Liquid Nucleation at Superheated Grain Boundaries

T. Frolov and Y. Mishin

Phys. Rev. Lett. **106**, 155702 — Published 14 April 2011

DOI: 10.1103/PhysRevLett.106.155702

Liquid nucleation at superheated grain boundaries

T. Frolov[1,*] and Y. Mishin[1,†]

[1]*Department of Physics and Astronomy, MSN 3F3,*
George Mason University, Fairfax, Virginia 22030, USA

Grain boundaries with relatively low energies can be superheated above the melting temperature and eventually melt by heterogeneous nucleation of liquid droplets. We propose a thermodynamic model of this process based on the sharp interface approximation with a disjoining potential. The distinct feature of the model is its ability to predict the shape and size of the critical nucleus using a variational approach. The model reduces to the classical nucleation theory in the limit of large nuclei but is more general and remains valid for small nuclei. Contrary to the classical nucleation theory, the model predicts the existence of a critical temperature of superheating and offers a simple formula for its calculation. The model is tested against molecular dynamic simulations in which liquid nuclei at a superheated boundary were obtained by an adiabatic trapping procedure. The simulation results demonstrate a reassuring consistency with the model.

PACS numbers: 64.60.qe, 64.70.D-, 68.08.Bc, 68.35.Rh

Keywords: Grain boundary, melting, phase nucleation theory, molecular dynamics.

Solids are difficult to superheat above the melting point T_m due to the relative easiness of heterogeneous nucleation of the liquid phase on the surface, at grain boundaries (GBs) and at other defects. Diffuse-interface modeling [1–4] and molecular dynamics (MD) simulations [5] reveal two different modes of GB melting, depending on the relation between the GB free energy γ_{GB} and the solid-liquid interface free energy γ_{SL} at T_m. If $\gamma_{GB} > 2\gamma_{SL}$, the GB cannot be superheated and its thickness diverges when temperature T approaches T_m. If $\gamma_{GB} < 2\gamma_{SL}$, the GB thickness remains finite at T_m and the boundary can be superheated. Both modes of GB melting can be reproduced within a sharp interface model representing the premelted GB by a thin liquid layer with interactions between the two solid-liquid interfaces described by a disjoining potential (DP). A repulsive DP leads to continuous GB melting while a DP with a minimum reproduces the superheating. Both types of DPs were found in MD simulations of different GBs [5].

The previous DP-based models assumed uniform thickness of the stable or metastable GB, precluding direct comparison with the classical nucleation theory (CNT) [6]. Here we propose a more general model enabling calculations of the size and shape of the critical nucleus, as well as the nucleation barrier, as functions of the superheating $T - T_m$. The same quantities are computed in the heterogeneous CNT using a purely geometric treatment of the interfaces. The proposed model adopts the sharp-interface approach with a DP but makes the critical step of performing a variational calculation of the nucleus shape and size. This step was inspired by

Cahn's 1957 paper on nucleation on dislocations [7]. Furthermore, a known limitation of CNT is that it predicts a finite nucleation barrier at arbitrarily high temperatures [6, 8]. The proposed model removes this limitation by incorporating a DP which accounts for the atomistic nature of the GB in a rather general way. This leads to prediction of a critical point of superheating at which the nucleation barrier vanishes.

The GB is modeled by a liquid layer of a width W separated from the grains by two solid-liquid interfaces. The interfaces interact by a DP $\Psi(W)$ with a minimum at a thickness W_0. For definitiveness, we will adopt the Morse potential

$$\Psi(W) = (2\gamma_{SL} - \gamma_{GB}) \left[e^{-2a(W-W_0)} - 2e^{-a(W-W_0)} \right], \tag{1}$$

which has a minimum of depth $\Psi(W_0) = (\gamma_{GB} - 2\gamma_{SL}) < 0$. Here γ_{GB} and γ_{SL} refer to T_m and are assumed to be constant; a^{-1} defines the range of the potential. The free energy per unit area of a uniform GB is

$$\gamma(W) = \Delta G_V W + 2\gamma_{SL} + \Psi(W), \tag{2}$$

where ΔG_V is the difference between Gibbs free energies per unit volume of the solid and liquid phases [15]. At temperatures close to T_m, $\Delta G_V \approx H_m(T_m - T)/T_m$, where H_m is the latent heat of melting per unit volume. At T_m, $\Delta G_V = 0$ and $\gamma(W)$ reaches the minimum value γ_{GB} at $W = W_0$.

