Correlation Between Thermodynamic and Kinetic Fragilities in Non-Polymeric Glass-Forming Liquids (Preprint)

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Correlation between thermodynamic and kinetic fragilities in nonpolymeric glass-forming liquids

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A phenomenological relationship between reduced excess heat capacity of supercooled liquid $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ at the glass transition temperature T_g, fragility index m, and reduced glass transition temperature $T_{\mathrm{rg}} = T_g/T_m$, where T_m is the melting (liquidus) temperature, was derived for fragile nonpolymeric glass-forming liquids under the assumptions that the fragile behavior of these liquids is described by the Vogel–Fulcher–Tammann (VFT) equation; the excess heat capacity of liquid is inversely proportional to the absolute temperature and the VFT temperature T_0 is equal to the Kauzmann temperature T_K. It was found that $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ is a composite function of m and T_{rg}, which indicates that the empirical correlation $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m = 0.025m$ recently identified by Wang *et al.* [J. Chem Phys. **125**, 074505 (2006)] is probably valid only for liquids which have nearly the same values of T_{rg}. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2890726]

INTRODUCTION

In their recent work, Wang *et al.*[1] have analyzed the behavior of 54 glass-forming nonpolymeric liquids and found an empirical correlation between the heat capacity step $\Delta C_p(T_g) = C_p^{\mathrm{liquid}}(T_g) - C_p^{\mathrm{glass}}(T_g)$, which was measured at the glass transition temperature T_g and reduced by the entropy of fusion ΔS_m, and the liquid fragility index m. This correlation is shown in Fig. 1 and can be expressed using the following relation:[1]

$$\frac{\Delta C_p^{\mathrm{exc}}(T_g)}{\Delta S_m} = 0.025m. \tag{1}$$

The fragility index m, which is also called as kinetic fragility index or the steepness index, is defined as the slope of the curve $\log_{10}\tau$ vs T_g/T in a fragility plot at the glass transition temperature T_g,[2]

$$m = \left.\frac{d\log_{10}\tau}{d(T_g/T)}\right|_{T=T_g},$$

where τ is the Maxwell relaxation time and T is the absolute temperature. Although relation (1) fits the most of the experimental data rather well (see Fig. 1), several glass-forming liquids, such as selenium, toluene, triphenilphosphite (TPP), and decalin [decahydronaphtalene], show large deviation from this simple dependence, which leads to a rather low coefficient of determination ($R^2 = 0.353$) of the fit of all data points, and Wang *et al.*[1] had a difficulty in explaining such "anomalous" behavior.

In the present work, we have identified a phenomenological relationship between $\Delta C_p(T_g)/\Delta S_m$ and m for the nonpolymeric liquids and found that $\Delta C_p(T_g)/\Delta S_m$ is not a single linear function of m, as relation (1) suggests but it is a composite function of both m and the reduced glass transition temperature $T_{\mathrm{rg}} = T_g/T_m$, where T_m is the melting (liquidus) temperature. Therefore, liquids with the same m but different T_{rg} values may have quite different $\Delta C_p(T_g)/\Delta S_m$ values, which explain the large deviation of several glass-forming liquids from relation (1).

ANALYSIS

Thermodynamic fragility

The heat capacity of the supercooled liquid $C_p^{\mathrm{liquid}}(T)$ is known to be higher than that of the respective crystal $C_p^{\mathrm{crystal}}(T)$. Because of this, the entropy of liquid $S^{\mathrm{liquid}}(T)$ decreases faster than that of crystal $S^{\mathrm{crystal}}(T)$, with a decrease in the temperature, which eventually would lead S^{liquid} to become smaller than S^{crystal} below the Kauzmann temperature T_K.[3] This entropy crisis is, however, avoided by liquid-glass transition at $T_g > T_K$, with the glass having nearly the same heat capacity as crystal. The excess heat capacity of the liquid, $\Delta C_p^{\mathrm{exc}}(T) = C_p^{\mathrm{liquid}}(T) - C_p^{\mathrm{crystal}}(T)$, can therefore be determined as $\Delta C_p^{\mathrm{exc}}(T) = Td\Delta S^{\mathrm{exc}}(T)/dT$, where $\Delta S^{\mathrm{exc}}(T) = S^{\mathrm{liquid}}(T) - S^{\mathrm{crystal}}(T)$. The latter equation can be modified in the following way:

