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Excess thermodynamic properties of glassforming liquids: The rational scaling of heat capacities, and the thermodynamic fragility dilemma resolved

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ABSTRACT

With the overall objective of clarifying some perennial issues with the concept of liquid fragility, and with thermodynamic fragility in particular focus, we review the determination of excess thermodynamic properties of liquids as the temperature rises above T_g . We treat the compressibility first, as it is the one most commonly encountered in theory where it may be derived from the radial distribution function (specifically, from its Fourier transform (the structure factor) at zero wave vector), and is known to be proportional to the mean square density fluctuation. We show that the compressibility of glassforming liquids, and also the difference in compressibility between liquid and glass, always decreases as T_g is approached with the exception of a few water-like (anomalous) liquids. Secondly we examine the heat capacity which is favored in the analysis of glassforming liquid behavior. Contrasting with the compressibility, the excess heat capacity (determined by entropy fluctuations), mostly increases as temperature approaches T_g (with the same exceptions). But here we encounter the problem of the appropriate scaling of the measured molar quantity, which plagues comparisons of ΔC_p between different substances. We solve this problem by defining C_p as an entropy derivative and scaling by the absolute excess entropy at T_g - which avoids the need for “beads” or other artificial scaling methods. Finally, we revisit the subject of thermodynamic fragility, which has been discussed before using a related scaling strategy.

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1. Introduction

The concept of fragility in liquids [1,2] has been given a great deal of attention by workers in the viscous liquid and glasses field. While the basic phenomenon has been widely used to classify liquids (and also the related plastic crystal phases that freeze-in orientational degrees of freedom during extended cooling [3–5]), the full understanding of fragility itself is proving slow to arrive.

A development that should have been of help but has instead become a source of confusion, was the proposal of a thermodynamic equivalent of the kinetic quantity, viz. the “thermodynamic fragility” [6]. Thermodynamic fragility was defined initially using a dimensionless quantity $S_{ex}(T_g)/S_{ex}(T)$ that was shown to yield a pattern similar to that for the liquid viscosity (log plot) vs scaled temperature T_g/T . Studies showed that this quantity, or a more easily determined variant of it (in which $S_{ex}(T_g)$ was replaced by $\Delta H_m/T_g$) [7], correlated quite well with the dynamic quantity $\log(\text{viscosity})$. The thermodynamic fragility has the advantage that it could be understood in terms of the molecular parameters of simple excitation models for glassformer thermodynamics [8,9].

Unfortunately several groups have taken the position that thermodynamic fragility should be represented by the excess heat capacity, in unscaled or unsuitably scaled, form. Works like the impressive data collection of Huang and McKenna [10] that illustrate the lack of correlation of this excess quantity with the kinetic fragility, have become highly cited, and assist in creating a state of disenchantment in the field with thermodynamic fragility as a concept. A primary purpose of this contribution is to point out as strongly as possible that excess heat capacity should **not** be expected to correlate with kinetic fragility unless it is first subjected to a rational scaling, which has so far not been properly documented.

We commence with a general, and much needed, review of the different sorts of fluctuations that get “frozen in” in the glass transition process, (and indeed define that process) and their connection to response functions that are better known as derivatives of extensive thermodynamic properties, like volume and enthalpy. After all, the glass transition is not only the temperature at which the structure becomes fixed during cooling, but also the temperature at which the slow component of the fluctuations in extensive thermodynamic properties become frozen. Remember that each of the response functions is a sum of components that are collision-based (vibrational time-scale) fluctuations and configuration-based (structural relaxation time scale) and only the latter component time scale is diverging as T_g is approached.

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The configuration-based derivative quantities behave very differently from each other with increase of temperature above T_g , and this is not often discussed, probably because it is neither well studied nor well understood. We recently showed, for one “model” system, orthoterphenyl (OTP), how the compressibility (particularly the excess over the vibrational component) increases as T rises above T_g , while the excess heat capacity, scaled as we elaborate in this article, does the opposite [11]. The expansion coefficient, being proportional to the product of entropy and volume fluctuations is, not surprisingly, nearly temperature independent.

The common derivative functions, and also their relation to fluctuations according to Landau and Lifschitz [12], are:

$$\begin{aligned} \text{Isothermal compressibility, } \kappa_T &= -1/V(\partial V/\partial P)_T \\ &= -\langle(\Delta V)^2\rangle/Vk_B T \end{aligned} \quad (1)$$

$$\text{Constant volume heat capacity, } C_V = (\partial E/\partial T)_V = k_B T^2 \langle(\Delta T)^2\rangle \quad (2)$$

$$\text{Constant pressure heat capacity, } C_P = (\partial H/\partial T)_P = \langle(\Delta S)^2\rangle/k_B \quad (3)$$

$$\begin{aligned} \text{Isobaric expansion coefficient, } \alpha_P &= 1/V(\partial V/\partial T)_P \\ &= \langle(\Delta S \cdot \Delta V)\rangle/Vk_B T \end{aligned} \quad (4)$$

In each case, there will be fast and slow components of the response function, determined by fast fluctuations (like sound waves - fast damping shear modes and slow-damping longitudinal waves - and librations) and slow fluctuations that change the local structure, and potential energy, and entropy. We now examine their behavior in the order compressibility, heat capacity (which is our main concern), and expansivity, before applying the results of our considerations to the question of thermodynamic fragility.