Introducing the dimensionless variables $w = W/W_0$, $\Gamma = \gamma/\gamma_{GB}$, $g = -\Delta G_V W_0/\gamma_{GB}$, $\beta = (2\gamma_{SL} - \gamma_{GB})/\gamma_{GB}$, $\alpha = aW_0$ and $\varphi = \Psi/\gamma_{GB}$, Eq. (2) becomes

$$\Gamma(w) = -gw + (1+\beta) + \varphi(w). \tag{3}$$

In these variables, length is measured in units of W_0 and free energy per unit area in units of γ_{GB}. The equilibrium GB thickness w_e is obtained from the condition $\Gamma'(w_e) = 0$, giving

$$w_e = 1 + (\beta/2g_c)\ln 2 - (\beta/2g_c)\ln\left(1 \pm \sqrt{1 - g/g_c}\right), \tag{4}$$

where $g_c = \beta\alpha/2$. The positive sign gives the stable or metastable GB thickness (minimum of Γ), whereas the negative sign corresponds to unstable equilibrium (maximum of Γ) existing only at $g > 0$ (superheating). The two solutions merge at $g = g_c$ when a critical temperature $T_c > T_m$ is reached. This temperature sets the upper bound of possible superheating of the GB. Above T_c, Γ is a monotonically decreasing function of w and the GB is absolutely unstable against melting. The GB thickness at the critical point is

$$w_e^c = 1 + (\beta/2g_c)\ln 2, \tag{5}$$

i.e., $W_e^c = W_0 + a^{-1}\ln 2$. Physically a^{-1} is comparable with W_0, thus the critical GB thickness is not expected to be much greater than W_0. Inserting (4) in (3), one obtains an analytical expression for the equilibrium GB free energy as a function of g and thus temperature.

At temperatures $T_m < T < T_c$, the superheated GB melts by heterogeneous nucleation of a liquid droplet. Calculation of the shape of the critical nucleus and the associated free energy barrier is a variation problem that can be formulated and solved as follows (see [9] for detail). For an isotropic GB, the nucleus shape is described by a function $W(r)$, where r is the radial distance parallel to the GB (Fig. 1). The excess free energy of the GB containing the nucleus, relative to the metastable GB, is

$$G = \gamma_{GB} W_0^2 \int_0^\infty \left\{ -g(w-w_e) + (1+\beta)\left[\sqrt{(w')^2/4+1} - 1\right] + \varphi(w) - \varphi(w_e) \right\} 2\pi\rho d\rho, \tag{6}$$

where $\rho = r/W_0$. The expression in the square brackets is the penalty for increase in the solid-liquid interface area relative to the plane geometry. The critical nucleus shape $w(\rho)$ corresponds to the saddle point of G, at which the variational derivative of functional (6) is zero. This leads to the Euler-Lagrange equation

$$\left[\varphi'(w) - g\right]\rho - \frac{(1+\beta)\left[w' + (w')^3/4 + \rho w''\right]}{4\left[1 + (w')^2/4\right]^{3/2}} = 0 \tag{7}$$

with the boundary conditions (1) $w' = 0$ at $\rho = 0$ and (2) $w' \to 0$ at $w \to w_e$, where w_e corresponds to the positive sign in Eq. (4). This equation has two solutions: one with $w' \equiv 0$ for the metastable state and the other for the critical nucleus. This equation has been integrated numerically to give the nucleus shape and thickness $w^* = w(0)$. Inserting the solution in (6) gives the nucleation barrier G^*.

In a two-dimensional (2D) version of this model, the nucleus shape is defined by a function $w(x)$, x being the distance parallel to the GB in the units of W_0 (Fig. 1). This function is obtained from the zero variational derivative of the excess free energy

$$G = \gamma_{GB} W_0 L \int_0^\infty \left\{ -g(w-w_e) + (1+\beta)\left[\sqrt{(w')^2/4+1} - 1\right] + \varphi(w) - \varphi(w_e) \right\} dx, \tag{8}$$

(L being the GB dimension normal to x) with similar boundary conditions. Since the integrand does not depend on x explicitly, we can apply the Beltrami identity. Due to the boundary conditions, the integration constant is zero and we obtain the differential equation

$$w' = 2\sqrt{q^2 - 1} \tag{9}$$

where

$$q = \frac{-(\beta+1)}{-(\beta+1) - g(w-w_e) + \varphi(w) - \varphi(w_e)} \tag{10}$$

