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1992 J. Phys.: Condens. Matter 4 L429

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LETTER TO THE EDITOR

**A simple connection between the melting temperature and the glass temperature in a kinetic theory of the glass transition**

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Received 14 May 1992

**Abstract.** The relationship of the glass transition temperature  $T_g$  to transport properties has been established. Simple arguments relating transport to distributions of barrier heights, barrier heights to random potential reliefs, and typical potential fluctuations to crystalline potentials allows the establishment of a relationship between  $T_g$  and the melting temperature,  $T_m$ , by application of the Lindemann criterion for melting.

A recent Letter to the Editor (Malinovsky and Novikov 1992), referred to hereafter as I, discusses an experimental relationship between the glass temperature  $T_g$  and the melting temperature  $T_m$  of vitreous and crystalline substances respectively. The relationship is

$$T_g \approx 2T_m/3 \tag{1}$$

and the proportionality is assumed to result from the excess low-energy density of states (LEDOS) found in glasses. An alternative viewpoint is given here.

The empirical relationship for the viscosity

$$\eta \approx \eta_0 \exp(T_0/T)^2 \tag{2}$$

with  $\eta_0$  and  $T_0$  system-dependent parameters has been demonstrated (Richert and Baessler (1990), referred to hereafter as II) to hold for a large number of viscous liquids and glasses over many orders of magnitude of  $\eta$ , including the glass transition region, and has been interpreted in II in terms of a random walk theory to result from a Gaussian distribution of barrier heights encountered by a random walker. That  $\eta$  has risen by roughly 13 orders of magnitude compared to its high-temperature liquid value implies a relevant experimental (percolation) relaxation time of

$$t_{\text{exp}} = 10^{13} \nu_{\text{ph}}^{-1} = 10^{13} 10^{-12} \text{ s} = 10 \text{ s}$$

with  $\nu_{\text{ph}} \approx 10^{12}$  Hz a nearly universal vibrational frequency (consistent with a relaxation time map emphasized by Angell (1990)). This typical experimental time frame defines the glass temperature. Such a picture has been shown in II (similarly to Hunt (1989)) to lead to (for  $\eta$  given in equation (1))

$$T_g = T_0 / [\ln(t_{\text{exp}} \nu_{\text{ph}})]^{1/2} = T_0 / [\ln 10^{13}]^{1/2} = T_0/5. \tag{3}$$

Application of the Lindemann criterion for melting (equivalent to equation (9) of I) gives

$$(1/2)k_s r_0^2 = (3/2)k_B T_m \quad (4)$$

where  $r_0$  is a nearest neighbour distance,  $k_s$  is an effective spring constant and  $k_B$  is the Boltzmann constant. If the interatomic (interionic) forces are assumed to be primarily Coulombic (ionic and superionic glasses), one has

$$k_s \approx |dF/dr|_{r_0} = 2e^2/\epsilon r_0^3 \quad (5)$$

(with  $e$  the electronic charge and  $\epsilon$  the dielectric constant) and

$$e^2/\epsilon r_0 = (3/2)k_B T_m \quad (6)$$

i.e. melting occurs when the thermal energy per particle is of the order of the Madelung energy (numerical Madelung factors of say 1.75 appear in both  $T_0$  and  $T_m$  and therefore cancel) per particle. If this same energy is expected to play an important role in transport (viscosity!) then one calculates (Hunt 1990, Henn and Elliott 1992) for a typical barrier height  $\langle E_b \rangle$  encountered by a hopping ion (with separation still roughly  $r_0$  and hopping distance of the order of  $r_0$ )

$$\langle E_b \rangle \approx 2e^2/\epsilon r_0 \quad (7)$$

(assuming that an ion must pass roughly halfway between other ions to hop over the next barrier). The distribution of such barrier heights, if roughly Gaussian (as assumed in II) will also have a width  $\sigma$  proportional to  $\langle E_b \rangle$  (for the distribution to be approximately Gaussian,  $\sigma$  cannot be much larger than  $\langle E_b \rangle$  as negative barrier heights make no sense)

$$\sigma \approx 2e^2/\epsilon r_0. \quad (8)$$

But in II  $T_0$  is

$$k_B T_0 = (2/3)\sigma \approx (4/3)k_B T_m. \quad (9)$$

So, putting together all the proportionalities leads to

$$T_g \approx 0.4T_m \quad (10)$$

and the rule  $T_m \propto T_g$  is demonstrated to follow from a kinetic theory of the glass transition.

The proportionality of  $T_g$  and  $T_m$  is thus demonstrated for ionic and superionic glasses, although in this exceedingly naive calculation the proportionality constant is 40% too small. The restriction to ionic and superionic conductors was made for the purpose of ease of calculation; the relationship between  $T_g$  and  $T_0$  is independent of the nature of conduction, i.e. of the nature of the molecular bonding. Whether a similar calculation can be performed for covalently bonded crystals/glasses is not clear, but at least in dipole glasses a large fraction of the bonding as well as of the barrier heights will involve similar electrostatic interactions.

Reasons for the discrepancy in the numerical constant of proportionality are not difficult to imagine. The Lindemann condition itself is known to be inaccurate, while the rough equality of  $\langle E_b \rangle$  and  $\sigma$  already indicates that the approximation of a Gaussian distribution of barrier heights is not quantitatively accurate. Moreover, using  $r_0$  for hopping distances, and for separations in both the crystal and in the glass is not quantitatively accurate. The main point of this work is to clarify the physical origin of the 'glass transition'. The ability of a kinetic theory to predict quantitatively glass transition temperatures in many systems, their dependences on experimentally determined parameters (i.e.  $T_0$ ) and on the cooling rate as well as the dependence of the width of the 'glass transition' region on the cooling rate could be set against e.g. the observed correlation between  $T_g$  and  $T_m$  which was 'explained' in terms of the extra LEDOS or against the correlation between the dynamic heat capacity jump  $\Delta C_{\text{dyn}}$  and the heat of fusion  $H$ . But a demonstration that the latter two correlations are also easily understood within a unified conceptual approach based on a purely kinetic interpretation removes the impetus to examine alternative theories. Such a correlation between  $T_g$  and  $T_m$  being now qualitatively understood, the most important need is to demonstrate the existence (or non-existence) of a proportionality between  $\Delta C_{\text{dyn}}$  and  $H$ . Since it has already been demonstrated that  $\Delta C_{\text{dyn}}$  is always a well-defined numerical fraction of the (quasi-) equilibrium heat capacity  $C_{\text{eq}}$  of a super-cooled liquid, a proportionality between  $H$  and  $C_{\text{eq}}$  remains to be demonstrated.

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