



Research paper

Nucleation kinetics in supercooled Ni₅₀Ti₅₀: Computer simulation data corroborate the validity of the Classical Nucleation Theory

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HIGHLIGHTS

- The crystallization kinetics in NiTi were analyzed by the Classical Nucleation Theory.
- The nucleus/supercooled liquid interfacial free energy was estimated by fitting.
- The critical crystal nuclei sizes are well described by the Classical Nucleation Theory.
- The crystal nucleation rates are well described by the Classical Nucleation Theory.

ARTICLE INFO

Keywords:

Crystallization
Nucleation
Interfacial free energy
Classical nucleation theory
Metallic alloy

ABSTRACT

Understanding the crystal nucleation mechanism and kinetics is essential for predicting and controlling numerous natural and industrial processes. However, it is extremely difficult to experimentally determine certain key parameters, such as the critical nucleus size, the interfacial free energy, and the diffusion coefficient in multicomponent liquids. In this work, we used MD data on nucleation rates and diffusion coefficient to analyze the nucleation kinetics in a Ni₅₀Ti₅₀ alloy in the framework of the Classical Nucleation Theory (CNT). Our analysis validates the CNT as a good descriptor of the crystal nucleation rates in this supercooled alloy, corroborating recent results of MD simulation of supercooled Lennard-Jones and BaS liquids.

1. Introduction

Crystallization is a ubiquitous, key phenomenon in human lives, science, and technology. Accurate measurements, calculations or simulations of the crystal nucleation mechanism and kinetics are necessary to understand and control numerous natural and industrial processes, such as ice and mineral formation, pharmaceutical drug degradation, metal solidification, crystallization of organic, metallic, semiconducting and inorganic substances, vitrification, and glass-ceramic development [1–4]. The kinetics of homogeneous crystal nucleation in supercooled liquids has frequently been (semi-quantitatively) described by the Classical Nucleation Theory, CNT. However, there has been a growing number of conflicting reports (especially on experimental versus computer simulation research) regarding its validity [5]. These conflicting views happen because it is extremely difficult to experimentally determine certain fundamental quantities, such as the (nanometric) critical nucleus, the interfacial free energy, and the diffusion coefficients in multicomponent supercooled liquids.

Recently, in a comprehensive paper [6], spontaneous crystallization of supercooled Ni₅₀Ti₅₀ alloy – a widely used shape memory material [7] – was investigated by molecular dynamics (MD) simulation. The authors obtained the nucleation time, homogeneous nucleation rate, the critical nucleus size, crystal growth rate, viscosity and diffusivity in the 700–825 K range, as well as the heat of melting Δh_m , and the equilibrium melting point T_m . However, their work focused on crystal growth rates and diffusion; they did not analyze the nucleation kinetics. Thus, their dataset provides a rare, valuable opportunity to test theories and complement their results on crystallization of this supercooled liquid alloy. Therefore, in this article, we use the MD data of Ref. [6] to analyze the crystal nucleation kinetics in the framework of the Classical Nucleation Theory. Our main objective is to test the validity of the CNT further to describe crystal nucleation rates in supercooled liquids.

2. Theory

In accordance with the Classical Nucleation Theory, in a

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Received 19 August 2019; Received in revised form 6 September 2019; Accepted 7 September 2019

Available online 09 September 2019

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Table 1

Crystallization parameters of Ni₅₀Ti₅₀ for $p = 0$ at six temperatures, T : n_* = number of atoms in the critical nucleus (corrected order); $\Delta\mu/k_B T$ = thermodynamic driving force, $W_*/k_B T$ = reduced work of critical nucleus formation, D = self-diffusion coefficient, J^{md} = nucleation rate, obtained by MD simulation.

