass balance. However, this approach has the drawback that its numerical implementation is complex. The second approach is called the phase field method [2], and it connects the behavior of the interfaces between phases fundamental thermodynamics. This method has been extensively used in applied physics to explain microstructure evolution [3,4]. In this context, Cahn–Hilliard equation and the Allen–Cahn equation are common in literature; they are both based on a diffuse interface approach [5–7], that is, interfacial energy is included in the total free energy by taking into account the square of the concentration gradient norm. While this approach has become quite standard, there are other effects that may lead to a diffuse interface. A plausible alternative points to the memory [8] and time relaxation of the chemical driving potentials. Numerous articles on this topic have appeared in the literature. For example, early work conducted by

Crank [9] revealed that the diffusion coefficient of small molecules diffusing into polymer is history-dependent. In the 1980s, Jäckle and Frisch [10,11] showed that a time relaxation can be derived from a time convolution of chemical potential. Motivated by this insight, we postulate that in a diffusion-controlled system the constitutive laws of transport should also exhibit memory and we derive a general model that explains how memory could impact phase transition and how the Cahn–Hilliard interfacial energy interplays with path dependent contributions.

## 2. Theory

We start by taking the Cahn–Hilliard equation in the following form [12]:

$$\frac{\partial u}{\partial t} = \nabla^2 (\Phi(u) - \kappa \nabla^2 u) \quad (1)$$

where  $u$  is the dimensionless concentration, a quantity obtained by dividing the concentration by its maximum value, and  $\Phi(u)$  is a driving potential. As a consequence of interfacial energy, the overall driving potential becomes  $\Phi(u) - \kappa \nabla^2 u$ , where the coefficient  $\kappa$  is a positive number, tuning the contribution to the aforementioned interfacial energy.

To connect the current driving potential of the system to its history, we follow the work by Jäckle and Frisch [10] and suppose that a generalized driving potential exists and satisfies the following relation:

$$\mathcal{E}(u(t, \mathbf{x})) = \Phi(u(t, \mathbf{x})) - \kappa \nabla^2 u(t, \mathbf{x})$$

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**Table 1**  
List of the physical properties.

Symbol	Physical property
$u$	Normalized concentration
$\Phi(u)$	Driving potential
$\Psi(u)$	Auxiliary potential
$\mu(u)$	Homogeneous chemical potential in the regular solution model
$\mathcal{E}(u)$	Generalized driving potential
$\varepsilon$	Viscosity parameter
$\kappa$	Interfacial energy coefficient
$\tau$	Relaxation time
$g$	Interaction parameter in the regular solution model
$T$	Injection period

$$+ \int_{-\infty}^t \theta(t-s) \frac{\partial}{\partial s} (\Psi(u(s, \mathbf{x})) - \Phi(u(s, \mathbf{x}))) ds \quad (2)$$

The memory effect emerges from a convolution between an auxiliary potential  $\Psi(u)$  and the time relaxation function  $\theta(t)$ . In the remainder of the Letter, the function  $\theta(t)$  is taken from the Maxwell–Debye model [13], i.e.,  $\theta(t) = e^{-t/\tau}$ .

We substitute the terms inside the outer Laplacian of Eq. (1) with the new driving term  $\mathcal{E}(u)$  of Eq. (2). After taking the time derivative and subsequent algebraic manipulation, we obtain the following [13] expression:

$$\tau \frac{\partial^2 u}{\partial t^2} + \frac{\partial u}{\partial t} = \nabla^2 (\Phi(u) - \kappa \nabla^2 u) + \tau \nabla^2 \left( \frac{\partial \Psi(u)}{\partial t} - \kappa \nabla^2 \frac{\partial u}{\partial t} \right) \quad (3)$$

The auxiliary potential  $\Psi(u)$  is taken it to be linear with respect to  $u$ , i.e.,  $\Psi(u) = \frac{\varepsilon}{\tau} u$ , where  $\varepsilon \geq 0$ .<sup>1</sup> If we substitute  $\Psi(u)$  back into Eq. (3) and neglect the term of order  $\tau \kappa$  [13,14] then we obtain the following PDE:

$$\tau \frac{\partial^2 u}{\partial t^2} + \frac{\partial u}{\partial t} = \nabla^2 \Phi(u) - \kappa \nabla^4 u + \varepsilon \nabla^2 \frac{\partial u}{\partial t} \quad (4)$$

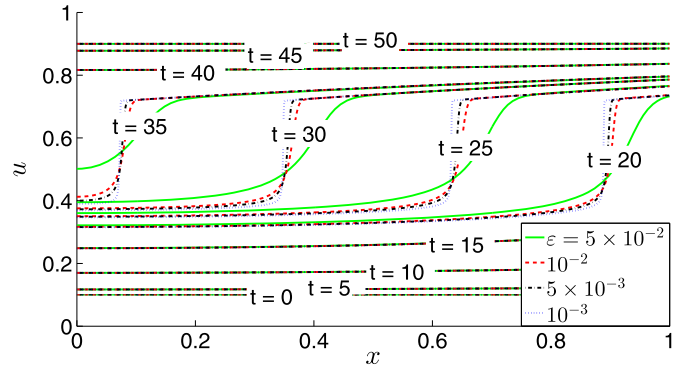
We note that the first term  $\tau \frac{\partial^2 u}{\partial t^2}$  on the left-hand side of Eq. (4) corresponds to Cattaneo’s correction to Fick’s Law [15]. This term was originally derived as a phenomenological relaxation effect of the concentration flux. The second term on the left-hand side  $-\kappa \nabla^4 u$  is the classical Cahn–Hilliard diffuse interface contribution. The last term,  $\varepsilon \nabla^2 \frac{\partial u}{\partial t}$ , which we shall refer to as viscosity contribution, can also be found in fluid flow [16] and heat transfer models [17].

