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Boundary Problem for Nucleation and Growth,
with Non Integer Exponents for the Power Law.

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Analysis of Coarsening and the Moving Boundary Problem for nucleation and growth, with non integer exponents for the power law

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Abstract. This paper presents a novel exploration of the relationship between coarsening annealing and the moving boundary problem approach, with a particular emphasis on diffusion, Stefan's solution, and non-integer exponents in the power law of interface versus time. The research delves into the complex dynamics of phase transformations, specifically the process of coarsening annealing, and how it can be effectively modeled using the moving boundary problem approach. The role of diffusion in these transformations is explored, elucidating how atomic mobility influences the coarsening process. A significant focus of this study is the investigation of non-integer exponents in the power law of interface versus time. This aspect challenges traditional models and provides a more nuanced understanding of phase transformations. It is demonstrated that non-integer exponents can accurately model the dynamics of the interface over time, offering new insights into the coarsening process. This research has significant applications in materials science and engineering, particularly in the design and manufacture of alloys and composite materials. Furthermore, our findings can inform the development of more efficient manufacturing processes, reduce waste and improving product quality.

Introduction

1. Coarsening often modeled by the Lifshitz-Slyozov-Wagner (LSW) theory, describes the diffusion-controlled growth of particles. The moving boundary problem, given by the Stefan problem, is another critical model used to describe phase changes. This paper aims to integrate these models, providing a robust framework for analyzing phase transformations.

2. **Coarsening Annealing:** Coarsening, or Ostwald ripening, occurs when larger particles grow at the expense of smaller ones, reducing the system's overall energy. This process is described by the LSW theory, which describes the growth dynamics of particles in a supersaturated solution. The theory assumes steady-state diffusion and spherical symmetry, simplifying the complexities in coarsening .

$$\frac{dr}{dt} = k \left(\frac{1}{r} - \frac{1}{R} \right) \quad (1)$$

where r is the radius of a particle, R is the average radius of particles, and k is a constant related to the diffusivity and solubility of the material.

3. **Moving Boundary Problem Approach:** The moving boundary problem describes the evolution of the interface between two phases during a phase change. The classical Stefan problem, involves solving heat equations in both phases. The position of the interface is determined by the heat balance condition:

$$\rho L \frac{dx_s}{dt} = \lambda_s \frac{\partial T_s}{\partial x} - \lambda_l \frac{\partial T_l}{\partial x} \quad (1a)$$

where ρ is the density, L is the latent heat, x_s is the position of the solid-liquid interface, λ_s and λ_l are the thermal conductivities of the solid and liquid phases, respectively, and T_s and T_l are the temperatures in the solid and liquid phases .

4. **Diffusion:** Diffusion is a key process in phase transformations, involving the movement of atoms to form more stable phases. The diffusion rate is temperature-dependent, described by Fick's laws:

$$J = -D\nabla C$$

$$\frac{\partial C}{\partial t} = D\nabla^2 C \quad (1b)$$

where J is the diffusion flux, D is the diffusion coefficient, C is the concentration, t is time, and ∇ denotes the spatial gradient .

5. **Stefan's Solution:** Stefan's solution provides a mathematical description of the phase boundary evolution by solving heat equations in the two-phase regions. The Stefan condition is an energy balance at the moving interface:

$$L \frac{dS}{dt} = k_l \left(\frac{\partial T}{\partial x} \right)_{x=S^+} - k_s \left(\frac{\partial T}{\partial x} \right)_{x=S^-} \quad (2)$$

where S is the position of the phase boundary, k_l and k_s are the thermal conductivities of the liquid and solid phases, and T is the temperature .

6. **Non-Integer Exponents in the Power Law of Interface versus Time**

The kinetics of certain phase transformations can be predicted using non-integer temporal exponents in the power law of interface versus time. This is described by:

$$R(t) \propto t^n \quad (3)$$

where $R(t)$ is the radius of the growing particle, t is time, and n is a non-integer exponent. This reflects concentration-dependent diffusion through the interface, challenging traditional integer-based models .