T , K	n_* MFPT [6]	n_* Eq. (4)	$\Delta\mu/k_B T$ Eq. (3)	$W_*/k_B T$ Eq. (1)	D , $10^{-9}\text{m}^2\text{s}^{-1}$ Ref. [6]	J^{md} , $10^{34}\text{m}^{-3}\text{s}^{-1}$ Ref. [6]
700	19	21	1.23	13.7	0.94	3.36
725	23	24	1.14	14.5	1.17	3.62
750	33	27	1.05	14.1	1.57	2.22
775	34	31	0.98	14.6	1.94	1.44
800	39	35	0.90	14.6	2.50	0.42
825	63	41	0.83	16.1	2.85	0.14

These values of D vary very little (only $\sim 3X$) with temperature in this temperature range of 125 K. However, they are consistent with reported data by other authors for different metallic liquids — both in the order of magnitude and temperature variation. Moreover, the self-diffusion coefficient is relatively easy to obtain in MD simulation, since it is only necessary to work with the atom coordinates in relatively short time intervals.

Furthermore, the nucleation rates seem to vary little (only $\sim 10X$) in this temperature range of 125 K. We do not have a clear explanation for this behavior.

supercooled liquid system at constant temperature T , and pressure p , the stationary nucleation rate, J (the average number of viable crystal nuclei formed per unit time per unit volume), is given by

$$J = \rho B \exp\left(-\frac{W_*}{k_B T}\right) \quad (1)$$

where ρ [m^{-3}] is the number of atoms per unit volume in the supercooled liquid, i.e. the inverse of the molecular volume; B [s^{-1}] is a kinetic coefficient, which characterizes the average rate of the embryo-nucleus transition through a critical size; k_B is the Boltzmann constant; W_* [J] is the work of formation of a critical nucleus, given by

$$W_* = \frac{16\pi}{3} \frac{\gamma^3}{\rho_*^2 \Delta\mu^2} \quad (2)$$

where γ [J/m^2] is the interfacial free energy of the critical crystal nucleus/liquid, ρ_* [m^{-3}] is the number of atoms in the critical crystal nucleus per unit volume, $\Delta\mu$ [J] is the difference between the chemical potentials of the crystal phase and the supercooled liquid. In the case of isobaric supercooling, $\Delta\mu$ can be approximated by a widely used expression that gives an upper bound [8]

$$\Delta\mu = \frac{\Delta h_m (T_m - T)}{T_m} \quad (3)$$

The thermodynamic work of nucleation, Eq. (2), corresponds to a number of atoms in the critical nucleus n_* , given by

$$n_* = \frac{32\pi}{3} \frac{\gamma^3}{\rho_*^2 \Delta\mu^3} \quad (4)$$

In the case of the crystallization of supercooled liquids, the kinetic coefficient is given by [8]

$$B = \mathcal{Z} \frac{24Dn_*^{2/3}}{\lambda^2} \quad (5)$$

where D [m^2/s] is the self-diffusion coefficient in the supercooled liquid, λ [m] is the characteristic diffusion length or jump distance, and \mathcal{Z} is the (dimensionless) Zeldovich factor, given by

$$\mathcal{Z} = \left(\frac{W_*/k_B T}{3\pi n_*^2}\right)^{1/2} = \left(\frac{|\Delta\mu|}{6\pi n_* k_B T}\right)^{1/2} \quad (6)$$

By combining Eqs. (2), (3), and (5), we can write Eq. (1) as

$$J = \rho \mathcal{Z} \frac{24Dn_*^{2/3}}{\lambda^2} \exp\left(-\frac{16\pi}{3} \frac{\gamma^3 T_m^2}{k_B T \rho_*^2 \Delta h_m^2 (T_m - T)^2}\right) \quad (7)$$

Unfortunately, experimental determination of all physical quantities

of Eq. (7) is not yet possible. Crystallization parameter measurements, such as the size of critical nuclei, their composition, and structure are very complicated due to their nanometric size. Furthermore, the difficulty of determining the diffusion coefficient in multicomponent glass-forming liquids often leads to using the Stokes-Einstein equation, which connects the kinetic barrier of nucleation with the liquid viscosity [5]. Hence, in most experimental tests of the CNT, these hypotheses and other necessary extra assumptions could invalidate them [5].

