# A Few Progress in Predicting Solidification Kinetics Using the Time-Dependent Ginzburg-Landau Solidification Theory

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## Introduction

The crystal–melt interface (CMI) kinetic coefficient $\mu_{\hat{n}}$ is one of the key parameters govern the solidification process. It is defined as the constant of proportionality between the steady-state solidification interface velocity $V_{\hat{n}}$ and the degree of the interface undercooling $\Delta T$. The anisotropy of kinetic coefficient among different CMI orientations, plays a leading role in the solidification microstructure evolution.

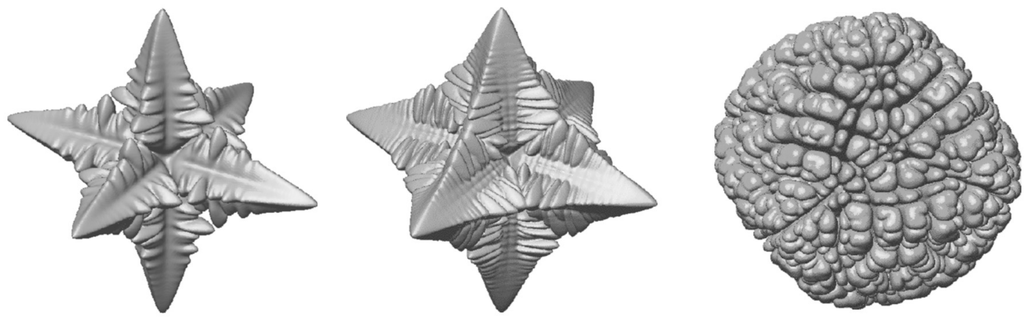


**FIG.1 Dendrite morphology for the crystal grown from melt, predicted by phase field simulations in** [*Interface Sci.* 10, 121 (2002)], **employing different magnitudes of CMI kinetic and thermodynamic anisotropy.**

## Progress I : Theoretical Extension

We extended the TDGL theory to FCC and BCO CMI systems and verified it by comparing with the non-equilibrium molecular dynamics (NEMD) simulations of a model dipolar particles.[*Cryst. Growth Des.* 20, 7862 (2020)]. $\mu_{\hat{n}} = \frac{L}{k_B T_m^2 A_{\hat{n}}}$

$$A_{\hat{n}} = \int dz \left[ \varsigma_{1a} \sum_{\vec{K}_i, u_a} \left(\frac{du_i}{dz}\right)^2 + \varsigma_{1b} \sum_{\vec{K}_i, u_b} \left(\frac{du_i}{dz}\right)^2 + \varsigma_{2a} \sum_{\vec{G}_i, v_a} \left(\frac{dv_i}{dz}\right)^2 + \varsigma_{2b} \sum_{\vec{G}_i, v_b} \left(\frac{dv_i}{dz}\right)^2 + \varsigma_3 \frac{1}{\varepsilon_0(\varepsilon_r - 1) n_0 k_B |T_C - T_m|} \left(\frac{do}{dz}\right)^2 \right]$$

Represents our formalism of TDGL theory for the crystal growth kinetic coefficients for the dipolar particle system. $\varsigma$ are the dissipative time constants, $u$, $v$, $o$ are the Ginzburg–Landau (GL) order parameters. The vacuum and relative dielectric permittivities, are included to count the free energy dissipation due to polarization concurrently process with the solidification. $T_C$ is the Curie temperature.

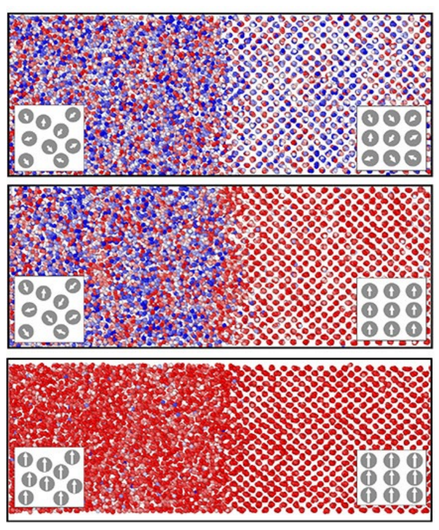


**FIG.2 Simulation snapshots for CMIs**

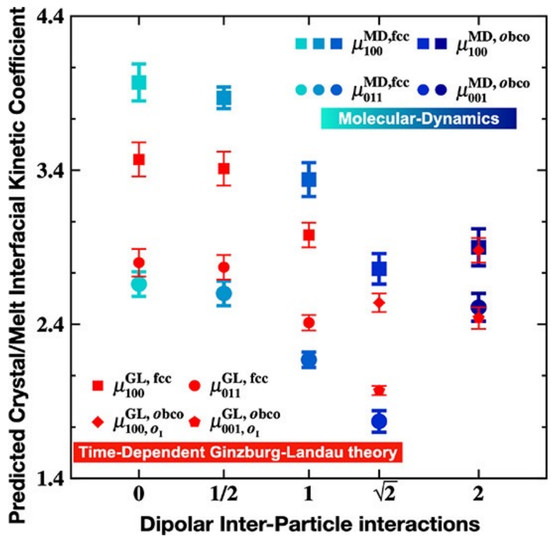



**FIG.3 Kinetic coefficients measured and predicted as function of $M^*$**

## Progress II : Kinetic Anisotropy of BCC

We predicted the kinetic coefficients for the BCC soft-sphere (SS) model systems with inverse-power repulsive potential through NEMD simulations and the TDGL theory respectively, and compared the results with the previous reported data of BCC metal systems, see in **TABLE I**.[*J. Phys.: Condens. Matter* 34, 264004 (2022)]

