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LETTER TO THE EDITOR

Homogeneous nucleation for superheated crystalMasao Iwamatsu[†]Department of Computer Engineering, Hiroshima City University, 3-4-1 Ozuka-higashi,
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Abstract. Homogeneous nucleation of liquid droplets in superheated crystals is considered in order to estimate the maximum superheating of crystals. Using the previously derived universal order parameter model of the crystal–melt transition (Iwamatsu M and Horii K 1996 *J. Phys. Soc. Japan* **65** 2311), it is determined that the catastrophic homogeneous nucleation occurs at $T_{\text{super}} \sim 1.11 T_m$, where T_m is the equilibrium melting point. This numerical estimation is consistent with the results of maximum-superheating experiments.

Superheating experiments have indicated [1] that melting usually starts at heterogeneous nucleation sites such as grain boundaries and free surfaces. If heterogeneous nucleation could be avoided, it might be supposed that crystals could be superheated above their equilibrium melting points. There have been several attempts at estimating the upper limit for the superheating of crystals. For example, Fecht and Johnson [2] have argued that the upper limit is defined by the isentropic temperature T_i^s , at which the entropies for a superheated crystal and a liquid become equal. Their numerical estimation shows that this isentropic temperature occurs at $T_i^s \sim 1.38 T_m$ for Al above the thermodynamic melting point T_m . Following the ideas of Fecht and Johnson, Lele *et al* [3] have estimated the isentropic temperature T_i^s for all of the alkali metals from Li to Cs. They have found these alkali metals to have a rather high superheating temperature $T_i^s \sim 2.0 T_m$, and they have argued that vaporization will intervene before this metastability limit is reached. Subsequently, Tallon [4] has suggested another inner instability point T_i^v , where the entropy for a superheated crystal becomes equal to that for a glass (a diffusionless liquid) rather than that for a liquid. On the basis of a numerical estimation of the entropy difference between liquid and glass, Tallon has suggested that this inner instability point T_i^v is slightly lower than T_i^s . However, the superheating observed experimentally in metallic crystals is typically $T_{\text{super}} \sim 1.1 T_m$ [5], which is far below the predictions based on entropic instability.

Recently, Lu and Li [5] have proposed a new type of instability related to the catastrophic homogeneous nucleation [6] of melts in superheated crystals. They have found that a massive homogeneous nucleation catastrophe occurs in superheated crystals at a critical temperature $T_{\text{super}} \sim 1.2 T_m$ which is much lower than the previously estimated instability points T_i^s and T_i^v . Because they used the *classical nucleation theory* and neglected the differences between the thermodynamics of crystals and liquids, they obtained maximum superheating $\Delta T_{\text{super}} \sim 0.2 T_m$, which is close to the maximum undercooling $\Delta T_{\text{under}} \sim 0.18 T_m$ [7]. However, it has long been recognized that whereas a liquid can be easily undercooled so long as heterogeneous nucleation is avoided, a crystal cannot be superheated [8]. In fact, such

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an asymmetry has already been predicted for liquid–vapour nucleation, where the sign of the so-called Tolman length [9] for the surface tension of liquid droplets becomes negative. Such an asymmetry is further confirmed by recent theoretical calculations [10]. On the basis of the density functional theory of the crystal–liquid interface for bcc metals [11], we have constructed a universal order parameter theory of the crystal–melt transition [14]. This model has been used to study homogeneous nucleation [14] and the steady-state kinetics of melting and freezing [15]. We have successfully explained the empirical relation between the maximum undercooling and the melting temperature proposed by Turnbull [7] half a century ago, and have found a remarkable asymmetry between the freezing and melting behaviour [15]. In particular, we can explain the observed asymmetry in the interfacial velocity of a freezing and melting front [15]. In this letter, we reconsider this *non-classical nucleation theory* on the basis of the order parameter model [14] in order to examine the homogeneous nucleation of melting in superheated crystal.

Using a simple Landau-type expansion of the density functional for the crystal–melt interface, and assuming several universal relations derived from the experimental results for various molten metals, we have derived a universal free energy ΔF of a crystal–melt system given by [14]

$$\Delta F \simeq \alpha \Delta H_f \left(\frac{T}{T_m} \right) \Delta \Phi \quad (1)$$

where $\Delta H_f = T_m \Delta S_f$ is the heat of fusion, and α is a universal constant: $\alpha \simeq 0.45$ [7] for a number of liquid metals. The non-dimensional model free-energy functional $\Delta \Phi$ is given by

$$\Delta \Phi[\phi] = \int [(\nabla \phi)^2 + \epsilon \phi^2 + \phi^2(1 - \phi)^2] d^3x \quad (2)$$