The nucleus thickness w^* is obtained by solving the equation $w' = 0$, i.e. $q = 1$:

$$-g(w^* - w_e) + \varphi(w^*) - \varphi(w_e) = 0. \tag{11}$$

The 2D nucleation barrier is computed by numerical integration,

$$G^* = \gamma_{GB} W_0 L (1+\beta) \int_{w_e}^{w^*} \frac{\sqrt{q^2-1}}{q} dw. \tag{12}$$

It can be shown analytically that this model reduces to CNT when the superheating is small and thus $w^* \gg 1$. In this limit the model recovers the CNT results

$$W^* = 2\frac{\gamma_{GB} - 2\gamma_{SL}}{\Delta G_V}, \tag{13}$$

$$G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\left(1 - \frac{3}{2}\cos\frac{\theta}{2} + \frac{1}{2}\cos^3\frac{\theta}{2}\right) \tag{14}$$

in the 3D model and

$$W^* = \frac{\gamma_{GB} - 2\gamma_{SL}}{\Delta G_V}, \tag{15}$$

$$G^* = -\frac{L\gamma_{SL}^2}{\Delta G_V}(\theta - \sin\theta) \tag{16}$$

in 2D. Here, θ is the contact angle satisfying the Young relation $2\gamma_{SL}\cos(\theta/2) = \gamma_{GB}$. For homogeneous nucleation, the diameter of the spherical droplet W^* and the barrier $G^*$are obtained from (13) and (14) with $\gamma_{GB} = 0$ and $\theta = \pi$.

We tested our model by atomistic simulations of the $(540)[001]$ symmetrical tilt GB in Cu with the misoriention angle 77° and the reciprocal density of coincidence sites $\sum = 41$. The GB was created in a simulation block with dimensions $20 \times 20 \times 20\,\mathrm{nm}^3$ (543296 atoms). The block had periodic boundary conditions parallel to the GB and terminated at open surfaces in the normal direction. The atoms in thin layers near the surfaces were constrained to move only in the normal direction, imposing zero normal stress. The atomic interactions were modeled with an embedded-atom potential [10] giving $T_m = 1327$ K and $H_m = 9.72$ eV/nm^3. The GB structure consists if an array of closely spaced $(1/2)[110]$ dislocations aligned parallel to the tilt axis [001] (Fig. 4d in [11]).

The MD simulations were performed in the canonical and microcanonical ensembles for times up to 50 ns. The temperature was increased by steps starting from 0 K. The block was pre-expanded according to the thermal expansion factor and annealed to achieve point-defect equilibrium at each temperature. At temperatures approaching 1410 K, spontaneous melting was observed by nucleation and growth of a liquid droplet on the GB. Since it was impossible to superheat the GB above 1410 K, it was concluded that this temperature was approximately equal to the critical point T_c. The following procedure was applied to stabilize the critical nuclei below T_c. As soon as a nucleus began to grow in a canonical simulation, we switched the ensemble to microcanonical. The droplet slightly grew or shrunk until the temperature stabilized at a new value and the melting/crystallization stopped due to the adiabatic constraint. This resulted in an equilibrium finite-size droplet at a certain temperature T and nearly zero

stress. This droplet represented the critical nucleus at the temperature T stabilized by the adiabatic trap. To obtain a critical nucleus at a different superheating temperature, a small amount of heat was removed or added to the system followed by re-equilibration.[16] To visualize the nuclei, each atom was assigned to either the solid or the liquid according to its energy relative to a chosen discrimination level. This method was used to compute the GB and nucleus thicknesses W_e and W^*. Alternatively, the centrosymmetry method was applied to produce images revealing the nucleus shape and the surrounding vacancies (Fig. 2) [9]. To model a heterogeneous 2D nucleation, the block dimension parallel to the tilt axis was reduced by half, resulting in nucleation of droplets whose thickness was uniform in that direction. A similar procedure was used to create nearly spherical droplets representing homogeneous nuclei in the lattice. (The residual stresses were removed by a short isothermo-isobaric run with a switch back to the microcanonical ensemble.)