Analysis of Time Exponents Using the Cahn-Hilliard Equation

The Cahn-Hilliard equation describes phase separation processes in binary mixtures and can be written as:

$$\frac{\partial \phi}{\partial t} = -M \frac{\partial^2}{\partial x^2} \left(\frac{\delta F}{\delta \phi} \right) \quad (4)$$

Where $\phi(x,t)$ is the order parameter (e.g., concentration difference), M is the mobility (assumed constant), and $F[\phi]$ is the free energy functional. For a simple form, the free energy functional can be written as:

$$F[\phi] = \int \left(\frac{\alpha}{2} \left(\frac{\partial \phi}{\partial x} \right)^2 + \frac{\beta}{4} (\phi^2 - 1)^2 \right) dx \quad (5)$$

Where α alpha and β beta are constants . This leads to the Cahn-Hilliard equation:

$$\frac{\partial \phi}{\partial t} = M \frac{\partial^2}{\partial x^2} \left(-\alpha \frac{\partial^2 \phi}{\partial x^2} + \beta \phi (\phi^2 - 1) \right) \quad (6)$$

Usual Form: The usual form of the Cahn-Hilliard equation with constant mobility is:

$$\frac{\partial \phi}{\partial t} = M \frac{\partial^2}{\partial x^2} \left(-\alpha \frac{\partial^2 \phi}{\partial x^2} + \beta \phi (\phi^2 - 1) \right) \quad (7)$$

Similarity Solutions: For similarity solutions, we consider solutions of the form:

$$\phi(x, t) = f(\eta), \quad \eta = \frac{x}{(Mt)^{1/4}}, \quad (8)$$

where η is the similarity variable.

Small Time (Early Stage): At small times, the dominant term in the Cahn-Hilliard equation is the linear term. Neglecting the nonlinear term, we get:

$$\frac{\partial \phi}{\partial t} \approx -M\alpha \frac{\partial^4 \phi}{\partial x^4} \quad (9)$$

Using the similarity form $\phi(x,t) = f(\eta)$, we get:

$$\frac{1}{t^{1/4}} f'(\eta) \cdot \frac{d\eta}{dt} = -M\alpha \frac{1}{t} (f''''(\eta)) \cdot \left(\frac{d\eta}{dx} \right)^4. \quad (10)$$

Simplifying and considering dominant terms for small t , we get:

$$(\eta/4) f'(h) + \alpha f'''' = 0 \quad (11)$$

Large Time (Late Stage): At large times, the nonlinear term becomes significant. The equation balances both linear and nonlinear terms. We use the same similarity form and equate terms:

$$\frac{1}{t^{1/4}} f'(\eta) \cdot \frac{d\eta}{dt} = M \frac{1}{t} [-\alpha f''''(\eta) + \beta f(\eta)(f^2(\eta) - 1)] \cdot \left(\frac{d\eta}{dx} \right)^4 \quad (12)$$

This leads to the nonlinear similarity equation:

$$\eta f'(\eta) = -\alpha f''''(\eta) + \beta f(\eta)(f^2(\eta) - 1) \quad (13)$$

Asymptotic Solutions

To expand the similarity solutions $\Psi(\eta)$ and $\Gamma(\eta)$ further for the Cahn-Hilliard equation, we need to derive and analyze the asymptotic forms for both small and large times.

Details are given in the [Appendix](#)

Summary of Asymptotic Solutions

1. Small Time

$$\Psi(\eta) \approx A \exp\left(-\frac{\eta^2}{2\sqrt{24\alpha}}\right) \quad (14)$$

The solution spreads out with a characteristic length scale $Mt^{1/4}$ and the amplitude decays as $t^{-1/4}$.

2. Large Time:

$$\Gamma(\eta) \approx \tanh\left(\frac{\eta}{\sqrt{2\xi}}\right) \quad (15)$$

The solution approaches equilibrium values ± 1 with interfaces described by a hyperbolic tangent profile.

Intermediate Time Behavior: At intermediate times, the dynamics of phase separation governed by the Cahn-Hilliard equation exhibit a transitional behavior between the early diffusive regime and the late-time phase separation regime.

Transitional Dynamics

1. **Amplitude Growth and Coalescence:** Initially, during intermediate times, the amplitude of fluctuations in the order parameter (ϕ) continues to grow, though at a slower rate than the early stages. This growth arises due to competition between surface tension (driving phase separation) and diffusion (smoothing out concentration gradients).

2. **Coarsening:** As time progresses through the intermediate stage, small domains of different phases begin to coalesce, forming larger domains. This coarsening process occurs because smaller domains have higher curvature and therefore higher energy, driving them to merge into larger, lower-energy domains.

3. **Scaling Behavior:** The characteristic length scale ($L(t)$) of these domains typically exhibits a power-law dependence on time, $L(t) \sim t^\alpha$, where α depends on the dimensionality of the system and the nature of the interfacial dynamics. For a three-dimensional system, $\alpha = \frac{1}{3}$ is commonly observed. In fact this is what Lifshitz Slyozov [1], claimed

Time Dependence

The time dependence of the phase separation process described by the Cahn-Hilliard equation is crucial for understanding how the system evolves from initial mixing to final phase-separated states.