where $\phi(x)$ is the ‘crystallinity’ order parameter ($\phi = 0$ for liquid and $\phi \sim 1$ for solid) that represents the magnitude of the (110) Fourier component of the crystalline density [11]. All of the physical quantities are appropriately scaled by assuming various empirical universal formulae [14]. In particular, the undercooling $\Delta T < 0$ and the superheating $\Delta T > 0$ are expressed in terms of the non-dimensional temperature ϵ defined by [14]

$$\epsilon \simeq \frac{0.44}{T_m} \Delta T. \quad (3)$$

We should recall here that our model is based on the density functional model for bcc metal and, therefore, the target materials are alkali metals. However, the model can be applicable to other structures as well because the embryonic nucleus might have a structure similar to that of a bcc metal [12, 13].

The thermodynamic stability of a superheated crystal and an undercooled liquid can be seen from the local part of the free-energy density in (2):

$$f(\phi) = \epsilon \phi^2 + \phi^2(1 - \phi)^2 \quad (4)$$

which has three extrema at ϕ_+ , ϕ_- given by

$$\phi_+ = (3 + \sqrt{1 - 8\epsilon})/4 \quad (5)$$

$$\phi_- = (3 - \sqrt{1 - 8\epsilon})/4 \quad (6)$$

and $\phi = 0$. The thermodynamic stability limits, referred to as the spinodal points, are defined when the two minima lose absolute stability, which occurs at $\epsilon_{\text{spiu}} = -1$ (undercooling) and $\epsilon_{\text{spis}} = 1/8$ (superheating) (figure 1). It can be seen in figure 1 that the crystalline order is destroyed relatively easily. This asymmetry comes from the functional form of the model free energy (4), where the order parameter ϕ is coupled with the temperature ϵ in the form $\epsilon \phi^2$.

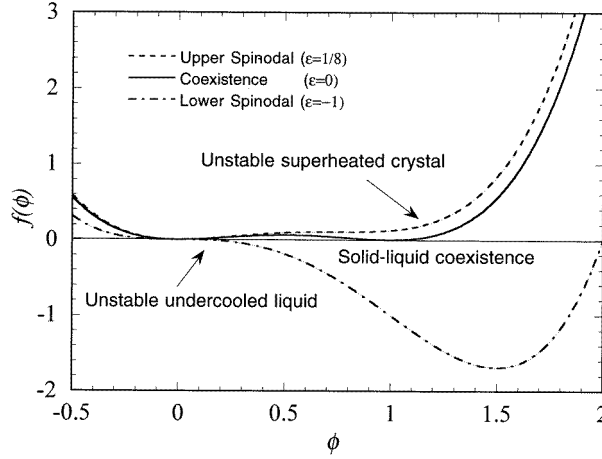


Figure 1. The model free-energy density $f(\phi)$ at the upper spinodal ($\epsilon = 1/8$, upper curve), at liquid–solid coexistence ($\epsilon = 0$, middle curve) and at the lower spinodal ($\epsilon = -1$, lower curve). This model intrinsically contains the asymmetry of the liquid and solid phases.

We would like to stress that this functional form is derived not on a phenomenological basis but from the microscopic density functional theory [11].

Our simple model predicts the classical upper spinodal temperature T_{spis} for superheated crystals at

$$T_{\text{spis}} \simeq 1.28 T_m \quad (7)$$

from the universal relation (3) and $\epsilon_{\text{spis}} = 1/8$. Therefore, our thermodynamic stability limit (7) for superheated crystals predicted from our model free energy (4) is similar in magnitude to the entropic stability limit suggested by Fecht and Johnson [2], but significantly smaller than those suggested by Lele *et al* [3]. We also note again that figure 1 predicts significant asymmetry between superheating and undercooling. The *classical nucleation theory* used by Lu and Li [5], however, can predict neither these spinodals nor this asymmetry.

In the *non-classical nucleation theory*, the order parameter profile $\phi(x)$ of a spherical critical nucleus of homogeneous nucleation is determined from the stationary condition

$$\frac{\delta \Delta \Phi}{\delta \phi(x)} = 0 \quad (8)$$

which leads to a simple differential equation for spherical geometry with appropriate boundary conditions [14]. We consider the spherical crystallites in an undercooled liquid and the spherical liquid droplets in superheated crystals to be critical nuclei. The calculated density profile is ‘*soliton*’-like [14] with diffuse interfaces and, therefore, the nucleus cannot be considered to be a spherical bulk phase separated by a sharp interface as is assumed in the classical nucleation theory. The work of formation for the critical nucleus $\Delta \Phi^*$ of homogeneous nucleation is the free energy of the nucleus whose density profile satisfies the extremum given by (8).

