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Homogeneous *vs.* Heterogeneous Nucleation Modes of Solidification at Strong Driving Force Conditions

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Abstract: We summarize and numerically estimate, in a simple form, the major relationship and parameters of classical nucleation theory (CNT) toward the problem of solidification under extreme conditions of large driving force. The effect of reduced quantities such as the interfacial free energy and chemical potential difference is explored under both heterogeneous and homogeneous modes of nucleation. It is shown when under strong driving force conditions, total homogeneous nuclei production within the bulk may exceed the production by heterogeneous nucleation sources.

Discrimination between homogeneous and heterogeneous nucleation was the subject of numerous studies since beginning of the 20th century. In earlier experiments, to exclude the hetero-nucleation of the melt, solution or vapor were thoroughly purified physically and chemically, and selection of the maximal undercooling achieved in series of experiments were practiced. “Sterilization” of the samples from the active nucleation centers in the fluids or on the container walls was also used by essentially overheating the melt or solution above the melting or saturation temperatures to reach maximal deviation from equilibrium before fast crystallization of the whole sample is triggered by nucleation. See, for example the books: [J.A. Danzig and M. Rappaz, “Solidification” EPFL/CRC Press (2009); A.A. Chernov, “Crystal Growth (Modern Crystallography III)”, Springer Series in Solid State, Vol. 36, (1984); J.W. Mullin, “Crystallization”, 4th Edition, Elsevier (2001); I. Gutzov and J.S. Schmelzer, “The Vitreous State”, Springer, (1995)] and the review [S. Toshev, “Homogeneous nucleation” in P. Hartman, ed. “Crystal Growth: an introduction”, North Holland, (1973), pp. 1-49].

The most effective technique was pioneered by D. Turnbull in 1950s. In this technique, the sample melt is separated into microns-scale droplets spread in a nucleation-inert

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environment so that the active nucleation centers may be eliminated because the droplets containing these centers are observed to crystallize earlier then the contamination-free droplets and excluded from further analyses. Numerous experiments with pure simple melts (mainly metals) led to the general conclusion that the maximal reached relative undercooling is $(T_m - T)/T_m \sim 0.2 \div 0.5$ where T_m is the melting point and T is the lowest temperature resulting in nucleation for the material under investigation. The linear dependence of the nucleation rate logarithm $\ln J(cm^{-3}s^{-1})$ on the inverse square of undercooling predicted by the classical nucleation theory (CNT) showed that the crystal-melt interfacial free energy γ follows the expectable rule $\gamma = \kappa\omega^{-2/3}T_m\Delta s$ where the empirical coefficient $\kappa = 0.5 \div 0.3$, while $\omega(cm^3)$ and $\Delta s(erg/K)$ are the specific atomic volume in solid the melting entropy rise. The empirical surface energies are in general agreement with the data found by independent techniques like dihedral angles at the grain boundary grooves and melting point depression.

In the CNT, the rate of the *homogeneous nucleation* in the bulk melt is:

$$\begin{aligned} & J_{\hom}(cm^{-3}s^{-1}) = \\ & = 4\pi(2\omega\gamma/\Delta\mu)^2(\omega^{1/3})n^2\nu\exp(-E/kT)Z\exp[-16\pi\omega^2\gamma^3/3(kT)^3(\Delta\mu/kT)^2] \equiv \\ & \equiv B_{\hom}\exp[-G_c/kT] \end{aligned} \qquad (1)$$

where the dimensionless nucleation driving force g, specific free interfacial energy ε, nucleation work G_c, and the Zel'dovich delay factor Z, respectively, are:

$$g \equiv \Delta\mu/kT,\ \ \varepsilon \equiv \omega^{2/3}\gamma/kT,\ G_c/kT = 16\pi\varepsilon^3/3g^2,\ Z = (1/8\pi)(g^2/\varepsilon^{3/2})$$

$$r\_c = 2\omega\gamma/kT\Delta\mu = (2\omega\text{^}(2/3)\ \varepsilon)/g, \qquad B_{hom} = 2\varepsilon^{1/2}D/\omega^{5/3}(2)$$

The chemical potential difference $\Delta\mu(erg)$ is taken between the bulk metastable melt and the crystal. The pre-exponent in (1) is designated as $B_{\hom}$.

The exponent in (1) shows the thermodynamic probability of a fluctuation needed to create a critical size cluster of the more stable crystalline phase despite of the appearance of the interfacial energy and consequent increase in the Gibbs potential. The "critical size" (a sphere of the radius $2\omega\gamma/\Delta\mu$) means that the Gibbs potential of the system as a function of the cluster size is at maximum for this size. The height of this barrier is the minimal nucleation work. The critical cluster is supposed to be formed by addition of an extra atom to the cluster with the size only slightly to the left from the flat top of the barrier. This extra atom frustrates on the flat top of the barrier between returning to the melt and joining the crystal nucleus. These frustrations decrease Z times the average attachment flux $\sim (\omega^{1/3}/2)n\nu\exp(-E/kT)$ between the critical cluster and the melt where n is the atomic number density in the melt while ν and E respectively are the vibration frequency of a melt atom at the cluster interface and the local barrier for hopping to the cluster. This flux may be rewritten via the melt self-diffusivity $D=\omega^{2/3}\nu\exp(-E/kT)$. Typically, for simple liquids at room condition, $D=10^{-5}cm^2/s$ and is a weak function of temperature. Alternatively, the exchange flux may be replaced by kinetic coefficient of proportionality between the growth rate R of an atomically rough interface and undercooling immediately at the interface. This undercooling and thus the coefficient is very difficult to measure (especially for simple metals characterized by the largest kinetic coefficients). However, density wave theory [L.V. Mikheev, A.A. Chernov, “Mobility of a diffuse simple metal – melt interface”, *J. Crystal Growth* 112:591 (1991)] gives an estimate $R\approx 2(kT/m)^{1/2}g$, not far away from some measurements and modeling.

