

Rings, chains and planes: Variation of T_g with composition in chalcogenide glasses

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Abstract. We propose a microscopic, phenomenological model for the decrease in the viscosity observed at glass transition. Our model is primarily applicable to chalcogenide glasses. According to this model, the decrease in the viscosity at glass transition is mainly due to the breaking of the Van der Waals bonds in the chalcogenides. Using this model, we derive a relationship between the glass transition temperature, T_g , and the molar volume V_m . The validity of this relation is checked using experimental data available in the literature for two binary systems (Ge–Se and As–S) and a pseudo-binary system ($\text{As}_{40}\text{Se}_x\text{Te}_{60-x}$).

Keywords. Glass transition; chalcogenide glasses; Van der Waals interaction.

1. Introduction

The phenomenon of glass transition has been widely studied (Zallen 1983; Jackle 1986) in the past, but a complete understanding is still lacking.

There have been numerous efforts to relate T_g to some easily measurable quantity. In the case of chalcogenide glasses, T_g is thought to depend on the degree of cross-linking in the glass. One such effort resulted in the Varshneya–Gibbs–DiMarzio (VGDM) equation, which relates T_g and mean coordination number ($\langle r \rangle$) (Varshneya *et al* 1993).

$$T_g = \frac{T_0}{1 - b(\langle r \rangle - 2)},$$

where T_0 and b are constants.

Recently, a stochastic approach has been used to support this equation and calculate the parameter, b (Micoulaud and Naumis 1999). The VGDM equation and the stochastic approach break down in the low chalcogen limit, due to the presence of chemical order. According to the VGDM equation, T_g is only a function of $\langle r \rangle$. However, there is now sufficient evidence indicating that most physical properties of glasses are not universal functions of $\langle r \rangle$ (Tatsumisago *et al* 1990).

2. Microscopic model for glass transition

The VGDM equation fits the experimental data in the high chalcogen (or low $\langle r \rangle$ limit). The stochastic approach and

the VGDM equation break down at high $\langle r \rangle$ (where there is chemical ordering).

We take a slightly different approach and derive a relation between T_g and the molar volume of the glass using the fact that there is a huge decrease in the viscosity of glass when it undergoes a transition from the supercooled liquid to the glassy state (Zallen 1983). This decrease in viscosity is a vital clue to the structural changes happening at T_g . Since the viscosity in the supercooled liquid state is much lower than that in the glassy state, it is obvious that relative motion of atoms/molecules is possible in the supercooled liquid state. The relative motion of atoms requires the breaking of the bonds holding them together. Since in this paper our interest is confined only to chalcogenide glasses, we propose a model, which is specific to such a system. It is known that chalcogenide glasses consist of one-dimensional or two-dimensional covalent networks (Phillips 1979; Zallen 1983). These lower dimensional structures are held together by Van der Waals forces. Since the Van der Waals bonds are much weaker than the covalent bonds, we expect them to break at a much lower temperature. We assume here that the decrease in viscosity observed at the glass transition is due to the breaking of the Van der Waals bonds. There are a few experimental results to support our assumptions. Busse (1984) measured the X-ray diffraction pattern of chalcogenide glasses, below and above T_g . The changes observed in the X-ray intensity were interpreted as being due to the relative motion of the chalcogenide planes.

In this paper, we calculate the energy required for breaking a Van der Waals bond and relate it to the molar volume of the glass. It is known that the Van der Waals interaction between two atoms varies as $1/r^6$ (Kittel 1971), where r is the interatomic distance. However, if the Van der

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Waals interaction is between planes or chains, the dependence of the interaction on inter-planar or inter-chain distance is quite different.

First, we work out the Van der Waals interaction energy between chains (this is relevant for selenium-rich glasses which consist primarily of selenium chains). The Van der Waals interaction between any one atom on one of the chains and all the atoms of another chain is given by

$$E_{\text{chain}} \sim \int_{-\infty}^{+\infty} \frac{Pdx}{r^6}, \quad (1)$$

where P is the number of dipoles per unit length and r the distance between an atom on one chain and any atom on the other chain. For convenience we have considered an infinite chain, but the results are not altered in a significant way for the case of finite chains.