Fortunately, however, all physical parameters of Eq. (7) in principle can be directly obtained from computer simulations. Indeed, spontaneous nucleation of a supercooled Ni₅₀Ti₅₀ alloy was investigated by a molecular dynamics simulation [6]. These authors obtained all the necessary quantities in a certain supercooling interval, but have not yet analyzed the nucleation kinetics in terms of theoretical models. Therefore, in this article, we use their data to test the validity of the CNT.

3. Results and discussion

As we briefly mentioned before, the kinetics of spontaneous crystallization of a supercooled Ni₅₀Ti₅₀ alloy was studied in Ref. [6] by classical molecular dynamics at constant (zero) pressure in the temperature range $T = (700 - 825)$ K. The melting temperature $T_m = 1325$ K at $p = 0$ was estimated using the two-phase simulation technique. The temperature dependence of the steady-state nucleation rate, $J(T)$, was obtained in their MD experiments via the mean first passage time (MFPT) method [9]. The nucleation rate J increases with decreasing temperature, reaching $(10^{33} - 10^{35}) \text{s}^{-1}\text{m}^{-3}$ in the investigated temperature range, $T = (0.53 - 0.62)T_m$.

First of all, before proceeding with the intended analysis of nucleation data from Ref. [6], we noted that the values of the critical nucleus sizes n_* , were (likely inadvertently) tabulated in an incorrect order, viz. $n_*(T)$ is a decreasing function of temperature (Table 1 in Ref. [6]). Thus, there is an obvious contradiction of the tabulated temperature dependence with the well-accepted behavior of n_* , which increases with temperature [2]. Therefore, in this article, we altered the order of n_* from Ref. [6], in line with the CNT. In the corrected table, $n_*(T)$ is a monotonically increasing function of temperature in the studied undercooling interval (our Table 1).

For the theoretical calculation of nucleation rates according to Eq. (7), it is necessary to know the values of n_* , T , \mathcal{Z} , D , ρ , T_m , Δh_m , ρ_* , and γ . Finally, a physically reasonable value of the jump distance, λ , should be chosen. The temperature dependence of the first five quantities was obtained directly from the MD simulations in Ref. [6]. The values of the equilibrium melting temperature, $T_m = 1325$ K, and the

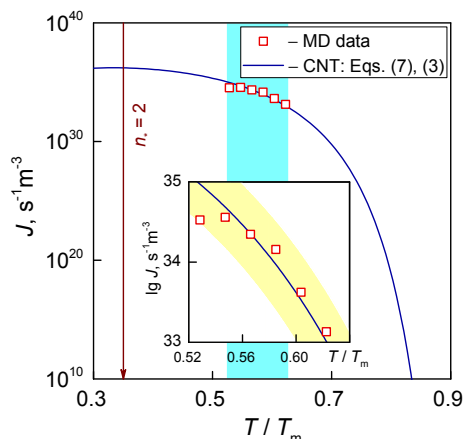


Fig. 1. Temperature dependence of the steady-state nucleation rates: squares – obtained by MD simulations [6]; solid line – fitted using CNT, Eqs. (7) and (3), with an average value of $\gamma = 0.296 \text{ J/m}^2$. The vertical line for $n_* = 2$ (number of atoms in the crystalline bcc unit cell) indicates the upper bound, $T \approx 0.35T_m$, where the CNT likely breaks down. The temperature range of homogeneous nucleation determined by MD [6] is highlighted in cyan blue and amplified in the inset. The estimated error of J due to the uncertainty in γ is shown in yellow.

heat of melting, $\Delta h_m = 0.157 \text{ eV/atom}$, were also determined in Ref. [6].