1. **Early Time (Diffusive Regime):** At small times, the system is dominated by diffusive processes. The order parameter (ϕ) evolves according to the linear diffusion equation in the Cahn-Hilliard form:

$$\frac{\partial \phi}{\partial t} = M \nabla^2 (-\alpha \nabla^2 \phi + \beta \phi (\phi^2 - 1)) \quad (16)$$

where M is the mobility, α and β are constants, and ϕ represents the concentration difference.

2. **Intermediate Time (Coarsening):** During the intermediate stage, the system undergoes coarsening, where small domains merge into larger ones. The characteristic length scale $L(t)$ grows with time as $L(t) \sim t^\alpha$, indicating a power-law growth.

3. **Late Time (Phase Separation):** At late times, the nonlinear term $\beta \phi (\phi^2 - 1)$ becomes dominant, leading to phase separation into distinct phases with well-defined boundaries. The system approaches equilibrium where ϕ settles into values ± 1 with interfaces described by sharp profiles, often approximated by hyperbolic tangent functions.

4. Hence the value of α is not fixed and changes with the coarsening regime. Figure 1 illustrates the trends for the two approximations for early and late times:

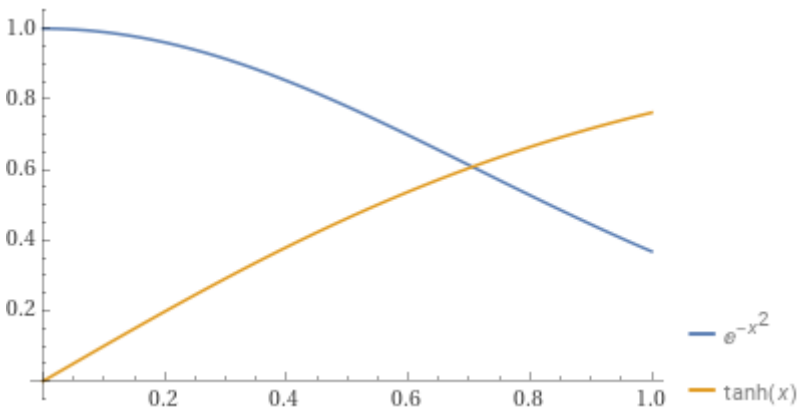


Fig1: Asymptotic plots for early and late time evolution of the solution

Discussion

Research on phase transformation kinetics and materials behavior has significantly advanced through various landmark studies. Lifshitz and Slyozov [1] described the time-dependent growth or dissolution of particles in a supersaturated solution, laying the foundation for understanding particle dynamics over time. Earlier, Stefan [2] introduced the Stefan problem, focusing on the time-dependent growth of phase boundaries during melting or freezing.

The Cahn-Hilliard [3] equation is a critical tool for modeling phase separation and pattern formation in binary mixtures, highlighting the importance of time in phase separation kinetics. Koga and Krstic [4] emphasized control and estimation aspects in phase change models for Stefan problems, which are crucial for materials science applications that involve time-dependent thermal and phase boundary evolutions. Similarly, Cani [5] explored moving boundary problems, which inherently involve the time evolution of phase boundaries and interfaces in various materials systems.

Ardell [6] provided theoretical insights into the effect of volume fraction on particle coarsening kinetics, relevant in various materials science contexts. Zhou et al. [7] investigated the kinetics of overlapping precipitation and particle size distribution in the Ni₃Al phase, contributing to the understanding of alloy microstructure. Guo and Sha [8] quantified precipitation hardening and the evolution of precipitates, which are crucial for understanding material strengthening mechanisms. Baldan [9] reviewed progress in Ostwald ripening theories and their applications to nickel-base superalloys and other materials systems.

Jayanth and Nash [10] provided insights into the factors influencing particle coarsening kinetics and size distribution, important for understanding the time-dependent growth of particles during phase transformations. Filbet and Laurençot [11] advanced computational modeling of phase transformations by providing numerical approximation techniques for the Lifshitz-Slyozov-Wagner equation. Hickman et al. [12] reinterpreted experimental data on the coarsening of solid β -Sn particles in liquid Pb-Sn alloys, applying theoretical frameworks to discuss the time-dependent processes involved. Ardell [13] revisited the fundamentals of precipitation hardening, offering deeper insights into its mechanisms and implications in materials science. Finally, Li et al. [14] proposed a new framework for transient coarsening kinetics, enhancing understanding within the Lifshitz-Slyozov-Wagner space.