Now

$$r = \sqrt{d^2 + x^2}, \quad (2)$$

where d is the perpendicular distance between the chains and x the distance along the chain.

Substituting (2) in (1), we have,

$$E_{\text{chain}} \sim \int_{-\infty}^{+\infty} \frac{Pdx}{(d^2 + x^2)^3}. \quad (3)$$

This integral can be written as

$$E_{\text{chain}} \sim \frac{1}{d^5} \int_{-\infty}^{+\infty} \frac{Pdx'}{(1 + x'^2)^3}, \quad (4)$$

where we have used the change of variables $x' = x/d$.

The integral in the above equation can be evaluated to be

$$= \frac{1}{8} \left(\frac{x'(3x'^2 + 5)}{(1 + x'^2)^2} + 3 \tan^{-1} x' \right)_{-\infty}^{+\infty} = \frac{3P}{8}. \quad (5)$$

Therefore, it is seen that the Van der Waals interaction between an atom and an adjacent chain varies as $1/d^5$. In a similar manner, it can be shown that the interaction between planes varies as $1/d^4$. Since we have assumed that the Van der Waals bond is broken at T_g , we equate the thermal energy (kT_g) at T_g to the Van der Waals bond energy

$$kT_g \sim \frac{1}{d^5} \sim \frac{1}{V_a^{5/3}} \sim \frac{N^{5/3}}{V_m^{5/3}}. \quad (6)$$

Here V_a is the atomic volume, V_m the molar volume and N the Avogadro number.

The above equation is relevant for the transition in selenium-rich glasses, which are predominantly made of selenium chains.

For the case of glasses, whose coordination number is slightly higher we have to use the formula for Van der Waals interaction between planes, i.e.

$$kT_g \sim \frac{N^{4/3}}{V_m^{4/3}}. \quad (7)$$

3. Comparison with experiments

In order to check the validity of the relations derived above, we compare them with available experimental data for different systems. Figure 1 shows the plot of T_g vs $1/V_m$ for the Ge–Se system. It is clearly seen that there is a sharp change of slope near $\langle r \rangle \sim 2.2$. The continuous line is a fit to (6) (for $\langle r \rangle$ less than 2.2) and (7) (for $\langle r \rangle$ greater than 2.2). In this system, the data (Borisova 1981) seems to fit (6) for compositions ranging from GeSe₂₄ to GeSe₁₄, while compositions ranging from GeSe₉ to GeSe₅ fit (7). This can be easily understood if we recall that selenium in the glassy state usually consists of chains which are held by Van der Waals interaction. As more and more Ge is added, the system develops a two-dimensional character, where the planes are held together by Van der Waals forces. The crossover point corresponds to the composition GeSe₉. The average coordination number for this composition is 2.2. It is interesting to note that the activation energy for viscosity also shows a decrease around this point (Phillips 1979).

Repeating the procedure followed in the previous section, we initially plot T_g vs $1/V_m$ (figure 2) for the As–S system. We can now discern at least three distinct regions (marked R, C and P) in the graph. To explain the significance of these three regions we have to recall the structural changes, which happen as we add arsenic to sulphur. It is known that the sulphur-rich glasses consist of rings of sulphur, made of 8 atoms. Since the ring is effectively of 0 dimension, one would expect that the Van der Waals interaction binding a ring is proportional to $1/r^3$ (extrapolating from (7)). Hence T_g in this system should vary as $1/V_m$. As arsenic is added to the sulphur-rich system, the rings might break down to form chains (region C). Hence the T_g variation in this region should follow (6). At higher arsenic concentrations, we see the transition to a 2-dimensional structure (region P). This transition takes place for the composition, AsSe_{3.5}, which corresponds to an average coordination number of 2.22. This is close to the value of the crossover point in the case of As–S.