However, the value of the number of atoms per unit volume of the supercooled melt $\rho = N/V$, for which spontaneous crystallization was studied, is not given in Ref. [6]. ρ can be estimated from their data on the average time of formation of the first critical nucleus $\langle \tau \rangle^{\text{mfpt}}$, and the homogeneous nucleation rate J^{mfpt} , both obtained by the MFPT method. It was previously shown [10] that the values of $\langle \tau \rangle$ and J , independently calculated by the MFPT and mean lifetime (MLT) [11] methods, coincide within the error: $\langle \tau \rangle^{\text{mlt}} \approx \langle \tau \rangle^{\text{mfpt}}$, $J^{\text{mlt}} \approx J^{\text{mfpt}}$. In accordance with the MLT approach, we have $J^{\text{mlt}} = 1/(\langle \tau \rangle^{\text{mlt}} \cdot V)$. Knowing the total number of atoms in the system, $N = 35125$, we calculated the values of ρ as $\rho \approx N \cdot \langle \tau \rangle^{\text{mfpt}} \cdot J^{\text{mfpt}}$. Quantity ρ increases with supercooling, from $\rho = 6.5 \cdot 10^{28} \text{ m}^{-3}$ to $1.5 \cdot 10^{29} \text{ m}^{-3}$ in the studied temperature range. Note that the value of ρ at the melting line can also be estimated from the density, $d = 6.17 \text{ g/cm}^3$ [12], and the molar mass, $\mu = 106.56 \text{ g/mol}$, of the liquid phase as $\rho = (d \cdot N_A)/\mu$, where N_A is the Avogadro number. This estimate yields $\rho = 0.3 \cdot 10^{29} \text{ m}^{-3}$, which is consistent with the previous evaluation.

The number of atoms in the critical crystal nucleus per unit volume, ρ_* , was then estimated as follows. At the melting point, $T_m = 1325 \text{ K}$, the density of the macro crystal is $d = 6.45 \text{ g/cm}^3$ [7], whereas the liquid density is $d = 6.17 \text{ g/cm}^3$ [12], leading to a ratio of ≈ 1.045 . Neglecting the weak temperature dependence of ρ_* , we assumed that ρ_* is 4.5% higher than the average value of ρ within the temperature range under study, thus $\rho_* = 1.5 \cdot 10^{29} \text{ m}^{-3}$.

Previous MD simulations indicated that the jump distance λ involved in crystallization is less than the lattice constant of the critical crystal nucleus [15,16]. As the lattice constant of the NiTi-austenite (B2) phase experimentally determined [13] and by computer simulation [14] is $\approx 3.0 \text{ \AA}$, here we use a constant value of $\lambda = 2(1) \text{ \AA}$ as the jump distance in Eq. (7). It should be noted that, according to Eq. (7), a variation of 3 times in λ leads to a change in the nucleation rate of less than one order of magnitude.

For a first estimate, we neglect the (typical) weak temperature dependence of the interfacial free energy, γ . Then, according to Eq. (7), a plot of $\ln(J/D)$ versus $1/T(T_m - T)^2$ should be almost linear. Using the MD data for J , this approach yields $\rho B = 10^{41(1)} \text{ s}^{-1} \text{ m}^{-3}$ and $\gamma = 0.296(8) \text{ J/m}^2$ (see Appendix). The number between brackets

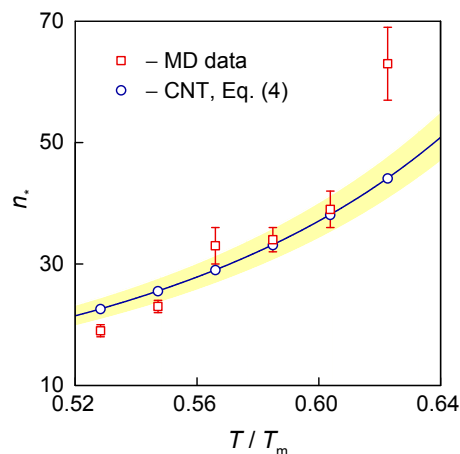


Fig. 2. Temperature dependence of the number of atoms in the critical crystal nuclei, n_* : squares – obtained by MD simulations using MFPT data [6], circles and solid line – calculated here using the CNT, Eq. (4), with a fitted average value of $\gamma = 0.296 \text{ J/m}^2$. The estimated error of n_* due to the uncertainty in γ is shown in yellow.

