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ON THE DYNAMICAL NATURE OF THE PHASE TRANSITION AND MELTING OF PLASTIC CRYSTALS

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Abstract A dynamical model as an extention of the Lindemann's law of melting has been presented in order to describe the rotational melting transition between non-plastic and plastic crystals.

The jump rate ν of the molecular translational diffusion in crystals has been described successfully by the Arrhenius activation process,

$$\nu = \nu_o \exp(-E_a/k_BT) \qquad (1)$$

where E_a is the activation energy of the diffusion.

Glyde[1] previously showed for metals that in the Debye model the following relation between vacancy migration energy E_m and the Debye temperature θ_D can directly be derived from the dynamical theories of diffusion,

$$E_m = (f/24)(k_B/h)^2 m\theta_D{}^2 a^2 \qquad (2)$$

where f is a constant which can be taken as unity, m the atomic mass and a is the nearest interatomic distance. He also showed that the pre-exponential factor ν_0 in Eq. (1) is proportional to θ_D. Very recently Couchman and Reynolds[2] found that by writing the Lindemann's law of melting as

$$T_m = Dm\theta_D{}^2a^2 \qquad (3)$$

where D is a constant, and by using Glyde's relation (2), E_m and T_m can be correlated as follows;

$$E_m = (1/24D)(k_B/h)^2T_m = c\ T_m. \qquad (4)$$

They determined c empirically as $0.66\cdot10^{-3}$ eV K^{-1} (63.6 J mol^{-1} K^{-1}) for metals.

On the other hand there has been revealed by nuclear magnetic resonance experiments that for crystals composed of globular molecules the translational correlation time $\tau(T_m)$ at the melting point in the plastic phase is about $2\cdot10^{-7}$ s, whereas the reorientational correlation time $\tau(T_r)$ in the rigid phase at the solid-solid transition temperature varies between $7\cdot10^{-9}$ s and $3\cdot10^{-11}$ s, depending on the individual materials.[3]

The purpose of the present note is to try to understand these unique properties of the plastic crystals by applying Glyde's model of diffusion (translational melting) and by proposing a relation for rotational melting which is an analogue of the Lindemann's law for melting.

In the case of translational diffusion in plastic crystals, it was suggested by Boden[4] that Eq. (4) should be replaced by a semi-empirical expression due to Gibbs[5]

$$\Delta G^* = \alpha k_B T_m \tag{5}$$

where ΔG^* is the free energy of diffusion, because both the entropies of fusion and of diffusion are not constant. In this case we can put $\alpha = 15.6$ for fcc and hcp and $\alpha = 13.6$ for bcc plastic crystals by averaging the NMR data.[4,6] According to Glyde[1,7] the pre-exponential factor for the translational diffusion may be evaluated to be

$$\begin{aligned} \nu_o &= (k_B T)^{1/2} \langle u^2 \rangle^{-1/2} (2\pi m)^{-1/2} \\ &= \theta_D (6\pi)^{-1/2} (k_B/h) = 4.8 \cdot 10^9 \theta_D \end{aligned} \tag{6}$$

where u is the vibrational displacement of molecules and ν_o is in the unit of Hz. By using Eqs. (5) and (6) the jump frequency at the melting point of a plastic crystal is given as

$$\nu(T_m) = 4.8 \cdot 10^9 \theta_D \exp(-\alpha). \tag{7}$$

Then we may obtain $\nu(T_m) = 806\ \theta_D$ (fcc and hcp) and $5956\ \theta_D$ (bcc). As θ_D ranges around 100 K in most of the plastic crystals,[8] $\tau(T_m)$ thus estimated falls in a range $2 \cdot 10^{-6}$ to $3 \cdot 10^{-7}$ s which approximately covers the values obtained by NMR.

As to the rotational melting from the rigid phase to the plastic phase, we will describe the libration of the molecules by a harmonic oscillator,[9] and introduce a new relation analogous to Eq. (3) between the transition temperature T_r and the Einstein temperature θ_E $(= \hbar\omega/k_B)$,

$$T_r = D' I \theta_E^2 \varphi_o^2 \tag{8}$$

where I is the average moment of inertia of the molecule and D' a constant. We considered that the rotational melting occurs when the amplitude of libration φ is some fraction of the angle φ_0 between the potential minima, so that Eq. (8) is understood as an extended Lindemann's law for the rotational melting.

If the molecular rotation or reorientation can be described by a hindered plane rotator,

$$V = (V_0/2)(1 - \cos n\varphi) \qquad (9)$$

where V_0 is the potential barrier to rotation and n the symmetry number, the pre-exponential factor ν_0'[10] and the activation energy E_r may be represented by

$$\begin{aligned} E_r \sim V_0 &= 2I\omega^2/n^2 = 8\pi^2 T_r/(D'n^2 \varphi_0^2)(k_B/h)^2 \\ &= \alpha' k_B T_r. \end{aligned} \qquad (10)$$

and

$$\begin{aligned} \nu_0' &= (n/2\pi)(V_0/2I)^{1/2} \\ &= (\alpha' k_B T_r/2I)^{1/2}(1/\varphi_0). \end{aligned} \qquad (11)$$

In these equations we have put $n\varphi_0 = 2\pi$. α' has been estimated[11] as 9.0 and we obtain

$$\nu(T_r) = 2.12(1/\varphi_0)(k_B T_r/I)^{1/2} \exp(-9.0). \qquad (12)$$

The values of $(k_B T_r/I)^{1/2}$ for various plastic crystals lying between $6 \cdot 10^{12}$ and $4 \cdot 10^{13}$ s^{-1} and φ_0 being of the order of π, Eq. (12) predicts that $\tau(T_r)$ is between $3.2 \cdot 10^{-10}$ and $4.8 \cdot 10^{-11}$ s. This range of values reasonably covers the experimental $\tau(T_r)$ values cited ealier although the lower bound is smaller by a factor of 20.

In short, it is our understanding that a cooperative rotational phase transition is triggered when the rotational correlation time reaches a certain value. This statement is, of course, not without some reservation about the mode or modes in which the molecules reorient themselves in the non-plastic phase. Thus, the seven compounds referred to in Ref. 3 undergo transitions as a result of overall molecular tumbling, whereas triethylenediamine[12] and t-butyl chloride[13] seem to require only an axial rotation to trigger the phase transition. Such crystals as trimethylacetonitrile[14] and hexamethylbenzene[15] do not have a plastic phase although their $\tau(T_r)$ values are shorter than 10^{-10} s probably because uniaxial rotation is not sufficient to make these crystals plastic. Anisotropic intermolecular interactions will play an important role in these apparently different behaviors.

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