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Relationship between crystallization temperature and melting temperature in crystalline materials

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The ratio of the absolute temperature at which the homogeneous nucleation rate or the crystal growth rate is maximum (T_{cmax}) to the absolute melting temperature (T_m) is analysed by two parameters: one is the ratio of the activation energy for migration (ΔE) and the heat of fusion (ΔH_m), the other is the ratio of mean molar surface energy ($\bar{\sigma}$) and ΔH_m. In analysing the crystallization data for a large number of crystalline materials such as metals and inorganic, organic and polymeric materials, the ratios $\bar{\sigma}/\Delta H_m$ and $\Delta E/\Delta H_m$ show roughly constant values for a given type of material. The constancy of the two parameters will then give rise to a constant value of T_{cmax}/T_m.

1. Introduction

It is well known that the ratio of the crystallization temperature at which the crystallization rate is maximum ($T_{\text{cmax}}(G)$ in K, as defined in Fig. 1) to the melting temperature (T_m in K) is nearly constant over many crystalline materials. For example, the ratio $T_{\text{cmax}}(G)/T_m$ for polymer crystal growth is ca. 0.8 to 0.9 [1] with an average value of 0.83 [2]. Also the ratios of the homogeneous nucleation temperature observed in small droplets of metals [3–6] and molecular liquids [4–8] to T_m lie in the range 0.7 to 0.9 and they fall close to a value of 0.82 [5]. This nucleation temperature, however, is unlike the above T_{cmax}.

According to classical crystallization theory [3, 9] for the temperature dependence of the homogeneous crystal nucleation rate (I) and that of the crystal growth rate (G) from the melt, I and G are generally described by the exponential equations

$$I = I_0 \exp\left(-\frac{\Delta E}{RT} - \frac{K_1 T_m^2}{RT(\Delta T)^2}\right) \tag{1}$$

$$G = G_0 \exp\left(-\frac{\Delta E}{RT} - \frac{K_2 T_m}{RT\Delta T}\right) \tag{2}$$

where ΔE is the activation energy for migration through the nucleus–melt interface, K_1 and K_2 are the nucleation parameters and ΔT is the degree of supercooling ($T_m - T$) where T is the crystallization temperature; I_0 and G_0 are constants and R is the gas constant. In Equations 1 and 2 the first and second terms in the exponential have opposing temperature dependences, thereby bringing about a maximum in the rate at a temperature T_{cmax} as seen in Fig. 1. The temperature T_{cmax} at which I or G is maximum can be obtained by equating to zero the derivative of Equation 1 or 2 with respect to the temperature [2].

For the maximum nucleation rate

$$\frac{T_{\text{cmax}}(I)}{T_m} = \frac{D^2 - D + 1}{D^2 + D + 1} \tag{3}$$

where

$$D = \left(\frac{B+1}{B-1}\right)^{1/3} \tag{4}$$

$$B = \left(1 + \frac{K_1}{\Delta E}\right)^{1/2} \tag{5}$$

For the crystal growth rate

$$\frac{T_{\text{cmax}}(G)}{T_m} = \frac{C}{C+1} \tag{6}$$

where

$$C = \left(1 + \frac{\Delta E}{K_2}\right)^{1/2} \tag{7}$$

The ratio T_{cmax}/T_m is only a function of the ratio $\Delta E/K$. Similar trials have been reported by Mandelkern *et al.* [10, 11], Hollomon and Turnbull [12] and Rowlands and James [13] for homogeneous nucleation; however, they could not get equations as simple as the above equations. The ratio T_{cmax}/T_m increases with an increase in the ratio $\Delta E/K$ as seen in Fig. 2; however, a large variation in $\Delta E/K$ in its high-value region causes little change in T_{cmax}/T_m. The minimum values of D and C are unity if the activation energy ΔE is put equal to zero. The minimum values of T_{cmax}/T_m for homogeneous nucleation and crystal growth are then 1/3 and 1/2, respectively. This clearly suggests that the maximum nucleation rate occurs at a temperature much lower than that of the maximum crystal growth rate.

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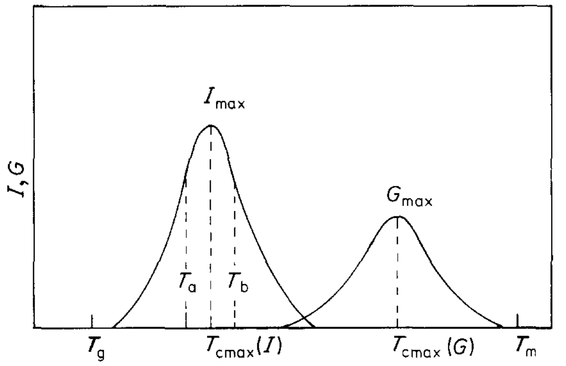

Figure 1 Schematic illustration of temperature dependence of nucleation rate (I) and crystal growth rate (G). $T_{cmax}(I)$ and $T_{cmax}(G)$ are the temperatures at which I and G are maxima, respectively. T_a and T_b are the temperatures at which nucleation rates become significantly measurable in annealing and droplet experiments, respectively.

