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LETTER TO THE EDITOR

A geometrical rationalization of frozen-in enthalpy and frozen-in entropy in glasses

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Abstract. A model based on a binary mixture of solid- and liquid-like phases can explain the empirical values for the frozen-in enthalpy and the frozen-in entropy in glasses. It is suggested that a binary mixture of equal amounts of the two phases can provide both spatially extended regions of high molecular mobility and structural rigidity on a macroscopic scale.

In thermodynamical terms, glass formation can be regarded as being incomplete crystallization from a melt. It has recently been shown [1] that the most probable values of frozen-in entropy and frozen-in enthalpy are $\Delta S_g = \Delta S_m/3$ and $\Delta H_g = \Delta H_m/2$ respectively where the subscript m denotes the thermodynamic values for the melting phase transition of the corresponding materials.

As the heat released by glass formation is about half the corresponding latent heat of crystallization, it may be suggested that the glass phase could be described as a mixture of equal amounts of quasi-liquid and crystalline phase regions. However, a homogeneous mixture of liquid-like and crystalline regions of equal size would imply that the frozen-in entropy or the excess entropy over a pure, crystalline phase, was equal to the mixing entropy of a binary mixture containing equal amounts of the two components. This excess entropy is then expected to be $k \ln 2$ per particle. It will be shown however that the typical values of the frozen-in entropy are closer to twice this value.

We propose a geometrical rationalization for the observed values for both the frozen-in enthalpy and the frozen-in entropy in glasses.

According to Trouton's rule [2], enthalpies of vaporization of different compounds increase almost linearly with the corresponding boiling-point temperatures. The rule implies that the entropy of vaporization is nearly constant, $\Delta S_v \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$. For a more limited range of compounds including glass formers such as hydrocarbons, alcohols and organic acids, a similar, approximate invariance in the values for the entropies of melting can be inferred from the experimental data (see table 8-1 in [2]). The most probable value for the entropy of melting is about $34 \text{ J K}^{-1} \text{ mol}^{-1}$ for a significant number of compounds including glass formers. Expressing this typical value in units of the Boltzmann constant, k , we arrive at $4.1 k$ per particle. As the frozen entropy for typical glasses is $1/3$ of the melting entropy [1], one can estimate the typical frozen-in entropy as $\sim 1.4 k$ per particle. A somewhat lower estimate for the typical residual entropy, $\sim 1 k$

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per molecule is used in a recent publication [3] on the basis of the available empirical data without assuming an approximate Trouton-like rule for melting.

Thus, a reasonable estimate for the residual entropy in typical glasses can be between $1 k$ and $1.4 k$ per particle which is almost twice the mixing entropy for a binary mixture containing equal amounts of the two components ($0.69 k$ per particle). The entropy excess over $0.69 k$ per particle can be incorporated by introducing an additional degree of freedom into a model for two-component mixing. An additional degree of freedom can be introduced in the form of a distribution in the sizes of solid phase subregions embedded in the remaining liquid-like region. In addition to accounting for the excess entropy, this distribution of sizes must accommodate half of the material.

The latter condition has been found to be satisfied by a simple distribution in which the largest solid-phase subregion is $1/3$ of the total space, the next largest is $1/9$ of the total space etc, the total size of the solid phase converges to half the total size:

$$1/3 + 1/3^2 + 1/3^3 + \dots = [1/(1 - 1/3)] - 1 = 1/2 \quad (1)$$

where the total size is taken as unity. The probability that a particle resides in the solid phase region is $1/2$ and by the normalizing condition of an overall probability of 1, the complementary probability of staying in the embedding liquid-like state region is also $1/2$. As the solid phase is a distribution of spatially defined subregions the sizes of which are members of a geometrical series by (1), the total configurational entropy can be expressed as:

$$S_{\text{config}} = -k \left(\sum_{n=1}^{\infty} (1/3)^n \ln(1/3)^n + (1/2) \ln(1/2) \right). \quad (2)$$

The first term in the square brackets is the configurational entropy of the solid-phase subregions while the second term is the complementary contribution from the liquid-like embedding phase. Denoting the configurational entropy of the solid-phase subregions as S^s , we arrive at

$$-(S^s/k) = \sum_{n=1}^{\infty} (1/3)^n \ln(1/3)^n = \ln(1/3)[1/3 + 2(1/3)^2 + 3(1/3)^3 + \dots]. \quad (3)$$

Multiplying both sides of (3) by 3,

$$-3(S^s/k) = \ln(1/3)[1 + 2(1/3) + 3(1/3)^2 + \dots]. \quad (4)$$

By subtracting (3) from (4) we arrive at

$$-(2S^s)/k \ln(1/3) = [1 + 1/3 + (1/3)^2 + \dots] = 1/(1 - 1/3) = 3/2. \quad (5)$$

Finally,

$$S^s = -(3/4)k \ln(1/3) \quad (6)$$

or, $S^s = 0.824k$ per particle. Adding $0.346k$ for the complementary entropy in (2), the total configurational entropy of the mixture is $1.17k$ per particle. This value is well within the empirical range as discussed above.

In summary, the simple geometrical model suggested here can explain the following empirical findings:

(i) The latent heat of vitrification is typically half the corresponding heat of crystallization. In our model this follows directly from (1) as crystallization affects only half the total size of the system.

(ii) The typical values for the frozen-in entropy in glasses are in the range $1k-1.4k$ per particle which is well above the entropy of mixing in binary systems containing equal amounts of the two components. This excess entropy is modelled by a distribution in the size of the solid-phase subregions (see (2)).

(iii) High molecular mobility in glasses can be rationalized [4] by the existence of disordered regions of defects or 'islands of mobility' at $T < T_g$ which, in our model, is simply the liquid-like phase. Spatial extension of high molecular mobility and similar transport properties over macroscopic length scales follows naturally from the model proposed here, as the fraction of the liquid-like phase ($p = 1/2$) is well above the percolation threshold in three dimensions and is at the percolation threshold in two dimensions for site percolation on a square lattice [5]. As the same holds for the solid-phase network, the mixture of the two phases is also structurally stable [6]. In other words, rigidity percolation can stabilize the glass against phase separation.

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