The MD results are summarized in Fig. 3. Homogeneous melting is characterized by a large nucleus size and can be treated within the CNT. Fitting the CNT equation $W^* = -2\gamma_{SL}/\Delta G_V$ to the MD points gives $\gamma_{SL} = 0.201$ J/m^2, a number which is in good agreement with the experimental value 0.177 J/m^2 [12] and recent direct calculations for the (110) solid-liquid Cu interface, 0.199 J/m^2 [13]. Using this γ_{SL}, the proposed model and CNT were fitted to the MD data for heterogeneous nucleation in 3D and 2D by optimizing the value of γ_{GB}. The numbers obtained (in J/m^2) are 0.332 (3D model), 0.341 (2D model), 0.331 (3D CNT) and 0.333 (2D CNT). They are remarkably consistent and are reasonably below the 0 K value of 0.595 J/m^2 in agreement with the established temperature trend [14]. The contact angle computed within CNT is $\theta = 67.8^\circ$. Fig. 1 illustrates typical shapes of critical nuclei predicted by the model, which are consistent with typical shapes observed in the MD simulations (Fig. 2). The DP parameters obtained from the fit are $W_0 = 0.5$ nm and $1/a = 0.36$ nm.

Despite the close agreement of the computed γ_{GB} values, the CNT and the proposed model show qualitatively different behaviors near T_c. While the model barrier vanishes at T_c, the CNT barrier continues to decrease with temperature and remains finite and as high as 3.6 eV at T_c (Fig. 4). The probability of overcoming this barrier is small, contradicting the MD observations. Overall the model demonstrates a reassuring agreement with the MD results.

The proposed model is more general than the heterogeneous CNT [6]. While the latter is not expected to be valid when the nucleus and the barrier are small, our model continues to give physically reasonable results due to the incorporation of the atomic-scale information via the DP. The particular Morse form (1) of the DP was used as an example. As shown in [9], the results remain qualitatively similar for other smooth functions with a single minimum and a single inflection point. All such functions predict a single critical temperature of superheating, which is obtained from the condition $g = g_c$:

$$T_c = T_m + T_m \left(2\gamma_{SL} - \gamma_{GB}\right)/2H_m l, \tag{17}$$

where l is a characteristic lengthscale of the DP (on the order of a nanometer) [9]. In the future,

the model could be applied for the analysis of the triple line effect. It could also incorporate the effect of applied mechanical stresses.

We are grateful to J. W. Cahn for helpful discussions. This work was supported by the US Department of Energy, Office of Basic Energy Sciences under grant DE-FG02-01ER45871. We acknowledge stimulating discussions at coordination meetings of the Computational Materials Science Network (CMSN) program sponsored by DOE/BES.

---

* Electronic address: tfrolov@gmu.edu

† Electronic address: ymishin@gmu.edu

[1] A. Lobkovsky and J. W. Warren, Physica D **164**, 202 (2002).

[2] M. Tang, W. C. Carter, and R. M. Cannon, Phys. Rev. B **73**, 024102 (2006).

[3] J. Mellenthin, A. Karma, and M. Plapp, Phys. Rev. B **78**, 184110 (2008).

[4] Y. Mishin, W. J. Boettinger, J. A. Warren, and G. B. McFadden, Acta Mater. **57**, 3771 (2009).

[5] S. J. Fensin et al., Phys. Rev. E **81**, 031601 (2010).

[6] D. A. Porter and K. E. Easterling, *Phase transformations in metals and alloys*, Taylor and Francis, second edition, 2004.

[7] J. W. Cahn, Acta Metall. **5**, 169 (1957).

[8] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).

[9] See EPAPS document No. xxx for further details of the model and animations of the growth and stabilization of liquid nuclei on grain boundaries in md simulations.

[10] Y. Mishin, M. J. Mehl, D. A. Papaconstantopoulos, A. F. Voter, and J. D. Kress, Phys. Rev. B **63**, 224106 (2001).

[11] J. W. Cahn, Y. Mishin, and A. Suzuki, Acta Mater. **54**, 4953 (2006).

[12] L. E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley, Reading, MA, 1975.

[13] T. Frolov and Y. Mishin, Phys. Rev. B **79**, 45430 (2009).

[14] S. M. Foiles, Scripta Mater. **62**, 231 (2010).

[15] In this model we neglect the volume effect of melting , so that ΔG_V is proportional to the chemical potential difference between the phases.

[16] This method stabilizing critical nuclei by adiabatic trapping is novel and can be applied to other materials and phase nucleation phenomena in the future.