Here, the ratios $\Delta E/K_1$ and $\Delta E/K_2$ are expressed as [2]

$$\frac{\Delta E}{K_1} = \frac{1}{n}\left(\frac{\Delta E}{\Delta H_m}\right)\left(\frac{\bar{\sigma}}{\Delta H_m}\right)^{-3} \tag{8}$$

$$\bar{\sigma} = (\sigma_e \sigma_u^2)^{1/3} \tag{9}$$

$$\frac{\Delta E}{K_2} = \frac{1}{n}\left(\frac{\Delta E}{\Delta H_m}\right)\left(\frac{\bar{\sigma}}{\Delta H_m}\right)^{-2} \tag{10}$$

$$\bar{\sigma} = (b_0 \sigma_e \sigma_u)^{1/2} \tag{11}$$

where σ is the surface free energy and the subscripts u and e denote the lateral and end-surface free energies, respectively; b_0 is the thickness of the depositing growth layer; $\bar{\sigma}$ is the mean molar surface free energy; ΔH_m is the heat of fusion and n is dependent on the mode of nucleation. Here, it is very interesting to note that the ratio of the molar surface energy to the molar latent heat of fusion ($\bar{\sigma}/\Delta H_m$, expressed hereafter as α) and the ratio of the activation energy for transport to the heat of fusion ($\Delta E/\Delta H_m$, expressed as β) are generally found to be constants for a given type of crystalline material. The constancy of α and β will then give rise to a constant value of T_{cmax}/T_m. For example, the values of $\Delta E/K_2$ lie between 10 and 40 with an average value of 23 for most polymers [2]. This results in the ratio $T_{cmax}(G)/T_m$ falling within the range 0.77 to 0.86 with an average value of 0.83 for crystal growth. The object of this paper is to explore the validity of the relationship between T_{cmax} and T_m as given by Equations 3 and 6, not only for polymers [2] but also for organic compounds, inorganic substances and metals.

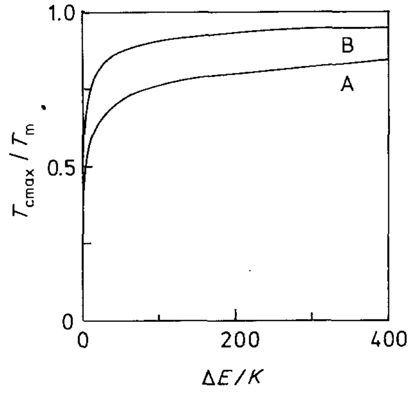

Figure 2 Ratios of the temperatures (T_{cmax} in K) at which (A) the nucleation rate and (B) the growth rate are maxima to the melting temperature (T_m in K) as a function of the ratio of the activation energy for transport (ΔE) to the nucleation parameter (K).

The main problem in relating the theory to experiments lies in evaluating $\bar{\sigma}$ and ΔE, which cannot be determined independently. The values of ΔE may be closely related to the activation energy of the self-diffusion of atoms or molecules; however, the value of $\bar{\sigma}$ cannot be measured in any other way. The constancy of α and β for many materials may be physically understandable and can be expected on independent grounds. The values of α and β and the ratio T_{cmax}/T_m will therefore be discussed in due course.

2. The ratio of $\bar{\sigma}$ and ΔH_m, α

2.1. Metals

Homogeneous nucleation in many metals has been extensively studied by Turnbull [3, 4] using the droplet technique. He has analysed the nucleation rates in metals as a function of temperature and found the ratio α to be approximately constant with a value of about 0.45 for most metals and a value of 0.32 for other substances including semi-metals. It has also been found that an analogous relation exists between the liquid–vapour interfacial energy and the heat of vaporization in metals [14]. The value of α for metals has been predicted to be 0.46 to 0.48 by theoretical calculation on the basis of a nearest-neighbour approximation [15, 16].

2.2. Inorganic substances

The nucleation and crystal growth rates can also be analysed for glass-forming systems whose compositions do not change during crystallization, such as silicate glass [13, 17–22] and germanium oxide [23]. In homogeneous nucleation data for $Li_2O \cdot 2SiO_2$, it has been found that α is in the range of 0.41 to 0.49 [13, 17 18]. Fig. 3 shows a linear relationship between the mean surface energy and the heat of fusion for silicate glass with a slope of 0.47 according to published data [13, 17–19].

2.3. Organic compounds

The droplet technique for homogeneous nucleation has also been applied to organic compounds, especially to molecular liquids. From the homogeneous nucleation results for many molecular liquids, α lies widely in the range 0.23–0.48, with the exception of white phosphorus at 0.68; however, its average value is roughly 1/3 [6, 7]. Also, the homogeneous nucleation of n-alkanes has been achieved by a droplet technique for a range of alkanes between C_5 and C_{36} [24–27]. It has been found that α decreases from 0.28 for C_5 to 0.07 for C_{16} and is then constant to C_{36}. The increase in α with decreasing chain length has been explained on the basis of chain localization effects in the liquid adjacent to the nucleus surface [28]. At very long chain length, as in linear polyethylene, α is about 0.31 to 0.37 [2] which is much larger than the value of 0.07 for the large n-alkanes. This large value in polymers is associated with the formation of chain folding on the crystal surface.