indicates the uncertainty in the last significant digit. This value of ρB is in good agreement with that obtained by CNT calculations using experimental data on the nucleation of metallic melts, $\rho B = (10^{38} - 10^{39}) \text{ s}^{-1} \text{ m}^{-3}$ [1]. The average value of the interfacial free energy for this particular alloy, $\gamma \approx 0.30 \text{ J/m}^2$ is somewhat higher, but not too far from the typical values reported from the analysis of homogeneous nucleation in oxide glasses, $0.10 < \gamma < 0.25 \text{ J/m}^2$ [5], and the value reported for a one-component metallic system $\gamma \approx 0.1 \text{ J/m}^2$ [17].

The theoretical value of the kinetic factor, ρB , is given by $\rho B = 24\rho \mathcal{D} n_*^{2/3} / \lambda^2$, Eq. (5). Using MD data for ρ , \mathcal{D} , and n_* from Ref. [6], and a fixed λ , we find that the quantity ρB is weakly dependent on temperature, and lies within the interval $\rho B = (10^{40} - 10^{41}) \text{ s}^{-1} \text{ m}^{-3}$. This theoretical value of ρB agrees very well with that obtained from the intercept of the linear dependence of $\ln(J/D)$ on $1/T(T_m - T)^2$.

Using the MD data for J and ρB , the work of critical nucleus formation is $W_c/k_B T = \ln(\rho B/J)$, Eq. (1). Thus, we find that within the supercooling range from $0.62 T_m$ to $0.53 T_m$ used in this research, the value of $W_c/k_B T$ decreases from 16.1 to 13.7 (Table 1). This range of $W_c/k_B T$ is typical to the values observed in other brute-force MD studies of crystallization. For example, in the case of homogeneous crystallization of a Lennard-Jones liquid, $W_c/k_B T = 11 - 22$ [16].

Finally, using Eq. (7), we calculated the theoretical nucleation rate curve, $J^{\text{cnt}}(T)$ using the fitted values of the pre-exponential factor ($\rho B = 10^{41(1)} \text{ s}^{-1} \text{ m}^{-3}$) and the interfacial free energy $\gamma = 0.296 \text{ J/m}^2$. We emphasize here that the classical approximations used by experimentalists for the kinetic coefficient, B , such as viscosity or nucleation induction times, were not used here. Instead, we used the average self-diffusion coefficient of Ni and Ti in the supercooled liquid, directly obtained by MD in Ref. [6] via the atomic mean-square displacements. Therefore, the only assumptions made for this test of CNT is the use of Eq. (3) for $\Delta\mu$, a fixed value of λ , and an average, fitted value of γ ; all the other parameters resulted directly from the MD simulations of Ref. [6].

Fig. 1 shows the temperature dependence of the steady-state nucleation rates, J^{md} , obtained directly from MD simulations [6] and the fitted curve calculated here using CNT Eq. (7). The theoretical $J(T)$ has the expected dome shape with a maximum of $J \approx 10^{36} \text{ s}^{-1} \text{ m}^{-3}$ at $T = T_m/3$.

A critical nucleus must have several unit cells to be considered a crystal. Using the MD data on $n_*^{\text{mfpt}}(T)$, we estimated the temperature

T_n , where n_* would reach its absolute minimum value, $n_* = 2$ (a single unit cell for a bcc lattice). Depending on the way the extrapolation of $n_*^{npt}(T)$ is carried out, the value of T_n lies in the range from $T = 0$ to $T \approx 0.35T_m$. Hence, the CNT should break down somewhere in this temperature range. The upper bound $T \approx 0.35T_m$ is shown by a vertical line in Fig. 1.