$$\frac{T_m}{T}\frac{\Delta C_p^{\mathrm{exc}}(T)}{\Delta S_m} = \frac{d(\Delta S^{\mathrm{exc}}/\Delta S_m)}{d(T/T_m)}. \tag{2}$$

The right part of Eq. (2) describes the rate of change of ΔS^{exc} with a decrease in the temperature or a slope of the so-called Kauzmann plot[3] of $\Delta S^{\mathrm{exc}}/\Delta S_m$ vs T/T_m. Correspondingly, the thermodynamic fragility index of a supercooled liquid m_T can be identified as the slope (or steepness) of the Kauzmann plot for this liquid at $T = T_g$,

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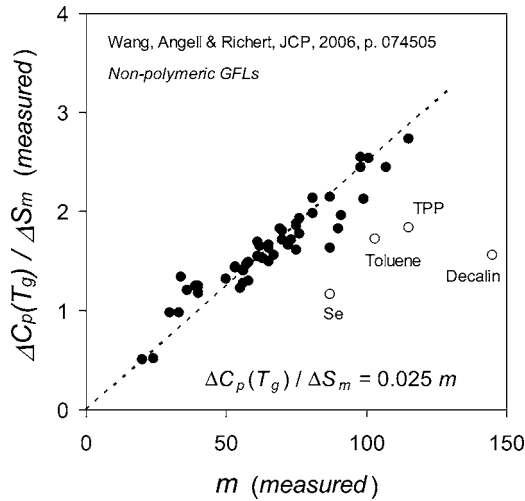
FIG. 1. Correlation of the heat capacity jump at T_g to melting entropy ratio $\Delta C_p(T_g)/\Delta S_m$ with kinetic fragility index m for 54 nonpolymeric glass-forming materials compiled by Wang *et al.* (Ref. 1).

$$m_T = \frac{d(\Delta S^{\mathrm{exc}}/S_m)}{d(T/T_m)}\bigg|_{T=T_g} \equiv \frac{T_m}{T_g}\frac{\Delta C_p^{\mathrm{exc}}(T_g)}{\Delta S_m}. \quad (3)$$

For a number of organic small molecule glass-forming liquids, including those analyzed by Wang *et al.*,[1] $\Delta C_p^{\mathrm{exc}}(T)$ $=A_1/T$,[4–6] where A_1 is a material constant, which can be determined using a boundary condition: $\Delta S^{\mathrm{exc}}(T_K)=0$. Indeed, integrating Eq. (2) in the range from T_K to T_m gives $\Delta S_m = \int_{T_k}^{T_m}(\Delta C_p^{\mathrm{exc}}/T)dT=A_1(T_m-T_K)/(T_mT_K)$, from which A_1 is obtained as $A_1=[T_mT_K/(T_m-T_K)]\Delta S_m$ and

$$\Delta S^{\mathrm{exc}} = \frac{T_m}{T}\frac{T-T_K}{T_m-T_K}\Delta S_m, \quad (4)$$

$$m_T = \frac{T_m}{T_g}\frac{\Delta C_p^{\mathrm{exc}}(T_g)}{\Delta S_m} = \left(\frac{T_m}{T_g}\right)^2\frac{T_K}{T_m-T_K} \equiv T_{\mathrm{rg}}^{-2}\frac{T_K/T_g}{T_{\mathrm{rg}}^{-1}-T_K/T_g}. \quad (5)$$

It can be seen from Eq. (5) that the thermodynamic fragility [and, therefore, $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$] increases when T_{rg} decreases and T_K/T_g increases.