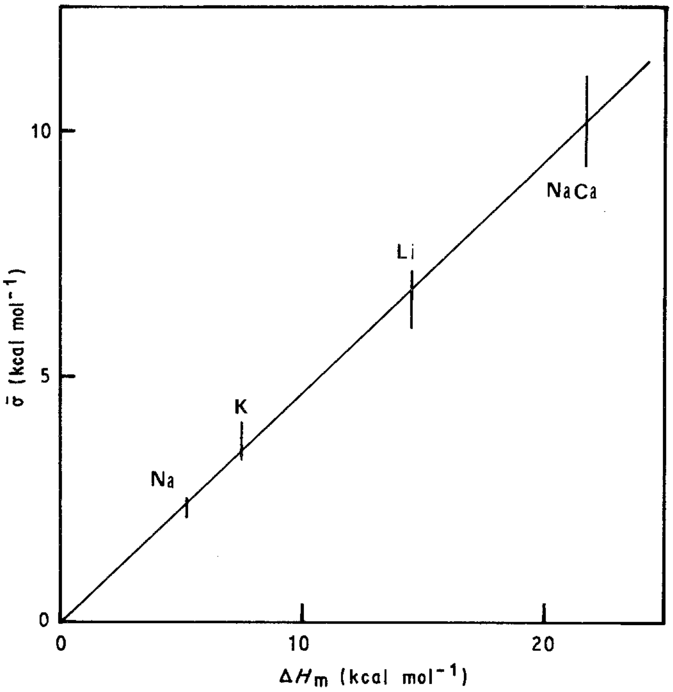

Figure 3 Relationship between the mean molar surface energy ($\bar{\sigma}$) and the heat of fusion (ΔH_m) in silicate glass, $X_2O \cdot 2SiO_2$ or $X_2O \cdot 2YO \cdot 3SiO_2$. 1 kcal = 4.19 kJ.

Homogeneous nucleation and crystal growth rates have been studied over the full range of temperature for many aromatic compounds. For example, crystal growth measurements in benzophenone [29], betol [30], 1,2-diphenylbenzene [31] and 1,3,5-tri-α-naphthylbenzene [32] show that α is about 0.05.

2.4. Polymers

A few homogeneous nucleation data for polymers are available in the literature. For example, using the nucleation data for polyethylene (PE) obtained from small droplet experiments [33, 34], α is calculated to be 0.31 to 0.32 [2]. In contrast with the homogeneous nucleation data, numbers of data are available for polymer crystal growth as listed in Table I. It has been found that in most of the polymers without hydrogen bonding groups, α lies in the range 0.2 to 0.4 and for polymers with hydrogen bonding groups, such as nylons, α lies between 0.1 and 0.2. The average values of α for polymers with and without hydrogen bonding groups, however, are 0.15 and 0.3, respectively.

3. The ratio of ΔE and ΔH_m, β

ΔE could be related to the principal motions in the

TABLE I Ratio of the temperature of maximum growth rate ($T_{cmax}(G)$ in K) to melting temperature (T_m in K) and the characteristic parameters α and β for various polymers.

Material*	T_{cmax}/T_m		$\bar{\sigma}/\Delta H_m = \alpha$	$\Delta E/\Delta H_m = \beta$	References
	Observation	Calculation†			
PClTFE		0.82 to 0.83	0.36 to 0.38	11.83	36, 37
PE		0.76 to 0.78	0.34 to 0.37	5.14	36–38
iso-PP		0.81	0.29	5.71	39
syd-PP		0.75	0.43	(5.71)	40
PB-1		0.81 to 0.82	0.29 to 0.30	6.24	41
PS	0.87 to 0.89	0.86	0.25 to 0.26	9.52	41–44
PVF_2		0.75	0.41	(5.5)	45
PTMPS	0.78 to 0.83	0.77 to 0.82	0.24 to 0.35	4.81	46, 47
PET	0.79 to 0.86	0.81 to 0.92	0.10 to 0.29	(5.5)	48–50
POM	0.79	0.82	0.26	5.44	51
PEO		0.76 to 0.79	0.22 to 0.26	2.39	52–54
PPO	0.82 to 0.88	0.82 to 0.85	0.20 to 0.25	4.85	55, 56
PESu	0.86	0.85	0.21	(5.5)	57
PPhAd	0.85	0.86	0.19	(5.5)	58
PDMS	0.82	0.82	0.14	1.65	59
N6	0.81 to 0.82	0.77 to 0.82	0.18 to 0.25	2.65	60–63
N56	0.85	0.80	0.16	1.53	64
N66	0.76	0.86	0.1	1.2	61
N12		0.76	0.18	(1.2)	63
N96	0.87	0.82	0.12	1.13	64

*PClTFE = poly(chlorotrifluororethylene), PE = poly(ethylene), iso-PP = isotactic poly(propylene), syd-PP = syndiotactic poly(propylene), PB-1 = poly(butene-1), PS = poly(styrene), PVF_2 = poly(vinylidene fluoride), PTMPS = poly(tetramethyl-p-silphenylene siloxane), PET = poly(ethylene terephthalate), POM = poly(methylene oxide), PEO = poly(ethylene oxide), PPO = poly(propylene oxide), PESu = poly(ethylene succinate), PPhAd = poly(tetrachloro-bis-phenol adipate), PDMS = poly(dimethyl siloxane), N6 = nylon 6, N56 = nylon 56, N66 = nylon 66, N12 = nylon 12, N96 = nylon 96.

†Values calculated from Equation 6 based on the values of α and β: values of α analysed from data in the literature, values of β based on the results of Mandelkern *et al.* [35]. Numbers in brackets refer to assumed values.