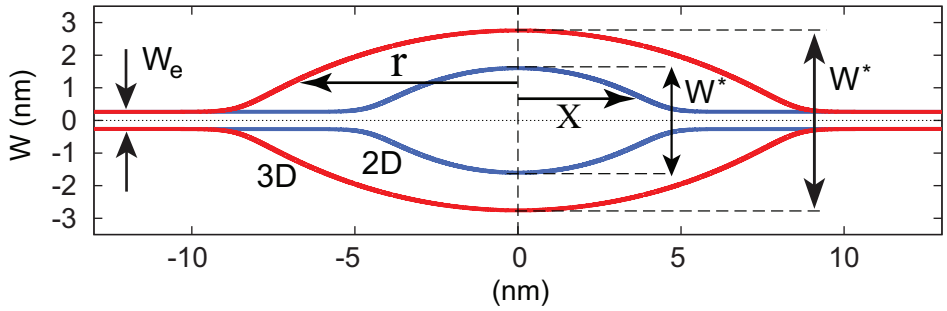

Figure 1: Shapes of the critical nuclei computed from the model at $T = 1349$ K for the 2D (blue) and 3D (red) geometries. The finite thickness away from the nuclei represents the premelted boundary and equals 0.5 nm at T_m.

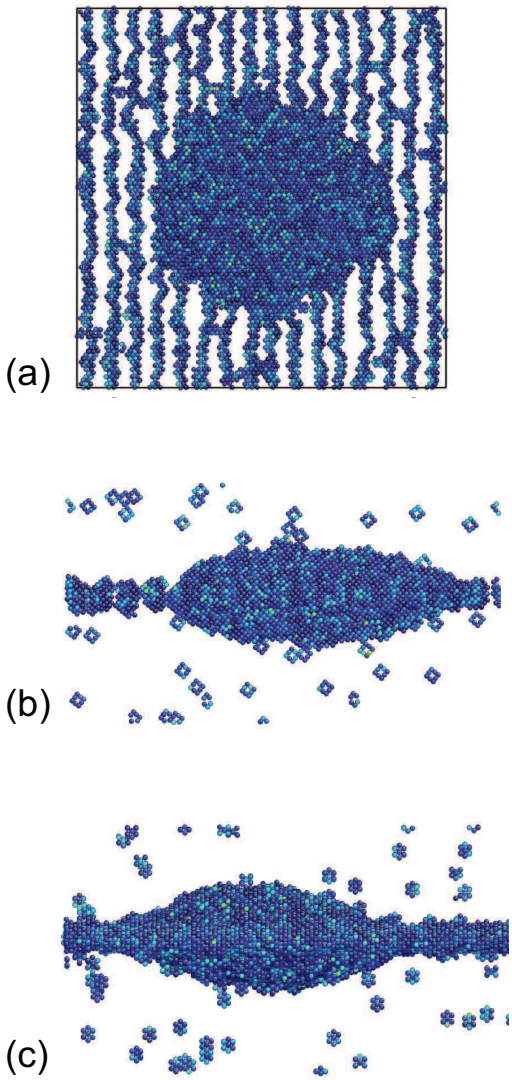

Figure 2: Premelted grain boundary (GB) with a three-dimensional critical nucleus at 1357 K stabilized by adiabatic trapping and visualized by centrosymmetry coloring. Atoms with fcc coordination are not shown for clarity. (a) Top view; the dislocation lines are vertical. (b) Dislocation lines are normal to the page. (c) Dislocation lines are horizontal. Although not apparent due to fluctuations, the average shape of the nucleus does not possess a twofold symmetry around the GB normal due to the lack of such symmetry in the GB structure and anisotropy of γ_{SL}. The dots in the grains mark vacancies. See supplementary materials for animations [9].