To capture phase transition behavior, we choose the potential  $\Phi(u)$  to be a nonmonotonic cubic function [18]. In the remainder of the Letter we assume that the driving potential  $\Phi(u)$  is a function derived from regular solution theory of the following form [19,20]:

$$\Phi(u) = u + \frac{1}{2} g u^2 - \frac{1}{3} g u^3 \quad (5)$$

where,  $g$  is the interaction parameter in the regular solution model. In Eq. (5) we note that  $\Phi(u)$  is non-monotonic only if  $g < -4$ . The homogeneous chemical potential  $\mu(u) = \log \frac{u}{1-u} + g(u - \frac{1}{2})$  is obtained from the regular solution model [19] and it corresponds to the driving potential  $\Phi(u)$  given above. Lastly, we point to Table 1 for a list of the quantities that are used in this work.

<sup>1</sup> In the expression for  $\Psi(u)$   $\varepsilon$  is divided by  $\tau$  in order to simplify the later notation.



**Fig. 1.** Spatial distribution of the normalized concentration  $u$  during the injecting half-cycle for  $T = 100$ ,  $\kappa = 0$ ,  $\tau = 0$  and  $g = -4.2$ .

### 3. Result and discussion

First, we consider the 1D version of Eq. (4) with  $\tau \rightarrow 0$  and  $\kappa = 0$

$$\frac{\partial u}{\partial t} = \frac{\partial^2}{\partial x^2} \Phi(u) + \varepsilon \frac{\partial^2}{\partial x^2} \frac{\partial u}{\partial t} \quad (6)$$

The domain under study spans from  $x = 0$  to  $x = 1$ , where  $x = 1$  denotes the surface where the reaction takes place. We set the initial condition to be  $u(x, t = 0) = u_0$ ; at the boundary the flux is equal to 0 at  $x = 0$  and to a function  $j(t)$  at  $x = 1$ , i.e.,  $-\frac{\partial}{\partial x} \Phi(u) - \varepsilon \frac{\partial}{\partial x} \frac{\partial u}{\partial t} = j(t)$ , where  $-j(t) = \frac{A\pi}{T} \sin(2\pi \frac{t}{T})$ . The flux will directly affect the average concentration of the system  $u_{avg} = \int_0^1 u(t, x) dx$ . In fact, the average concentration within half a period is independent of the period length, since  $A = -\int_0^{T/2} j(t) dt$ . Although the boundary flux condition is unusual in the Cahn–Hilliard literature, we can find several technologically-relevant applications. For example, in the lithium-ion batteries, phase transitions occur within the electrode particles and the process can be modeled by a shrinking-core model coupled with electrochemical reactions that occur at the electrode-electrolyte interface [21,22]. Those reactions allow for lithium to be stored within the material and the corresponding flux of lithium ion may be given by the boundary condition above. While the sinusoidal form greatly simplifies this electrochemical problems, it is still relevant since many practical electrochemical excitations are sinusoidal in nature such as alternating current AC voltammetry and electrochemical impedance spectroscopy.

We start all simulations from  $u_0 = 0.1$  and choose  $A = 0.8$ , meaning that the average concentration  $u_{avg}$  in the sample varies sinusoidally from 10% to 90%. In Fig. 1 we show the local concentration evolution in the injection half period with  $T = 100$ ,  $g = -4.2$  and for  $\varepsilon = 5 \times 10^{-2}, 10^{-2}, 5 \times 10^{-3}, 10^{-3}$ .

The phase change is characterized by the presence of regions of significantly different concentrations and by a sharp transition between them. We find that due to the boundary inward flux, the region near  $x = 1$  changes phase first during the injection phase, i.e.,  $0 \leq t \leq T/2$ . And at later times the diffuse interface travels towards  $x = 0$  as shown in Fig. 1. According to Fig. 1, the sharp interface is smoothed out when  $\varepsilon$  increases, stating that the presence of  $\varepsilon$  impedes backward diffusion, which is characterized by  $D_{eff} = \frac{\partial \Phi}{\partial u} < 0$  and would occur for  $\frac{g - \sqrt{g^2 + 4g}}{2g} < u < \frac{g + \sqrt{g^2 + 4g}}{2g}$ , and in addition it ensures the problem is physically feasible. The limit with  $\varepsilon \rightarrow 0^+$  leads to a sharp interface [23], as we can deduce from the figure.

We can also track the homogeneous chemical potential  $\mu(t, x = 1)$  at the surface. This is a quantity of interest in areas such as battery research because it can be linked directly to measurable

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