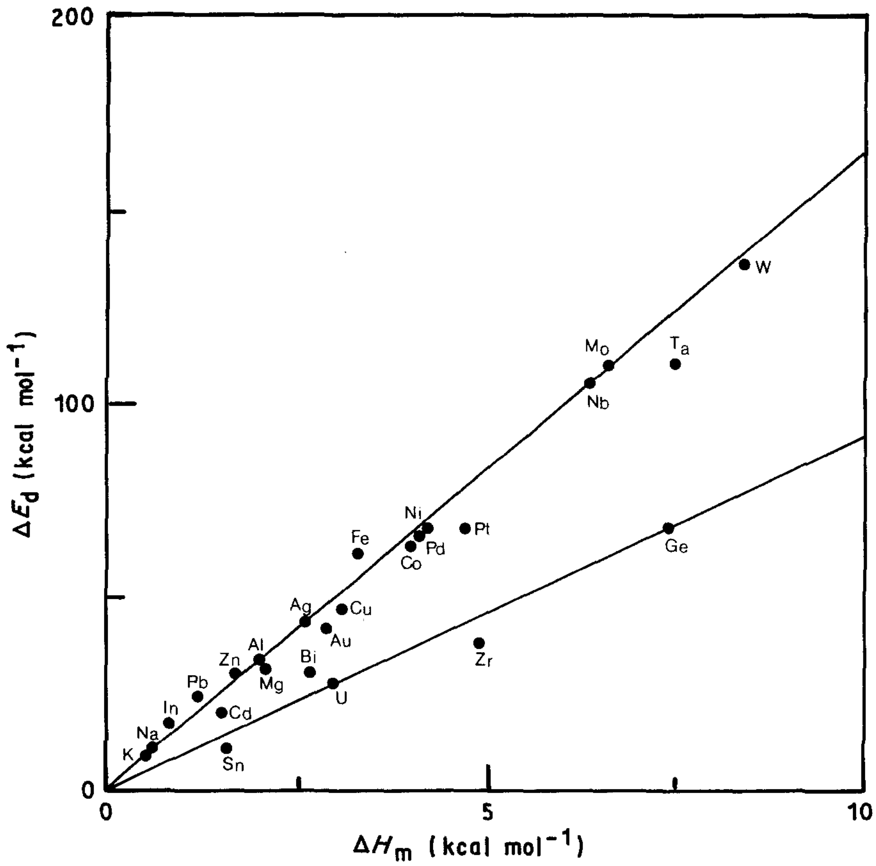

Figure 4 Relationship between the activation energy for self-diffusion (ΔE_d) and the heat of fusion (ΔH_m) for various metals.

vicinity of the nucleus surface which may be associated with the activation energy for self-diffusion (ΔE_d) or that for viscous flow (ΔE_{vis}) of atoms or molecules. ΔH_m could be thought of as a measure of intermolecular forces. In addition, ΔE and ΔH_m may be related to the cohesion energy. It is therefore worth discussing the ratios $\Delta E_d/\Delta H_m$ and $\Delta E_{vis}/\Delta H_m$ in many materials.

3.1. Metals

An empirical relationship between the activation energy of self-diffusion (ΔE_d) and the heat of fusion for metals has been pointed out by Shewmon [65]: $\Delta E_d/\Delta H_m = 16.5$. Fig. 4 shows such a relationship plotted together with a large number of data reported in the literature [66]. These plots show that there are two groups in analogy with the ratio α, and each group shows a fairly good linear relationship. The group for most metals yields the ratio ca. 16 and the other yields the ratio ca. 9. In addition, plots of the activation energy for viscous flow (ΔE_{vis}) against ΔH_m show a good linear relationship as seen in Fig. 5 according to the data in the literature [66, 67]. The values of the ratio are found to be ca. 3 for most metals and ca. 1.4 for semi-metals. It may be thought that ΔE lies between ΔE_d and ΔE_{vis}; that is, β may be in the range 3 to 16 for most metals and 1.4 to 9 for semi-metals.

3.2. Inorganic substances

The values of the activation energy for viscous flow for $Li_2O \cdot 2SiO_2$ are reported to be 105 to 107 kcal mol^{-1} (440 to 448 kJ mol^{-1}) by James [17] and 94 to 117 kcal mol^{-1} (394 to 490 kJ mol^{-1}) by Rowlands and James [13]. From these values, $\Delta E_{vis}/\Delta H_m$ is in the range 6.5 to 8.0. Rowlands and James [13] have also analysed silicate glass by the homogeneous nucleation theory, introducing the activation free energy for transport expressed as $\Delta E = \Delta H - T\Delta S$, where the activation enthalpy ΔH and that of entropy ΔS for transport are both independent of temperature. They were able to determine $\bar{\sigma}$ and ΔH and noted that a reasonable value of $\bar{\sigma}$ is observed and ΔH is much larger than ΔH_{vis}, the activation enthalpy for viscous flow. The ratio $\Delta H/\Delta H_m$ lies between 8 and 18.

3.3. Organic compounds

ΔE_{vis} for supercooled water is more than three times its value at the melting point [38]. A similar large increase in ΔE_{vis} may be shown by other supercooled organic liquids. If ΔE_{vis} for the supercooled liquids is employed as a kinetic barrier for ΔE, the values of β are estimated to be 3.6 for 1,3,5-tri-α-naphthylbenzene [32], and to 3.3 for water [68].