We also estimated the temperature interval where $W_*/k_B T = 1$, i.e. CNT would no longer be valid even if it did not collapse at a higher temperature. This temperature range, $T = (0.2 - 0.3)T_m$, was evaluated by smooth extrapolations of $W(T)$, calculated by Eq. (1) using MD data on J and ρB .

Luckily, all the analyzed “experimental” points, $J(T)$, are located at $T > 0.5T_m$, which is well above the forbidden region. The most relevant result is that the fitted values of the nucleation rates, $J^{nt}(T)$, are close, within the estimated uncertainty, to the values obtained directly by MD, $J^{md}(T)$. For this test, a fitted, average value of interfacial free energy, γ , was used, indicating that γ varies only a few percent with the temperature for this particular metallic alloy in the investigated range of state parameters. Moreover, the fitted pre-exponential parameter, ρB , agrees with its theoretical value.

In the following two paragraphs, we analyze the Zeldovich factor and the critical size of the crystal nucleus to check their consistency.

The Zeldovich factor, \mathcal{Z} , characterizes the curvature of the energy barrier versus the nucleus size at its top, taking into account not only the growth (survival) of the supercritical nuclei but also the possible dissolution of some of them. The MFPT method allows the direct calculation of this parameter. The theoretical value of \mathcal{Z} , calculated by Eq. (6), using Eq. (3) for $\Delta\mu$, monotonically increases with supercooling from 0.026 to 0.059. Whereas the MFPT values of \mathcal{Z} vary within the range 0.01–0.05. This relatively small variation has little influence on the magnitude of the calculated values of J .

The number of atoms in the critical crystal nucleus, n_* , was calculated by Eq. (4), using Eq. (3) for $\Delta\mu$ and a constant, fitted, value of the interfacial free energy, $\gamma = 0.296 \text{ J/m}^2$. Thus, in the investigated range of nucleation rates and temperatures, n_* varies from 20 to 40, and the radius $R_* = (0.32 - 0.40) \text{ nm}$. The CNT values of n_* thus agree with the MFPT determinations of Ref. 6, $n_* = 19 - 63$. In Fig. 2, the temperature dependence of the number of atoms on a crystal nucleus is shown, calculated by CNT and obtained by the MFPT method in Ref. [6].

The above described results corroborate the validity of the CNT in describing homogeneous nucleation rates in supercooled liquids when the correct values of interfacial free energy (or critical nucleus size), diffusivity, heat of melting, melting point, and jump distance are used. Similar results were recently described in tests of the CNT for supercooled LJ [18] and BaS [19] liquids.

In Ref. [6], the authors showed that crystal growth in supercooled Ni₅₀Ti₅₀ liquid is a diffusion-controlled process. Here we confirmed that the kinetics of homogeneous crystal nucleation in the same supercooled liquid also seems to be correctly described by CNT if the average self-

diffusion coefficient is used for the transport part in Eq. (1).

In this work, except for the thermodynamic driving force, $\Delta\mu$ (for which the traditional Eq. (3), was used), the fixed value of the jump distance, λ , and an average interfacial free energy, γ , all the other physical parameters needed to test the CNT were obtained directly from the MD simulations. However, as we had to swap the ordering of the published n_* shown in Table 1, this study stimulates further work. We should stress that the crystal/liquid interfacial free energy was obtained here by a fitting procedure. Independent methods for determination of γ warrants further research. Due to the problem with the original Table of Ref. [6], and the uncertainty about the calculated values of $\Delta\mu$, λ , and γ , we believe that further simulations, in a wider supercooling range, with enhanced statistics, more accurate interatomic potential [20], and also aiming to obtain $\Delta\mu$, should be performed with this same material to extend and validate the present estimates.