In figure 2 we reproduce the work of formation $\Delta \Phi^*$ of a critical nucleus calculated in [14] as a function of undercooling and superheating ϵ . The magnitude of maximum undercooling and superheating may be defined as the point at which the nucleation rate becomes $\simeq 1 \text{ cm}^{-3} \text{ s}^{-1}$ [6], which is given by [14]

$$\frac{\Delta F^*}{kT} \simeq 76. \quad (9)$$

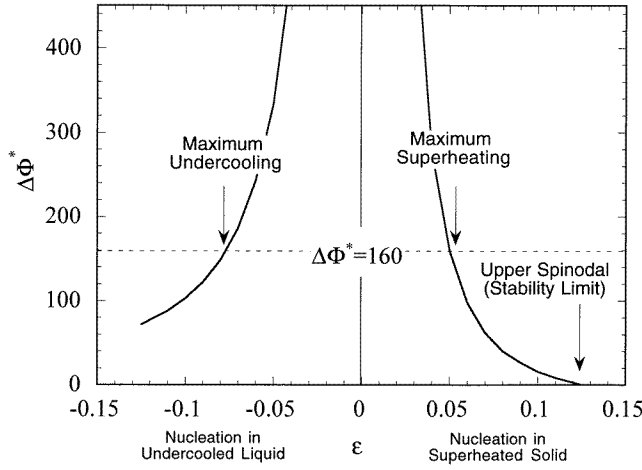


Figure 2. The calculated work of formation $\Delta\Phi^*$ of a spherical critical nucleus: the crystal cluster in an undercooled liquid ($\epsilon < 0$, left-hand portion), or the liquid droplet in a superheated crystal ($\epsilon > 0$, right-hand portion).

Table 1. Experimental data for the maximum superheating divided by the melting temperature $\Delta T_{\text{super}}/T_m$ for various metals. Note that the theoretical maximum superheating is $\Delta T_{\text{super}}/T_m \simeq 0.11$, and the thermodynamic stability limit of superheated crystal is given by $\Delta T_{\text{spis}}/T_m \simeq 0.28$.

Elements	T_m (K) [16]	ΔT_{super} (K)	$\Delta T_{\text{super}}/T_m$	Reference
Ag	1234	25	0.02	[17]
In	430	40	0.09	[18]
Bi	544	90	0.17	[19]
Pb	600	40	0.07	[20]
		40	0.07	[18]
		120	0.20	[21]

Using equation (1), this condition is written as

$$\alpha \frac{\Delta S_f}{k} \Delta\Phi^* \simeq 76. \quad (10)$$

Richard's rule [16] states that the entropy of fusion $N_{av} \Delta S_f$ (N_{av} is Avogadro's number) for liquid metals has an average value of $8.8 \text{ J K}^{-1} \text{ mol}^{-1}$, whose accuracy is about 30%, except for semiconductors and semimetals. Then the condition (9) is written as

$$\Delta\Phi^* \simeq 160 \quad (11)$$

using $\alpha = 0.45$. From figure 1, we find that the superheating and undercooling, which correspond to this condition, are roughly given by $\epsilon_{\text{super}} \simeq 0.05$ and $\epsilon_{\text{under}} \simeq -0.078$, respectively.

If we assume that equation (9) corresponds to the maximum undercooling ΔT_{under} and maximum superheating ΔT_{super} , then we find from equation (3) the universal relation for the maximum undercooling:

$$\frac{\Delta T_{\text{under}}}{T_m} \simeq 0.18 \quad (12)$$

which has been empirically derived by Turnbull [7]. Similarly, the maximum superheating is

given by

$$\frac{\Delta T_{\text{super}}}{T_m} \simeq 0.11. \quad (13)$$

In table 1, we show the recent data for maximum superheating $\Delta T_{\text{super}}/T_m$ for several metals. It seems that the magnitude of maximum superheating is mostly of the same order as our estimation $\Delta T_{\text{super}}/T_m \simeq 0.11$. Interestingly, the maximum undercooling observed for Pb is very close to our estimation of the upper spinodal $\Delta T_{\text{spis}}/T_m \simeq 0.28$ given by (7), which, however, might be merely fortuitous.

In conclusion, we have theoretically estimated the maximum superheating using an order parameter model derived from microscopic density functional theory. We found that the model predicts the universal superheating temperature $T_{\text{super}} \simeq 1.11 T_m$ by applying non-classical homogeneous nucleation theory. The thermodynamic stability limit of the superheated crystal is given by the upper spinodal located at $T_{\text{spiu}} \simeq 1.28 T_m$. Our theoretical results are consistent with the observed experimental results.

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