3.4. Polymers

In polymer crystallization, there are two expressions for the molecular transport term of ΔE. One is of simple Arrhenius type ($\Delta E/RT$) and the other is of WLF type ($C_1C_2/R(T - T_g + C_2)$), where C_1 and C_2 are adjustable parameters and T_g is the glass transition temperature. In analysing the crystallization data in bulk polymers, the WLF expression has been used much more often than the Arrhenius type, since it has been believed that the former expression fits the data better than the latter [42]. The validity of these two expressions can be judged by fitting to the data to determine which expression can yield the better fit. Meanwhile, Mandelkern *et al.* [35] have proposed that ΔE could be sufficiently expressed by the Arrhenius type. Hoffman *et al.* [42] and Suzuki and Kovacs [69]

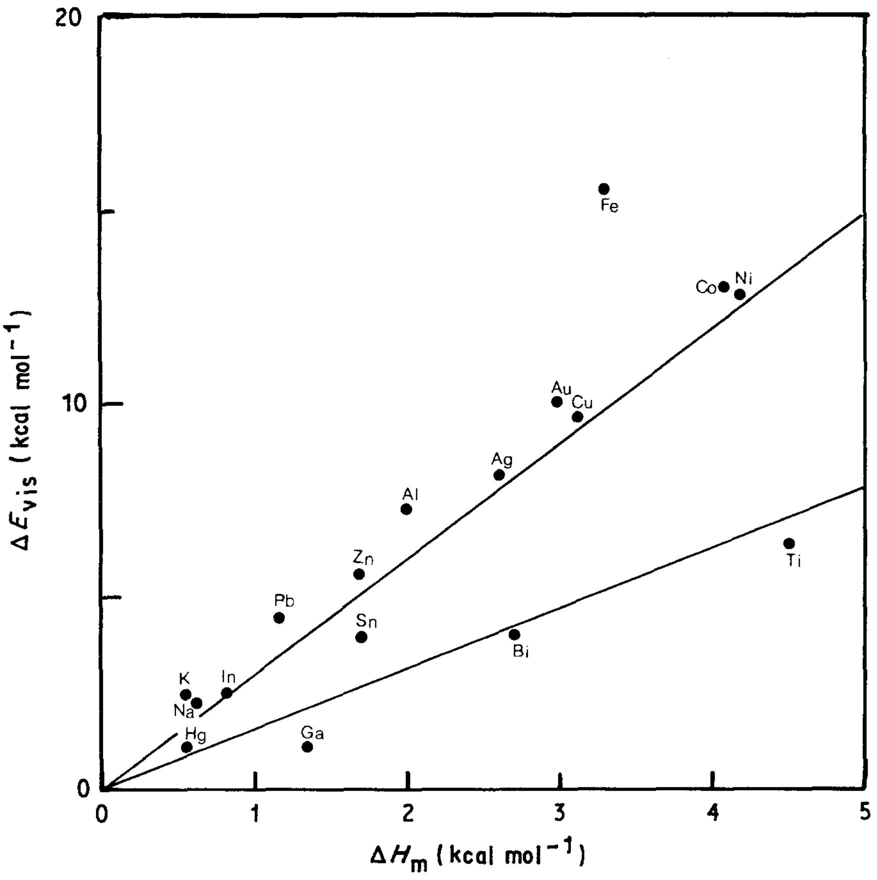

Figure 5 Relationship between the activation energy for viscous flow (ΔE_{vis}) and the heat of fusion (ΔH_{m}) for various metals.

have claimed that the Arrhenius-type expression yielded a far inferior fit to the data for polystyrene, while they also reported that most polymers could fit very well either the WLF or the Arrhenius expression with the sole exception of polystyrene. However, in analysing the crystallization data for various polymers including polystyrene, both expressions can fit the data very well with a high correlation coefficient in the least-squares method [70]. Consequently, either the WLF expression or the Arrhenius expression can be used for polymer crystallization from the melt. A simple expression of Arrhenius type is therefore employed in this study.

The crystal growth data for many polymers have been analysed by Mandelkern *et al.* [35] according to a possible nucleation mechanism and they have estimated ΔE by assuming an Arrhenius expression. It has been found that β is about 5.5 and 1.2 for polymers without and with hydrogen bonding groups, respectively, in the chemical structure. Here ΔE is also compared with ΔE_{d}. For example, the activation energy for reptation, which may be related to ΔE_{d}, is close to 5.5 kcal mol^{-1} (23 kJ mol^{-1}) for *n*-paraffin [71]. Thus obtained, $\Delta E_{\mathrm{d}}/\Delta H_{\mathrm{m}}$ is ca. 5.6 which is in satisfactory agreement with the value of 5.5 for β noted above. This may indicate that ΔE is very close to ΔE_{d}.

The constant value of $\Delta E_{\mathrm{d}}/\Delta H_{\mathrm{m}}$ may be brought about by the two well-known relations: one is the ratio $\Delta H_{\mathrm{m}}/RT_{\mathrm{m}}$ [72–74] and the other is that of $\Delta E_{\mathrm{d}}/RT_{\mathrm{m}}$ [65–67]. For most metals the ratio $\Delta H_{\mathrm{m}}/RT_{\mathrm{m}}$ (the so-called Richard's rule) lies between 1 and 2 with an average value of 1.06 excluding the semi-metals [74] and $\Delta E_{\mathrm{d}}/RT_{\mathrm{m}}$ is about 18 [65]. In addition, there are other empirical rules for most metals [74] such as the ratio of the heat of vaporization and boiling temperature (Trouton's rule), the ratio of the heat of evaporation and melting temperature, and the relationships between the apparent activation energy for self-diffusivity and melting temperature. Consequently, $\Delta E_{\mathrm{d}}/\Delta H_{\mathrm{m}}$ will be almost constant.