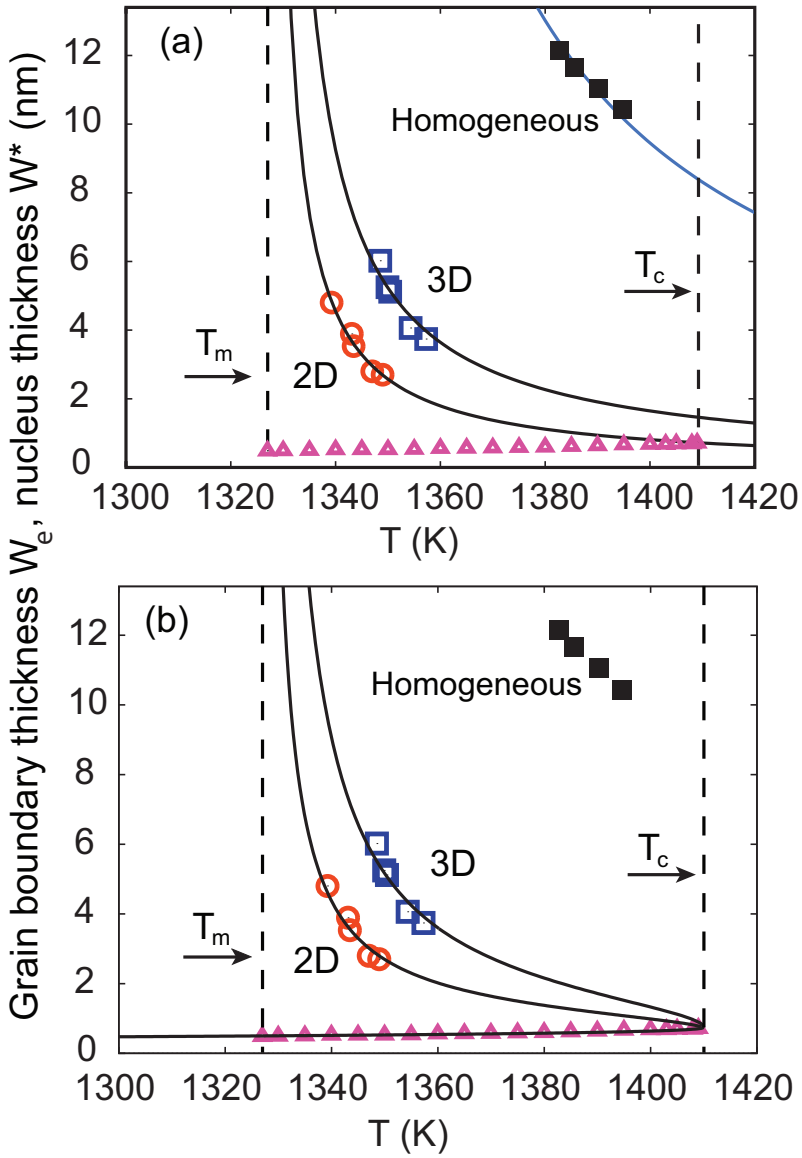

Figure 3: The grain boundary (GB) thickness W_e (△) and the nucleus thickness W^* (□,◯) as functions of temperature. The points are results of molecular dynamics (MD) simulations. The GB thickness increases from 0.5 nm at T_m to 0.75 nm at T_c. In (a) the lines are fits of the classical nucleation theory (CNT) to the MD data; in (b) the lines are fits of the proposed model. Note the qualitative difference at high temperatures.

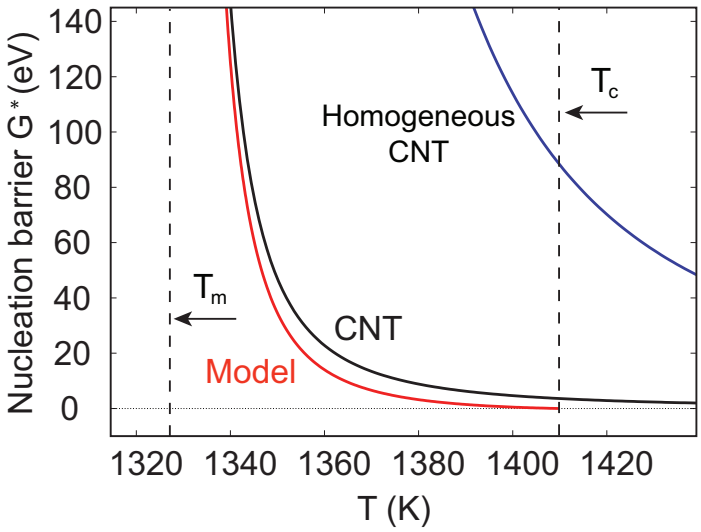

Figure 4: Nucleation barriers computed from the proposed model and classical nucleation theory (CNT). The model predicts a critical temperature of superheating at which the barrier vanishes and the boundary becomes unstable against melting. Note that CNT gives a finite barrier at all temperatures and is not capable of predicting a critical temperature.