At the real atomically rough crystal-melt interface, it is hard to distinguish between the “melt” and “solid” atoms since such interface is known to be a continuous transition between order and disorder – within several lattice layers. Therefore, more sophisticated approach beyond the CNT model is needed to describe the nucleus formation kinetics, both the pre-factor and the nucleation work of which small error results in much bigger change in the nucleation rate. For example, the exchange flux in the previous paragraph may be replaced by the ordering flux $\sim n(kT/m)^{1/2}$, like the one at the growing flat crystal-melt interface (Eq. 11 below). This subject will not be discussed here.

The ***heterogeneous nucleation*** rate may be written as,

$$J_{het}(cm^{-3}s^{-1})=(n_i\theta_i/n)B_{\hom}\exp[-16\pi\varepsilon^3 f/3g^2] \tag{3}$$

Here $n_i(cm^{-3})$ is the average volume density of the active nucleation centers that are “wet” by the crystal preferentially as compared to melt and therefore diminish the nucleation work f times. In other words, the number n of atoms as the points around which a nucleus may be formed is replaced by the number of centers n_i . In the CNT continuous approximation, the hetero-nucleus is just a part of the homogeneous nucleus cut off by the surface on which the active center is located. The smaller the part remained from the homo nucleus the less is the nucleation work and the part θ_i of its surface in contact with the melt. For example, if ϑ is the effective "wetting angle" between the (spherical) crystal and the flat active substrate surface (e.g. crucible wall, foreign particulates, and other impurities) then the work is reduced $f(\vartheta)$ times,

$$f(\vartheta) = (1-\cos\vartheta)^2(2+\cos\vartheta)/4 \qquad (4)$$

For the good wetting, $\vartheta = 0$ and f =0, so that the center is the most active – this is just a seed. For the poor wetting, that is, for passive foreign surfaces/center, $\vartheta = -\pi$ and f=1. Reduction of the cluster surface $0 < \theta_i < 1$ leads to reduction of the exchange flux at the subcritical cluster – melt interface.

Thus, the ratio of the nucleation rates,

$$J_{\text{hom}} / J_{het} = (n / n_i\theta_i)\exp[-16\pi\varepsilon^3(1-f)/3g^2] \qquad (5)$$

Evidently, the larger the driving force g the less important is the role of nucleation work and more important is the pre-exponent, that is, mainly kinetic factors.

To illustrate the importance of the driving force for the possibility of crossover between the homo- and hetero-nucleation, let us apply the Eq. 1 to an undercooled copper melt. At the experimental melting point $T_m = 1356K$, $\omega = 1.19.1.10^{-23}cm^3$, $n = 7.5.10^{22}cm^{-3}$, $\gamma = 200erg/cm^2$, the maximal experimentally achieved undercooling $\Delta T = T_m - T = 1356K - 1079K = 277K$. Then we get $\varepsilon = 0.58$, $g = 0.29$, nucleation work $16\pi\varepsilon^3/3g^2 = 34.4$, that is the exponent is 1.10^{-15}while the pre-exponent in Eq. 1 is

$$B_{\text{hom}} = 1.1.10^{33} 1/cm^3 s \qquad (6)$$

resulting in the $J_{\text{hom}} \approx 1cm^{-3}s^{-1}$. If a center lowering the nucleation work, say, twice is present ($f = 0.5$), the melt will crystallize nearly immediately due to the very high growth rate, $\sim 10^4 cm/s$ at $\Delta T \approx 300K$. Thus, the homogeneous nucleation rate is very low making its studying so difficult. However, the nucleation rate is the extremely steep function of the driving force g so that the nucleation work quickly decreases as the driving force rises. In particular, for Cu the nucleation work (in kT units)

$$16\pi\varepsilon^3 / 3g^2 = 1 \text{ at } g = 1.7. \tag{7}$$

At even larger driving force, the nucleation barrier nearly vanishes so that the nucleation rate is not limited by the nucleation barrier (like in spinodal decomposition of solid solutions). Instead, it is controlled by atomic kinetics remaining in the pre-exponent.

From the Eq. 5 with $\theta_i < 1$, the homogeneous nucleation might be overwhelming when

$$16\pi\varepsilon^3 / 3g^2(1-f) << \ln n / n_i \tag{8}$$

Earlier experiments with macro samples suggest the pre-exponential factor varies strongly depending on experimental conditions and may be on the order of $10^{15} cm^{-3} s^{-1}$ instead of the theoretical $\sim 10^{33} cm^{-3} s^{-1}$ or larger.