We now compare our approach with the VGDM equation. Most of our data, which we have fitted to (6) or (7), is for glasses with low coordination number. At higher coordination numbers our approach is likely to fail as the glass goes over to a 3-dimensional covalent network and we can no longer assume the presence of covalent bonds. Hence our equation fits the data in the same region as the VGDM equation. However, our approach has greater predictive power in certain cases. For example, consider the ternary system, As₄₀Se_xTe_(60-x)As, x is varied in this system, the mean coordination number $\langle r \rangle$ does not change as selenium (with a coordination number 2) is replaced by

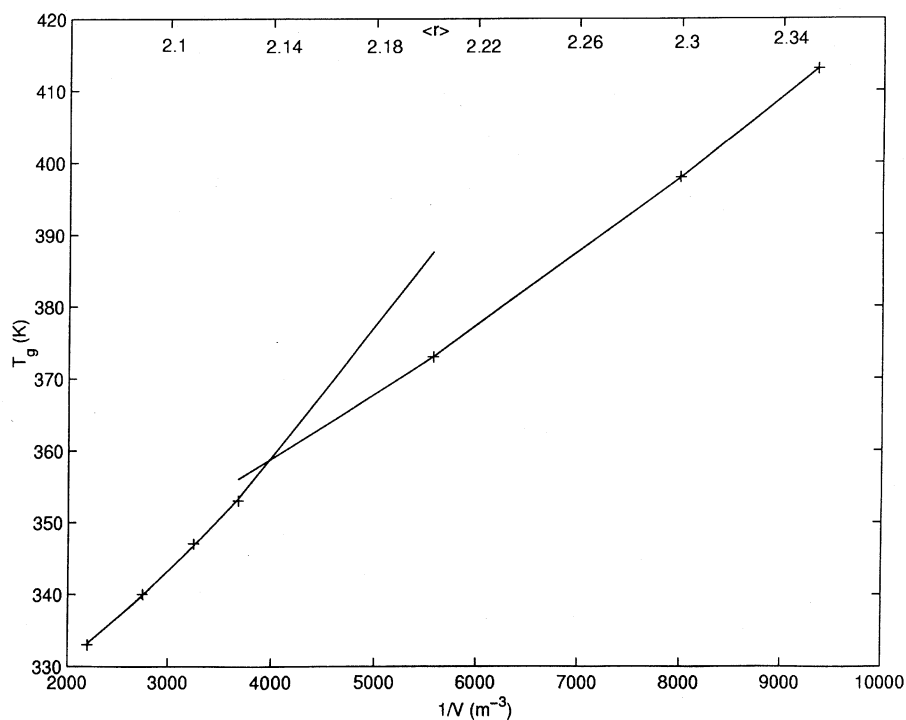


Figure 1. T_g vs $1/V_m$ for Ge-Se system. The corresponding coordination numbers are shown at the top. The molar volumes were calculated from the density values available (Borisova 1981) using the formula, $V_m = \text{molecular weight}/\text{density}$. Solid line is a fit to (6) and (7). Note the change in slope near $\langle r \rangle \sim 2.2$.