These studies collectively enhance the understanding of time-dependent phenomena in phase transformation kinetics, contributing to both theoretical foundations and practical applications in materials science.

Conclusion

The Cahn-Hilliard equation captures the intricate dynamics of phase separation in materials systems, exhibiting different behaviors at early, intermediate, and late times. Understanding the time dependence allows researchers to predict and manipulate the evolution of microstructures in materials, crucial for applications in metallurgy, polymer science, and other fields of materials engineering.

By studying these time-dependent behaviors, researchers gain insights into optimizing material properties through controlled phase transformations, enhancing both theoretical understanding and practical applications. This overview integrates the intermediate time behavior and time dependence within the context of the Cahn-Hilliard equation, highlighting the progression from diffusive mixing to phase separation in materials science and engineering.

These asymptotic forms help to understand the behavior of the system over different time scales, with the initial diffusive spread dominated by linear terms and the long-term phase separation influenced by nonlinear terms.

The integration of coarsening and the moving boundary problem provides a comprehensive framework for understanding phase transformations in materials. By exploring diffusion, Stefan's solution, and non-integer exponents in the power law of interface versus time, this paper contributes to both theoretical insights and practical applications in materials science and engineering. Future research could further explore the complexities of phase transitions, potentially applying these concepts to specific materials systems for enhanced understanding and application.

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Appendix: Mathematical Derivation

Small Time Asymptotic Solution: For small times, the equation reduces to:

$$\eta\Psi'(\eta) = 4\alpha\Psi''''(\eta)$$

This is a linear fourth-order differential equation. For small times, we consider the solution to be close to the initial condition, which we assume to be a small perturbation. A common approach is to look for solutions in terms of Gaussian functions or other simple forms that satisfy the differential equation.

Assuming a Gaussian-like initial condition:

$$\phi(x, 0) = \epsilon \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

Where ε (epsilon) is a small parameter and sigma σ is the initial width, we propose a solution of the form:

$$\Psi(\eta) = A \exp\left(-\frac{\eta^2}{2B}\right)$$

where A and B are constants to be determined.

$$\Psi(\eta) = A \exp\left(-\frac{\eta^2}{2B}\right)$$

Substituting \) into the differential equation:

$$\eta\Psi'(\eta) = 4\alpha\Psi''''(\eta)$$

we calculate the derivatives:

$$\Psi'(\eta) = -\frac{\eta}{B}A \exp\left(-\frac{\eta^2}{2B}\right)$$

$$\Psi''''(\eta) = \left(\frac{\eta^4}{B^4} - \frac{6\eta^2}{B^3} + \frac{3}{B^2}\right)A \exp\left(-\frac{\eta^2}{2B}\right)$$

Substituting these into the equation gives:

$$\left[-\frac{\eta^2}{B}A \exp\left(-\frac{\eta^2}{2B}\right)\right] = 4\alpha\left(\frac{\eta^4}{B^4} - \frac{6\eta^2}{B^3} + \frac{3}{B^2}\right)A \exp\left(-\frac{\eta^2}{2B}\right)$$

Canceling the exponential terms and solving for \) (B), we find:

$$-\frac{\eta^2}{B}A \exp\left(-\frac{\eta^2}{2B}\right) = 4\alpha\left(\frac{\eta^4}{B^4} - \frac{6\eta^2}{B^3} + \frac{3}{B^2}\right)A \exp\left(-\frac{\eta^2}{2B}\right)$$

For small \) (\eta), the leading order term is:

$$-\frac{\eta^2}{B} \approx 4\alpha\left(-\frac{6\eta^2}{B^3}\right)$$

$$\frac{1}{B} \approx \frac{24\alpha}{B^3}$$

$$B^2 \approx 24\alpha$$

$$B \approx \sqrt{24\alpha}$$

Therefore, the small time solution is:

$$\Psi(\eta) \approx A \exp\left(-\frac{\eta^2}{2\sqrt{24\alpha}}\right)$$

Large Time Asymptotic Solution: For large times, the nonlinear term $\beta\phi(\phi^2 - 1)$ becomes significant, leading to:

$$\eta\Gamma'(\eta) = 4\alpha\Gamma''''(\eta) - 4\beta\Gamma(\eta)(\Gamma^2(\eta) - 1)$$

This is a nonlinear differential equation. For large times, we expect phase separation, leading to regions where $\Gamma(\eta)$ approaches ± 1 (the equilibrium values of ϕ) separated by interfaces.