The relation between ΔE_{d} and ΔH_{m} has been established on the base of the idea that the activation energy for a vacancy mechanism of diffusion is equal numerically to the maximum change in the crystal internal energy [75]. In other words, the ratio $\Delta E_{\mathrm{d}}/\Delta H_{\mathrm{m}}$ equals the ratio of the activation volumes of fusion and diffusion [76]. Also, it is interesting to note that the ratio of the activation energy of vaporization (ΔE_{vap}) to that of viscous flow has been found to be a constant in metals and organic compounds [77]. These three activation energies and the heat of fusion are supposed to be functions of the cohesion energy, so the ratios between them will be constant. The value of $\Delta E/\Delta H_{\mathrm{m}}$ is very close to the value of $\Delta E_{\mathrm{d}}/\Delta H_{\mathrm{m}}$ rather than that of $\Delta E_{\mathrm{vis}}/\Delta H_{\mathrm{m}}$. Moreover, it has been pointed out that ΔE can be regarded as being equal to the activation energy for self-diffusion of molecules on the nucleus surface [78]. In the chain folding mechanism for polymer crystallization, part of a polymer molecule contacts a pre-existing nucleus surface and subsequently some other parts of the molecule in question deposit adjacently on the same nucleus surface. A translational shift along the chain axis needs self-diffusion energy to generate a crystalline packing finding a set of nearest lattice points. In fact, molecules cannot jump directly into the lattice points from the liquid phase. Such diffusion energy must be associated with the reptation energy of polymer molecules.

TABLE II Ratio T_{cmax}/T_m and the ratio of the mean molar surface energy ($\bar{\sigma}$) to the heat of fusion (ΔH_m) for inorganic substances

Material	T_{cmax}/T_m		$\alpha = \bar{\sigma}/\Delta H_m$		References
	Observation	Calculation*	Observation	Calculation*	
Nucleation					
$Li_2O \cdot 2SiO_2$	0.52 to 0.56	0.52 to 0.57	0.41 to 0.49		13, 17, 18
$Na_2O \cdot 2SiO_2$		0.53 to 0.57	0.41 to 0.47		18
$K_2O \cdot 2SiO_2$		0.50 to 0.54	0.45 to 0.53		18
$Na_2O \cdot 2CaO \cdot 3SiO_2$	0.57	0.51 to 0.55	0.43 to 0.51		19
Growth					
$Na_2O \cdot 2SiO_2$	0.94			0.11 to 0.12	20, 21
$Na_2O \cdot 3SiO_2$	0.94			0.11	22
GeO_2	0.95			0.10	23

*Values calculated from Equations 3 or 6 based on the value of 10 for β.

4. The ratio T_{cmax}/T_m

4.1. Metals

Even in the absence of experimental results for the temperature of maximum nucleation rate in most metals because of the very rapid nucleation rate, $T_{cmax}(I)/T_m$ can be evaluated according to Equation 3. That is, $T_{cmax}(I)/T_m$ is only a function of $\Delta E/K_1$ which is a function of α and β as discussed above. From the two empirical ratios discussed above, $T_{cmax}(I)/T_m$ thus calculated is in the range 0.45 to 0.58 for metals and in the range 0.46 to 0.62 for semi-metals. Here, Turnbull [3, 4] has drawn attention to the fact that the nucleation temperature obtained from droplet experiments is more than 0.8 times the melting temperature in most metals. Since the nucleation temperature (T_b) is in the range where the nucleation rate becomes measurable, T_b as defined in Fig. 1 must be located above $T_{cmax}(I)$. $T_{cmax}(I)$ is difficult to attain by the usual experimental methods because of the rapid nucleation rate. However, the existence of $T_{cmax}(I)$ in metals is valid since an amorphous metal can be achieved by an ultra-high speed quenching method from the molten state. Furthermore, there is an interesting empirical relationship in that the ratio to T_m of the nucleation temperature by annealing (T_a in Fig. 1), which may be located below $T_{cmax}(I)$, has a nearly constant value of 0.43 [79]. That is, $T_{cmax}(I)$ will be located between T_a and T_b. So, $T_{cmax}(I)/T_m$ as evaluated above in the range 0.45 to 0.62 may be fairly reasonable.

On the other hand, a few crystal growth data for metals are available in the literature. For example, $T_{cmax}(G)/T_m$ for the crystal growth of grey tin from the melt is ca. 0.85 [80]. This value is much higher than that for nucleation. If β is assumed to be of the same order as for nucleation, α can be estimated to be 0.12 to 0.3. This estimation suggests that the surface energy for growth is much smaller than that for nucleation.

4.2. Inorganic substances

In the homogeneous nucleation data for $Li_2O \cdot 2SiO_2$, it has been found that $T_{cmax}(I)/T_m$ is in the range 0.52 to 0.56 and α is in the range 0.41 to 0.49 as seen in Table II. In treating the ratio of β in the same way as for metals as discussed above, the value of 10 for β is assumed. Using the values of α listed in Table II and taking β as 10 for $Li_2O \cdot 2SiO_2$, $T_{cmax}(I)/T_m$ can be calculated to be 0.52 to 0.57, which fits very well with the experimental results of 0.52 to 0.56. If the value of 10 for β is assumed for other glasses, the values of $T_{cmax}(I)/T_m$ thus evaluated are in fairly good agreement with the experimental results given in Table II.