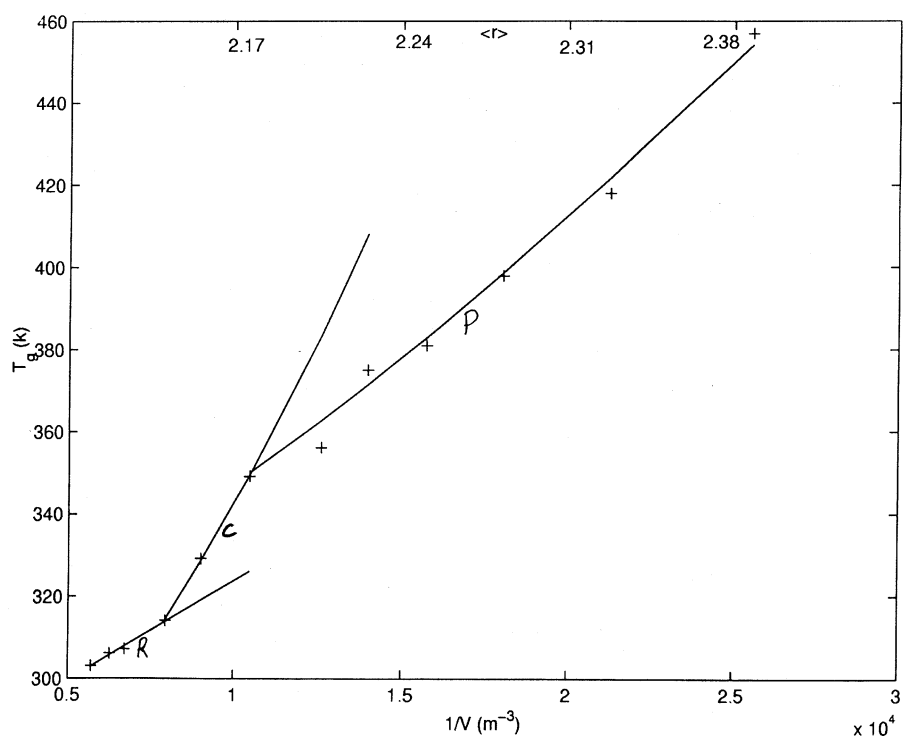


Figure 2. T_g vs $1/V_m$ for As-S system. Note the three distinct regions (marked R, C and P), corresponding to the formation of rings, chains and planes.

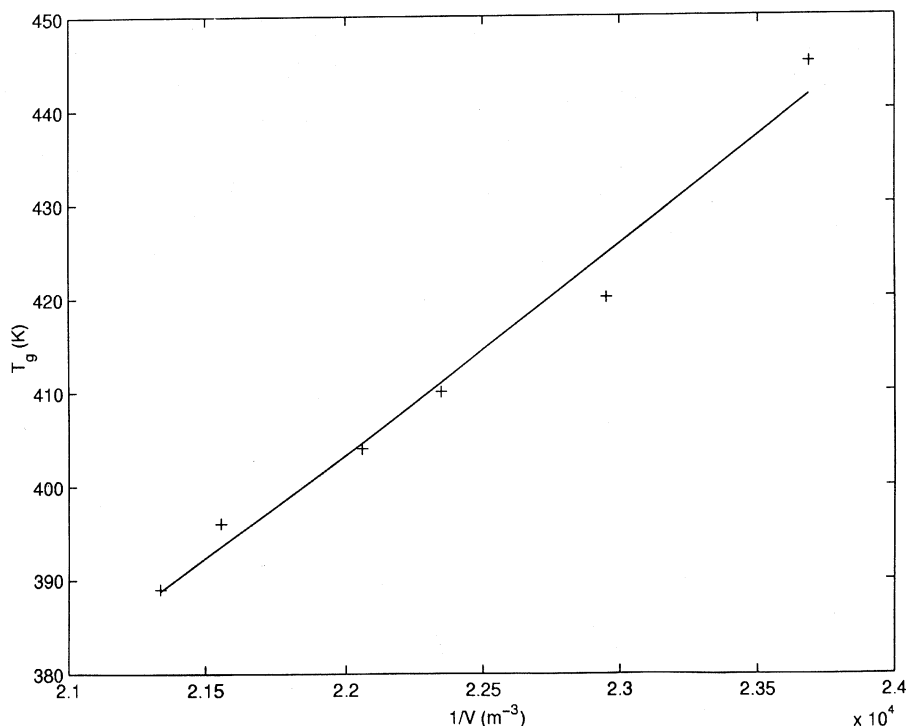


Figure 3. T_g vs $1/V^{4/3}$ for $\text{As}_{40}\text{Se}_x\text{Te}_{(60-x)}$. Solid line is a linear fit to the data.

tellurium (which also has the same coordination number). According to the VGDM equation, all these glasses should have the same T_g as they have the same value of $\langle r \rangle$. However, T_g in this system varies from 116°C for the glass $\text{As}_{40}\text{Se}_{12}\text{Te}_{48}$ to 172°C for $\text{As}_{40}\text{Se}_{60}$. This variation finds a ready explanation in our theory. As selenium is replaced by tellurium (which is a bigger atom), the molar volume (and the inter-atomic distances) will increase. This weakens the Van der Waals bond, leading to a lower T_g . The variation of T_g with molar volume is seen to fit (7) (figure 3).

In the present paper, we have not calculated the constants of proportionality occurring in the relations between T_g and molar volume. However, this should be possible since the microscopic basis for our model is quite clear.

4. Conclusions

We have proved the validity of our approach for both binary and ternary systems in the high chalcogen limit. Till now most of the theories (including the VGDM equation) concentrated on the degree of cross-linking (i.e. covalent bonding) in a glass while our approach stresses on the

strength of the Van der Waals bonding to understand the variation of T_g with composition in chalcogenide glasses.

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