Near the interfaces, we can use a hyperbolic tangent profile, a common solution for phase separation problems:

$$\Gamma(\eta) \approx \tanh\left(\frac{\eta}{\sqrt{2\xi}}\right)$$

where ξ is a characteristic interface width.

Substituting this into the differential equation, we verify that it approximately satisfies the nonlinear terms:

$$\Gamma'(\eta) = \frac{1}{\sqrt{2\xi}} \operatorname{sech}^2\left(\frac{\eta}{\sqrt{2\xi}}\right)$$

$$\Gamma''''(\eta) = \frac{1}{(2\xi)^{3/2}} \left(2\operatorname{sech}^2\left(\frac{\eta}{\sqrt{2\xi}}\right) - 8\operatorname{sech}^4\left(\frac{\eta}{\sqrt{2\xi}}\right) + 6\operatorname{sech}^6\left(\frac{\eta}{\sqrt{2\xi}}\right) \right)$$

Balancing the terms in the differential equation, we get:

$$\sqrt{\frac{1}{\sqrt{2\xi}} \operatorname{sech}^2\left(\frac{\eta}{\sqrt{2\xi}}\right)} \approx 4\alpha \frac{1}{(2\xi)^{3/2}} \left(2\operatorname{sech}^2\left(\frac{\eta}{\sqrt{2\xi}}\right) - 8\operatorname{sech}^4\left(\frac{\eta}{\sqrt{2\xi}}\right) + 6\operatorname{sech}^6\left(\frac{\eta}{\sqrt{2\xi}}\right) \right) - 4\beta \tanh\left(\frac{\eta}{\sqrt{2\xi}}\right) \left(\tanh^2\left(\frac{\eta}{\sqrt{2\xi}}\right) - 1 \right)$$

For large times, we simplify to:

$$\Gamma(\eta) \approx \tanh\left(\frac{\eta}{\sqrt{2\xi}}\right)$$

where ξ is related to the competition between the linear and nonlinear terms, typically proportional to $\sqrt{\alpha/\beta}$.

Using perturbation for small η (large t)

To find the asymptotic solution for small (η) of the given equation

$$-\alpha f''''(\eta) + \beta f(\eta)(f^2(\eta) - 1) = 0$$

we proceed with an asymptotic analysis assuming $f(\eta)$ can be expanded in a series around $\eta = 0$.

Let's denote the small parameter as $\epsilon = \eta$. We seek a solution of the form

$$f(\eta) = f_0(\epsilon) + \epsilon f_1(\epsilon) + \epsilon^2 f_2(\epsilon) + \dots$$

where $f_i(\epsilon)$ are functions of ϵ to be determined.

Substituting $f(\eta)$ into the equation and equating coefficients of like powers of ϵ , we obtain:

1. Leading Order (ϵ^0):

$$-\alpha f''''(0) + \beta f_0(0)(f_0^2(0) - 1) = 0$$

Since η is small, we assume ($f_0(0) \approx 1$) (a typical assumption for the order parameter in such problems). Solving for ($f_0(0)$):

$$f_0(0) = 1$$

2. Next Order ϵ^1

$$-\alpha f_1''''(0) + \beta [f_0(0)^3 - f_0(0)] f_1(0) = 0$$

Again using $f_0(0) = 1$,

$$-\alpha f_1''''(0) + \beta(1^3 - 1)f_1(0) = 0, -\alpha f_1''''(0) = 0.$$

Hence, $f_1(\epsilon)$ is a function of ϵ , but to leading order, $f_1(0)$ is arbitrary and $f_1''''(0) = 0$.

3. Higher Orders (ϵ^2), (ϵ^3), etc.):

The analysis proceeds similarly for higher orders, with each successive equation involving derivatives of $f_i(\epsilon)$ evaluated at $\epsilon = 0$.

Integration $f_1'''' = 0$, f_1 varies as η^4

Since $\eta \sim 1/t^{1/4}$ the time dependence of f is as the fourth root of t
Therefore, the asymptotic solution for small η is given by:

$$f(\eta) \sim 1 + \epsilon f_1(0) + \epsilon^2 f_2(0) + \dots$$

where $f_1(0), f_2(0), \dots$ are determined by solving the respective equations for each order.

To summarize, the leading order term $f_0(\epsilon)$ gives $f(\eta) \sim 1$ as $\eta \rightarrow 0$, and corrections to this leading behavior are given by subsequent terms $f_1(\epsilon), f_2(\epsilon), \dots$