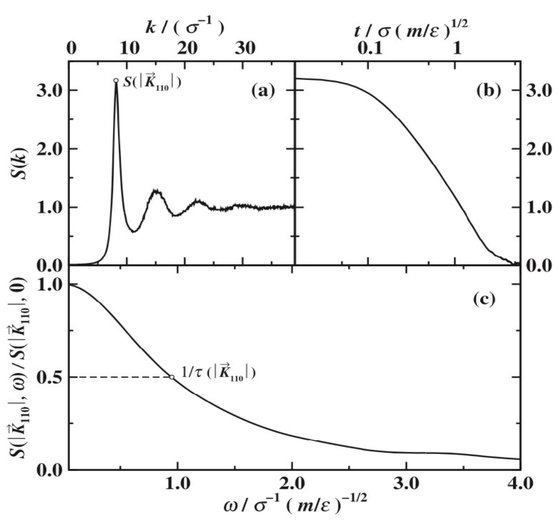



**FIG.4 Static/Dynamic structure factor**

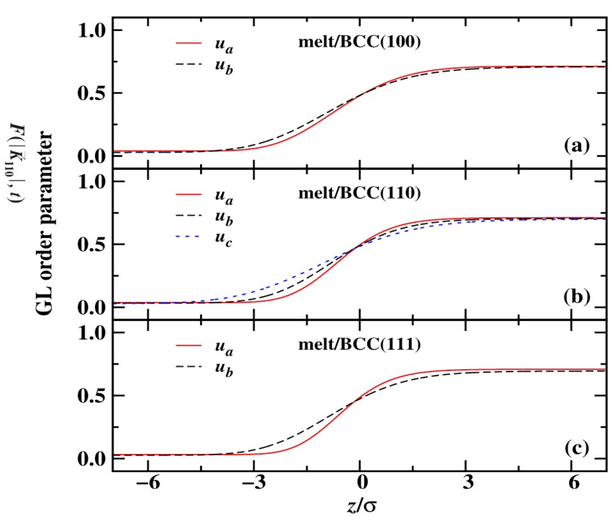



**FIG.5 GL order parameter profiles**

The calculations show the universality of the Ginzburg-Landau (GL) order parameter in same cubic structure systems. And a hypothesis that the density relaxation times for the interface melt phases to be anisotropic and material-dependent is then proposed.

## The TDGL Theory

Wu *et al* [*Phys. Rev. B* 91, 014107 (2015)] developed the time-dependent Ginzburg-Landau (TDGL) theory of solidification kinetics to quantitatively predict $\mu_{\hat{n}}$ for BCC systems,

$$\mu_{\hat{n}} = \frac{L}{k_B T_m^2 A_{\hat{n}}}, \quad A_{\hat{n}} = \int dz \left[ \varsigma \sum_{\vec{K}_i} \left(\frac{du_i}{dz}\right)^2 \right] \text{ (for BCC)}$$

where $L$ is the latent heat of fusion per particle, $A_{\hat{n}}$ is the anisotropy factor, $u_i$ is called the Ginzburg–Landau (GL) order parameter, and the dissipative time constant $\varsigma = \tau(|\vec{K}_{\langle 110\rangle}|)/S(|\vec{K}_{\langle 110\rangle}|)$.

| | $SS^{MD}$ $k_B/\sqrt{m\varepsilon}$ | $Fe^{MD}$ cm s$^{-1}$ K$^{-1}$ | $Mo^{MD}$ cm s$^{-1}$ K$^{-1}$ | $V^{MD}$ cm s$^{-1}$ K$^{-1}$ | $Fe^{GL}$ cm s$^{-1}$ K$^{-1}$ | $SS^{GL}$ $k_B/\sqrt{m\varepsilon}$ |
|---|---|---|---|---|---|---|
| $\mu_{100}$ | 2.59(9) | 78(5) | 11(1) | 9(2) | 67(6) | 2.4(1) |
| $\mu_{110}$ | 2.54(9) | 62(4) | 16(3) | 12(5) | 60(5) | 2.2(1) |
| $\mu_{111}$ | 2.13(7) | 62(2) | 12(3) | 10(1) | 51(5) | 1.9(1) |
| $\mu_{100}/\mu_{110}$ | 1.02(5) | 1.3(1) | 0.7(2) | 0.8(3) | 1.1(1) | 1.1(1) |
| $\mu_{100}/\mu_{111}$ | 1.2(1) | 1.26(9) | 0.9(2) | 0.9(2) | 1.3(2) | 1.2(1) |
| $\mu_{110}/\mu_{111}$ | 1.2(1) | 0.99(8) | 1.3(4) | 1.2(5) | 1.2(1) | 1.2(1) |