Kinetic fragility

The temperature dependence of the relaxation time of a supercooled liquid is generally well described by the Vogel–Fulcher–Tammann (VFT) equation,[7] which in the modified logarithmic form reads as[8]

$$\log_{10}\left(\frac{\tau}{\tau_\infty}\right) = m_{\min}\frac{T_g-T_0}{T-T_0}. \quad (6)$$

Here, T_0 is a VFT temperature at which $\tau \to \infty$, $\tau_\infty \approx 10^{-14}$ s (Ref. 2) is the relaxation time at infinitely high temperature, $m_{\min} \equiv \log_{10}(\tau_g/\tau_\infty) \approx 16$, and $\tau_g=100$ s is the relaxation time at T_g. Differentiating Eq. (6) by (T_g/T) at $T=T_g$, the kinetic fragility index is obtained as a function of T_g and T_0,

$$m = m_{\min}\frac{T_g}{T_g-T_0}. \quad (7)$$

From Eq. (7), one may conclude that the kinetic fragility increases with an increase in T_0/T_g, but it does not depend on the melting temperature (or T_{rg}), which is quite different from the behavior of the thermodynamic fragility [Eq. (5)]. One can therefore expect that, if it is present, the relationship between m_T or $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ and m should also involve the reduced glass transition temperature T_{rg}.

Correlation between kinetic and thermodynamic fragility indices

Comparing Eqs. (5) and (7), one can conclude that the correlation between the kinetic and thermodynamic fragility indeces has effect only if the characteristic temperatures T_0 and T_K are dependent parameters. Rationalization for this correlation comes from the Adams–Gibbs theory,[9] which predicts a dependence of the relaxation time on the liquid configurational entropy S_{conf},

$$\log_{10}\left(\frac{\tau}{\tau_\infty}\right) = \frac{A}{TS_{\mathrm{conf}}(T)}. \quad (8)$$

The parameter A in Eq. (8) can be shown as $A = m_{\min}T_gS_{\mathrm{conf}}(T_g)$. Comparing Eqs. (6) and (8) leads to the following temperature dependence of S_{conf}:

$$S_{\mathrm{conf}}(T) = \frac{T_g}{T}\frac{T-T_0}{T_g-T_0}S_{\mathrm{conf}}(T_g) \equiv \frac{T_m}{T}\frac{T-T_0}{T_m-T_0}S_{\mathrm{conf}}(T_m). \quad (9)$$

It has been widely assumed that S_{conf} is equal or at least proportional to ΔS^{exc} (i.e., $S_{\mathrm{conf}} \cong a\Delta S^{\mathrm{exc}}$, where a is a constant),[10] which can hold only if $T_0=T_K$ [e.g., compare Eqs. (4) and (9)]. Although the assumption $S_{\mathrm{conf}} \cong a\Delta S^{\mathrm{exc}}$ has recently been discussed to be problematic[11,12] and a large difference between T_0 and T_K has been found for strong glass-forming liquids, including bulk metallic glasses,[13] compilation of a number of experimental data[14,15] shows that the relation $T_0 \cong T_K$ is indeed valid for many fragile liquids, including nonpolymeric liquids. Assuming that $T_0 \cong T_K$ for the liquids analyzed by Wang *et al.*,[1] and combining Eqs. (5) and (7), one can find the following correlation between m_T and m:

$$m_T = \frac{1}{T_{\mathrm{rg}}}\frac{m-m_{\min}}{m(1-T_{\mathrm{rg}})+m_{\min}T_{\mathrm{rg}}}. \quad (10)$$

Taking into account relation between m_T and $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ [Eq. (3)], one can obtain the relationship between $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ and the kinetic fragility m,

$$\frac{\Delta C_p^{\mathrm{exc}}(T_g)}{\Delta S_m} = \frac{m-m_{\min}}{m(1-T_{\mathrm{rg}})+m_{\min}T_{\mathrm{rg}}}. \quad (11)$$

As it was expected, both m_T and $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ are functions of both m and T_{rg}.