In crystal growth, $T_{cmax}(G)/T_m$ has been shown to be constant within the range 0.94 to 0.95 [20–23] which is much higher than the values for nucleation. Such high values are also obtained in some organic substances [29–32] as seen in Table III. If β for crystal growth is assumed to be the same as for nucleation, then the estimated α is as listed in Table II. This estimation suggests that $T_{cmax}(G)$ increases with a decrease in the surface energy.

4.3. Organic compounds

In homogeneous nucleation studies on piperine

TABLE III Ratio T_{cmax}/T_m and the ratio of the mean molar surface energy ($\bar{\sigma}$) to the heat of fusion (ΔH_m) for organic compounds

Material	T_{cmax}/T_m		$\alpha = \bar{\sigma}/\Delta H_m$		References
	Observation	Calculation*	Observation	Calculation*	
Nucleation					
Piperine, $C_{17}H_{19}NO_3$	0.78			0.12	81
Betol, $C_{17}H_{12}O_3$	0.79			0.12	30
n-Alkanes: $C > C_{16}$		0.85 to 0.86	0.07 to 0.08		24, 25
$C_5 < C < C_{16}$		0.58 to 0.86	0.07 to 0.28		24, 25
Molecular liquids		0.39 to 0.63	0.23 to 0.68		6, 7
Growth					
Benzophenone, $C_{13}H_{10}O$	0.94			0.07	29
Betol, $C_{17}H_{12}O_3$	0.95			0.05	30
1,2,Diphenylbenzene, $C_{18}H_{14}$	0.95	0.95	0.05		31
1,3,5,Tri-α-naphthylbenzene, $C_{36}H_{24}$	0.95	0.95	0.05		32

*Values calculated from Equations 3 or 6 based on the value of 3.6 for β.

[81] and betol [30], $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}}$ is found to be 0.78 to 0.79. If β is assumed to be 3.6 for organic compounds in analogy with 1,3,5-tri-α-naphthylbenzene as noted above, $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}}$ or α can be estimated; the values obtained are listed in Table III. The calculated values of $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}}$ for homogeneous nucleation in n-alkanes are 0.85 to 0.86 for $\mathrm{C} > \mathrm{C}_{16}$ and 0.58 to 0.86 for $\mathrm{C}_5 < \mathrm{C} < \mathrm{C}_{16}$. On the other hand, the critical temperature is defined as the temperature (T_{b} in Fig. 1) at which the nucleation rate becomes significantly measurable, such as $10\,\mathrm{cm}^{-1}\,\mathrm{sec}^{-1}$ [26]. So, T_{b} is unlike $T_{\mathrm{cmax}}(I)$ and the ratio $T_{\mathrm{b}}/T_{\mathrm{m}}$ must be higher than that of $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}}$. In fact, the ratio $T_{\mathrm{b}}/T_{\mathrm{m}}$ lies between 0.8 and 0.95 depending on the alkane chain length [24–27].

Crystal growth measurements in benzophenone [29], betol [30], 1,2-diphenylbenzene [31] and 1,3,5-tri-α-naphthylbenzene [32] show that $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}}$ is in the range 0.94 to 0.95. Here, if β is also assumed to be 3.6, the ratios $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}}$ are calculated to be 0.95 for 1,2-diphenylbenzene and 1,3,5-tri-α-naphthylbenzene, values which are in fairly good agreement with the experimental results.

4.4. Polymers

Experimental results for $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}}$ existing in the literature for many polymers have been summarized by Godovskii [1], where $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}}$ lies almost between 0.8 and 0.9. $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}}$ can be calculated from the two parameters α and β listed in Table I and fits very well with the experimental results. From the nucleation data for PE crystals, α is ca. 0.31 to 0.32 as noted above. If β for PE in the nucleation process is of the same order as for crystal growth, $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}}$ thus estimated is 0.52. This estimation suggests that the maximum nucleation rate will occur at a temperature of about $-55^\circ\mathrm{C}$. In fact, PE is well known as an unquenchable polymer and amorphous PE can only be achieved by an ultra-high speed quenching method from the molten state [82]. Such amorphous PE begins to nucleate at above $-100^\circ\mathrm{C}$ [82], so the nucleation temperature evaluated above (in the vicinity of $-55^\circ\mathrm{C}$ at the maximum nucleation rate) is fairly considerable.

It is interesting to note that the ratio of the glass transition temperature (T_{g}) and T_{m} could also be expressed as a function of C: $T_{\mathrm{g}}/T_{\mathrm{m}} = (C-1)/(C+1)$ [70, 83]. In general, the mean value of C is roughly about 5 [2], so that the ratio of $T_{\mathrm{g}}/T_{\mathrm{m}}$ is 2/3. It is interesting to note that the previous empirical rule for $T_{\mathrm{g}}/T_{\mathrm{m}}$ shows 2/3 not only for polymers [84] but also for inorganic substances [85, 86] and organic compounds [85].

5. Critical nucleus size

In Table IV, the values for $T_{\mathrm{cmax}}/T_{\mathrm{m}}$, α and β are summarized. The values in brackets in Table IV are estimated on the basis of Equations 3 or 6. It is clear that the values of α for nucleation are larger than those for crystal growth, and the ratios $T_{\mathrm{cmax}}/T_{\mathrm{m}}$ for nucleation are smaller than those for growth. In other words, the value of $T_{\mathrm{cmax}}/T_{\mathrm{m}}$ increases with a decrease in the value of α or with an increase in β.