**TABLE 1 MD and GL prediction of the kinetic coefficients for a few BCC materials**

## Progress III : Algorithm Improvement

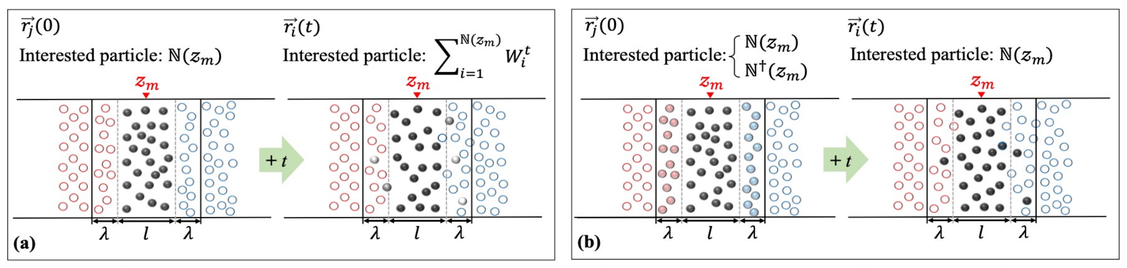
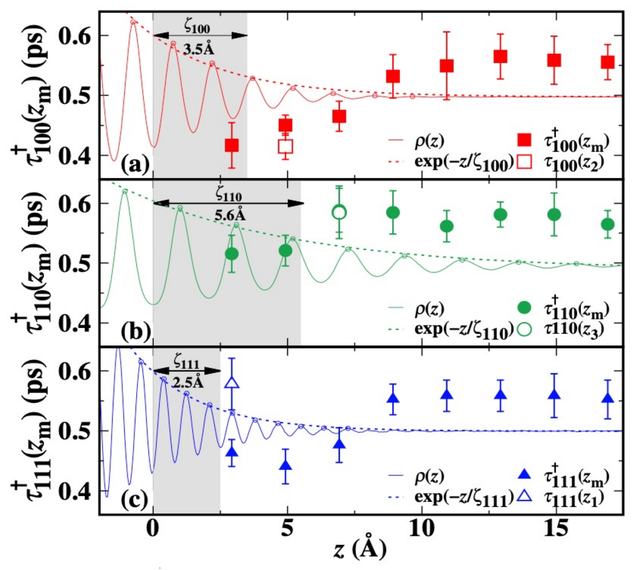



**FIG.6 Schematic diagrams for determine the local collective dynamics. Left: method by [Acta Mater. 198, 281 (2020)], Right: our method**

We introduce an algorithm for determining the density relaxation times for the interfacial liquids at CMI and its benefit in levitating the precision in the TDGL theory prediction of both $\mu_{\hat{n}}$ and the kinetic anisotropy.[*J. Chem. Phys.* 157, 084709 (2022)]

**FIG.7 Local density relaxation time profiles**




| | $\mu_{\hat{n}}^{MD}$ | $\mu_{\hat{n},M}^{GL}$ | $\mu_{\hat{n},I}^{GL}$ | $\mu_{\hat{n},I}^{\dagger GL}$ |
|---|---|---|---|---|
| $\mu_{100}$(cm/s/K) | 78(5) | 65(6) | 90(4) | 82(4) |
| $\mu_{110}$(cm/s/K) | 62(4) | 60(5) | 59(4) | 58(4) |
| $\mu_{111}$(cm/s/K) | 62(2) | 51(5) | 50(2) | 63(3) |
| $\mu_{100}/\mu_{110}$ | 1.27(16) | 1.08(13) | 1.53(12) | 1.41(12) |
| $\mu_{100}/\mu_{111}$ | 1.26(12) | 1.27(17) | 1.80(10) | 1.30(9) |
| $\mu_{110}/\mu_{111}$ | 0.99(8) | 1.18(15) | 1.18(9) | 0.92(7) |

**TABLE 2 Summary of the BCC Fe CMI kinetic coefficients and its anisotropy**

## Future Directions

- To examine whether the local collective dynamics is material dependent, for the final clarification for the reason why a similar solidification kinetic anisotropy is generally hold for FCC CMIs, yet not for BCC CMIs.
- Extend TDGL solidification theory to binary alloy system.
- Through the quantitative TDGL solidication theory, link the interatomic interaction to the CMI kinetic coefficients.

## Acknowledgements

NSFC (11504110 and 11874147), State Key Laboratory of Advanced Special Steel in Shanghai U (SKLASS 2021-10), State Key Laboratory of Solidification Processing in NWPU (SKLSP202105).

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