4. Conclusions

Using the published atomic self-diffusion coefficient directly obtained from MD simulations, calculated values of the thermodynamic driving force, and a fitted (constant) value of the interfacial free energy, we found that the crystal nucleation rates of Ni₅₀Ti₅₀ obtained by MD are well described by CNT. Therefore, our analysis corroborates the validity of the CNT for unfolding crystal nucleation rates in supercooled Ni₅₀Ti₅₀ alloy, reinforcing recent findings of MD simulations of supercooled LJ and BaS.

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.

Acknowledgments

A.O. Tıpeev acknowledges the São Paulo Research Foundation (FAPESP) for his postdoctoral fellowship (grant #2017/08350-1). E.D. Zanotto would also like to thank CNPq and FAPESP (contract CEPID #2013/07793-6) for the financial support of this research. Finally, we appreciate the critical comments from Alexander Abyzov and Vladimir Fokin.

Disclosure statement

No potential conflict of interest was reported by the authors. The authors of Ref. [6] were contacted twice regarding their incorrect Table 1, with no response.

Appendix

Using the MD data for temperature, T , equilibrium melting temperature, T_m , self-diffusion coefficient, D , and nucleation rate, J , we plotted $\ln(J/D)$ versus $1/T(T_m - T)^2$ in Fig. 1A. It shows that this dependence is almost linear. Thus, according to Eq. (7), in approximating by a straight line we can determine the pre-factor, ρB , from the intercept and the interfacial free energy, γ , from the slope. This approach yields $\rho B = 10^{41(1)} \text{ s}^{-1} \text{ m}^{-3}$ and an average value of $\gamma = 0.296(8) \text{ J/m}^2$ in the investigated supercooling range.

Using the MD data on nucleation rate, J , and viscosity, η , we calculated the $\ln(J\eta/T)$ plot – red points in Fig. 2A. This is a typical plot constructed by experimentalists when data for the diffusion coefficient are not available. In this case, due to the steep temperature dependence of η (Fig. S6a in Supplementary Materials of Ref. [6]), the $\ln(J\eta/T)$ vs. $1/T(T_m - T)^2$ plot is not a straight line. This result indicates that viscous flow and the mass transport mechanism controlling crystal nucleation in this particular metallic alloy are different.

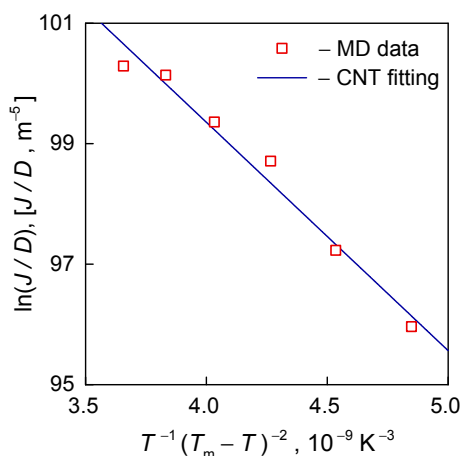


Fig. 1A. Linearized form of Eq. (7). The intercept on the y-axis compares quite well with the theoretical value calculated by CNT. The slope yields the average value of the crystal nucleus/liquid interfacial free energy, $\gamma = 0.30 \text{ J/m}^2$.

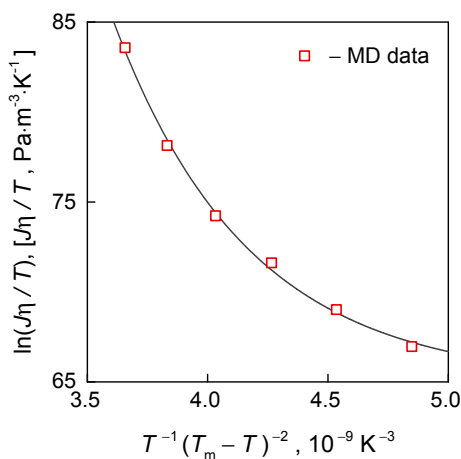


Fig. 2A. $\ln(J\eta/T)$ vs. $1/T(T_m - T)^2$ plot.

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