To reach the crossover between the heterogeneous to the homogeneous nucleation the activity f of the centers must be sufficiently low. However, by definition, $f \geq 0$. Therefore, this condition is met if

$$[3g^2 \ln(n./n_i)]/16\pi\varepsilon^3 > 1 \tag{9}$$

Evidently, however, that at the large driving force the growth rate may be very large so that even one center may induce crystallization of a very big sample (and not necessarily as a single crystal). For these reasons, it is probably impossible to fulfill the conditions (8) or (9) just by cooling of a macroscopic amount of melt because of low thermal conductivity – the nucleation and crystallization occurs in the course of cooling. That is why the droplet technique is widely employed to reach homogeneous nucleation in a conventional laboratory setting.

The situation is very different when shock wave compression is applied and much larger driving force $g \sim 1$ is quickly applied. In particular, at over-pressures of 3 -5 GPa in the 0.02mm thick flat cell, the ice crystals were observed in the flat water layer within the cell of which with both windows were made of quartz. On the opposite, in the cell with two sapphire windows nearly no solidification was optically recorded. The cell limited by one quartz and one sapphire window presents an intermediate case [D.H. Dolan and Y.M. Gupta. "Nanosecond freezing of water under multiple shock wave compression: optical transmission and imaging experiments", *J. Chem. Phys.* 121:9050 (2004)]. These data suggest heterogeneous nucleation on the quartz window. On the other hand, at

7GPa of pressure, ice was formed independently of the window materials [D.H. Dolan, M.D. Knudsen, C.A. Hall and C. Deeney, “A metastable limit for compressed liquid water”, *Nature Physics* 3:339 (2007)]. Thus, at 7GPa one may assume that either heterogeneous nucleation on quartz and on sapphire become met or the homogenous nucleation occurs, or both. The activity of quartz and sapphire are unknown, but it is possible to estimate the case of homogeneous nucleation. Namely, at $\gamma = 23 erg / cm^2$ and $T = 350K$ (the equilibrium temperature $T_e = 650K$), Eq. 2 provides $\varepsilon = 0.32$ while

$$g = (\Delta\omega\Delta P + \Delta s \Delta T) / kT = 1.5 \tag{10}$$

as it follows numerically from the equation of state. In this case, the criterion (8) or (9) may be qualitatively tested assuming that the heterogeneous nucleation sites on the windows may be artificially spread in the volume between the windows. These sites may have maximal surface density of $n_s \approx 10^{15} cm^{-2}$. For the water layer of $h = 0.02mm$ thick this density leads to the $\ln nh / n_s \approx 12$ on the left-hand side of the criterion (9). Then the criterion (9) becomes 82 >1, that is fulfilled with the big excess suggesting a possibility of homogeneous nucleation without special experimental precautions as well.

However, as the driving force rises the whole macroscopic concept of the CNT is becoming less applicable. Indeed, at $g = 1.5$ and $\varepsilon = 0.32$ the critical radius of a nucleus in water is

$$r_c = 2\omega\gamma / \Delta\mu = 2\omega^{1/3} \varepsilon / g = 0.55A \tag{11}$$

meaning less than one molecule size. The nucleation work, W, Eq. 2, is less than kT:

$$G_c = 0.2kT \tag{12}$$

The Zel’dovich factor in Eq. 1 is determined by the (negative) curvature of the nucleation barrier at its top, i.e. for the critical cluster:

$$Z = [\frac{1}{2\pi kT} (\frac{\partial^2 G}{\partial N^2})_{N_c}]^{1/2} = \frac{1}{8\pi} \frac{g^2}{\varepsilon^{3/2}} = 0.49 \tag{13}$$

The pre-exponent

$$B_{\mathrm{hom}o} \sim 2.10^{37} cm^{-3} s^{=1} < n / \tau_0 = \sim 10^{35} cm^{=3} s^{-1} \tag{14}$$

where $\tau_0 \sim 10^{-12} s$ is the maximal (optical) atomic vibration period.

The Eqs. (11-14) suggest that the whole CNT concept is applicable only qualitatively at the large driving force $g > 1$ when the critical nucleus is close to the molecular or atomic size and the nucleation barrier disappears. The accurate estimate depends on the dimensionless surface energy ε meaning the atomic “dangling bond” energy. On the other hand, the CNT is very productive at the driving force typical of maximal undercooling reached in numerous thermal experiments at room pressure. It is enough the critical nucleus to consist of N_c atoms equal only to several hundreds. For example, for Cu, at $\Delta T = 277K$, $\gamma = 200 erg/cm^2$ one has

$$g = 0.3,\ \ \varepsilon = 0.7.\ R_c = 1.06 nm,\ \ N_c = 425,\ \ G_c = 64kT,\ \ Z = 6.10^{-3} \qquad (15)$$

Despite of the applicability limitation at $g \sim 1$, the CNT is a good compass to orient ourselves in the parametric space.

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