The critical nucleus sizes for the length l^* and the lateral edge r^* (or the radius) could be expressed by $k\sigma_{\mathrm{e}}/\Delta f$ and $k\sigma_{\mathrm{u}}/\Delta f$, respectively. Δf is the thermodynamic driving force per unit volume for crystallization and can be approximated to $\Delta H_{\mathrm{m}}(T_{\mathrm{m}} - T)/T_{\mathrm{m}}$. The values of k are 4 and 2 for nucleation and for growth, respectively. The number of atoms (N^*) (or the number of repeating units of molecules) in the critical nucleus with the shape (l^*, r^*) can be given as $N^* = V^*/V_0 = l^* r^{*2}$ for nucleation and $N^* = b_0 l^* r^*$ for growth, respectively, where V^* and V_0 are the volume of the critical nucleus and the unit volume, respectively. Thus N^* is given by

$$N^* = (k\alpha T_{\mathrm{m}}/\Delta T)^m \qquad (12)$$

where $\Delta T\ (= T_{\mathrm{m}} - T)$ is the degree of supercooling and m is 3 for nucleation and 2 for crystal growth. Equation 12 indicates that N^* increases with a decrease in ΔT or with an increase in the mean surface energy $\bar{\sigma}$. Thus estimated numbers of atoms or repeating units of molecules in the critical nuclei at T_{cmax} are listed in Table IV. In analysing the droplet data at T_{b}, it has been reported that the nuclei contain 200 to 400 atoms for metals, less than 200 molecules for molecular compounds and about 300 ions for alkali halides [5, 73]. Here the values of N^* in Table IV are much lower than those for a droplet. This would not be surprising because of the different degree of supercooling owing to $T_{\mathrm{b}} > T_{\mathrm{cmax}}$. On the other hand, it might be thought that the values of N^* are reasonable in size for crystal

TABLE IV Characteristic ratios and critical nucleus sizes (N^*) for homogeneous nucleation and crystal growth in various materials†

Mode	Materials	$T_{\mathrm{cmax}}/T_{\mathrm{m}}$	$\bar{\sigma}/\Delta H_{\mathrm{m}} = \alpha$	$\Delta E/\Delta H_{\mathrm{m}} = \beta$	N^*
Nucleation	Metals	(0.45 to 0.58)	0.45	3 to 16	35 to 79
	Semi-metals	(0.46 to 0.62)	0.32	1.4 to 9	13 to 38
	Inorganic	0.56	0.46	10	73
	Aromatic compounds	0.79	(0.12)	3.6	12
	Molecular liquids	(0.39 to 0.63)	0.33 to 0.68	3.6	45 to 89
	n-Alkanes ($\mathrm{C} < \mathrm{C}_{16}$)	(0.58 to 0.86)	0.07 to 0.28	3.6	8 to 19
	n-Alkanes ($\mathrm{C} > \mathrm{C}_{16}$)	(0.85 to 0.86)	0.07 to 0.08	3.6	8 to 10
	Polymers (PE)	(0.52)	0.31	5.5	17
Growth	Semi-metals	0.85	(0.12 to 0.3)	1.4 to 9	3 to 16
	Inorganic	0.94	(0.11)	10	13
	Aromatic compounds	0.95	0.05	3.6	4
	Polymers with OH bonding	0.83	0.15	1.2	3
	Polymers without OH bonding	0.82	0.30	5.5	11

†Values in brackets are calculated from Equations 3 or 6.

growth based on surface nucleation, since the crystallographic planes at the crystal growth surface in metals are estimated to be constructed with 10 to 30 atoms [87] and the basic unit of polymer crystallization is considered to be a short sequence of chain, such as six CH_2 units of PE [88]. The fact that the values of N^* in homogeneous nuclei are larger than those in surface nuclei is physically understandable.

6. Conclusions

The ratio of the temperature at which the nucleation rate is maximum ($T_{\mathrm{cmax}}(I)$) to the melting temperature (T_{m}) was formulated as $T_{\mathrm{cmax}}(I)/T_{\mathrm{m}} = (D^2 - D + 1)/(D^2 + D + 1)$. Also, the ratio of the temperature at which the crystal growth rate is maximum ($T_{\mathrm{cmax}}(G)$) to the melting temperature was formulated as $T_{\mathrm{cmax}}(G)/T_{\mathrm{m}} = C/(C + 1)$. Here, C and D are a function of $\Delta E/K$. The ratio $\Delta E/K$ is divided into the two parameters $\bar{\sigma}/\Delta H_{\mathrm{m}}$ (denoted as α) and $\Delta E/\Delta H_{\mathrm{m}}$ (denoted as β). In analysing the crystallization data for a large number of crystalline materials such as metals and inorganic, organic and polymeric materials, the values of α and β show roughly constant values for a given type of material. The constancy of the above two parameters will then give rise to a constant value of $T_{\mathrm{cmax}}/T_{\mathrm{m}}$. The value of α for homogeneous nucleation is much larger than that for crystal growth. On the other hand, the ratio $T_{\mathrm{cmax}}/T_{\mathrm{m}}$ for homogeneous nucleation is smaller than that of crystal growth. A decrease in the surface energy therefore brings about an increase in T_{cmax}.

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