The presented analysis may require further modification for supercooled liquids with a considerable deviation of T_0 from T_K. For these liquids, the temperature dependences of
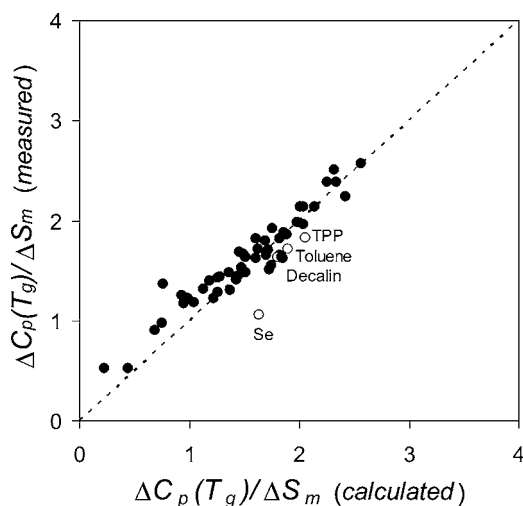
FIG. 2. Experimentally measured vs calculated [using Eq. (11)] values of $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ for 54 glass-forming liquids from Table I of Ref. 1 (see also Fig. 1).

the excess and configurational entropies can be quite different and the relation $S_{\mathrm{conf}} \cong a\Delta S^{\mathrm{exc}}$ may not be valid.[11,12,16]

Validation of Eq. (11) with experimental data

When the empirical relation suggested by Wang *et al.*[1] [Eq. (1)] is compared with the phenomenological relation derived in this work [Eq. (11)], a rather large difference can be seen. Indeed, Eq. (1) identifies a linear dependence between $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ and m, while Eq. (11) predicts a nonlinear dependence between these parameters, with $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ approaching the value of $(1-T_{\mathrm{rg}})^{-1} \approx 3.0$ when $m \to \infty$. Moreover, Eq. (11) predicts that $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ is a function of both m and T_{rg}, so that the glass-forming liquids with the same m but different T_{rg} should have different values of $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$. The analysis of Eq. (11) also shows that $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ increases with an increase in m and a decrease in T_{rg}. Figure 2 shows the dependence of the experimentally measured and calculated [using Eq. (11) and experimental data for m and T_{rg}] values of $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ for 54 liquids from Table I of Ref. 1. It can be seen that Eq. (11) describes the correlation between $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$, m, and T_{rg} much better than Eq. (1). TPP, decalin, and toluene are now in line with other glass-forming liquids and the coefficient of determination of the fit is R^2 =0.801. Selenium still deviates from the linear fit of the $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ (experimental) versus $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ (calculated); however, the deviation now is much smaller than in the case of the fit by Eq. (1) (compare Figs. 1 and 2).

The fact that the behavior of Se continues to deviate from the main trend [Eq. (11)] can be explained by different

values of T_0=236 K and T_K=264 K for this element.[17,18] This 12% difference between T_0 and T_K cannot be explained by the experimental error because these temperatures are quite close to T_g=303.4 K. Therefore, the approximation $T_0 = T_K$, which was used to derive Eq. (11), probably does not work well for Se.

CONCLUSIONS

A phenomenological relationship between $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$, m, and T_{rg} [Eq. (11)] was derived for fragile glass-forming liquids under the assumptions that (a) fragile behavior of these liquids is described by the VFT equation, (b) the excess heat capacity of liquid is inversely proportional to the absolute temperature, and (c) the VFT temperature T_0 is equal to the Kauzmann temperature T_K. It was found that $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m$ is a composite function of m and T_{rg}, which describes the behavior of nonpolymeric glass-forming liquids much better than the empirical linear dependence $\Delta C_p^{\mathrm{exc}}(T_g)/\Delta S_m=0.025m$ recently identified by Wang *et al.*[1] The latter correlation is probably valid for liquids which have nearly the same values of T_{rg}.

ACKNOWLEDGMENTS

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