2. Compressibilities of glassforming liquids

We have collected as many data on the compressibility of glassforming liquids as are readily available, and present them, together with some data on non-glassformers, in Fig. 1. Since the compressibility of solid phases is generally rather small by comparison with that of

liquids, the strongly increasing behavior with increasing temperature must be due to the slow density fluctuations characteristic of the liquid state in every case. This is quite striking to anyone familiar with the oppositely directed behavior of many glassforming liquid heat capacities, indeed almost all liquid heat capacities after the vibrational contribution has been subtracted and, in particular, after the appropriate scaling to which we draw attention in this paper, has been applied.

The increased compressibilities, and the temperature dependences of compressibility for liquids with low glass temperatures, are quite striking. It should be related to the observations made in negative pressure studies of liquids that show how, at ambient pressure, these less cohesive liquids are closer to their spinodal limits of mechanical stability (which lie at negative pressures hence are not much studied). The stability limit in question is the stability against cavitation under isotropic tension (which is the formally correct meaning of “negative pressure”). The cavitation event returns the system to its stable state of an ambient pressure liquid in equilibrium with its vapor. Simple theory (e.g. van der Waals) tells us that as the mechanical stability limit is approached, the compressibility must diverge, which is all we need to understand the pattern of Fig. 1.

There are experimental data to support the above reasoning. The experimental limits to stretching of simple liquids like heptane and ethanol at 25 °C, which agree with the theoretical expectations, are reported by Caupin et al. [13] to lie in the range -20 to -30 MPa (-200 to -300 atm), while that for OTP is much larger, namely at about -120 MPa [14,15,16,17]. Since ambient pressure (for which all Fig. 1 data are presented), is much further from the spinodal limit in the case of OTP than in the case of ethanol or heptane, the fluctuations in volume of the former should be much smaller than those of the latter. This would rationalize the relation between the κ_T values and also their temperature dependence, seen in Fig. 1.

3. Heat capacities of glassforming liquids, and a problem

The heat capacity “jump” observed at the glass transition, which is a consequence of the increase in mean square entropy fluctuation in the time window of the experiment in which “broken ergodicity” is being restored, is a highly variable quantity amongst different glassforming materials. For some glassformers, the liquid heat capacity at T_g can be

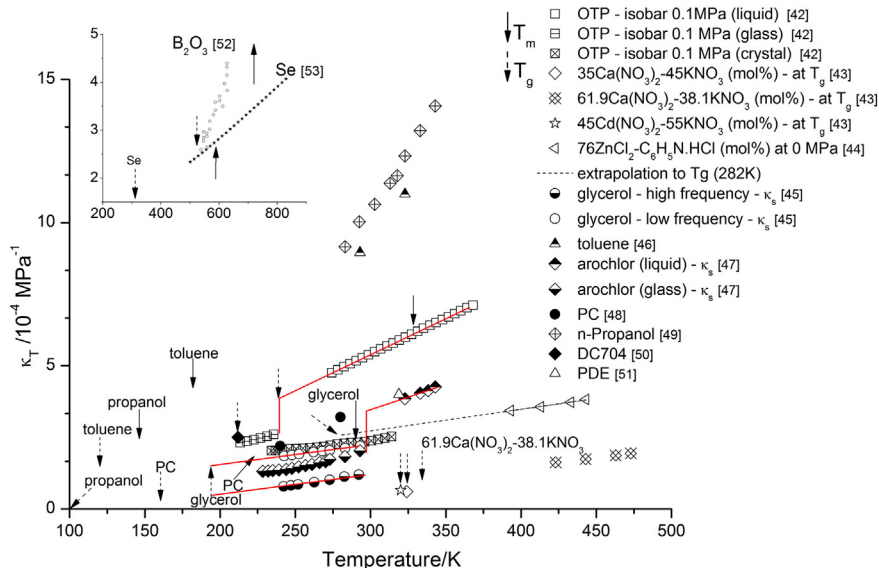


Fig. 1. Compressibilities of glassforming liquids. Solid arrows denote T_m and dashed arrows denote T_g . All examples show a jump at T_g and then a linear increase above T_g , with slope greater than that of glass or crystal. Extrapolations of available data to T_g would suggest rather small $\Delta\kappa_T$ values for the low T_g liquids like toluene and propanol. For glycerol, and arochlor, data are adiabatic values from sound velocity data, and high and low frequency points indicate the $\Delta\kappa_S$ values (in these cases, the label “glass” means non-relaxing on the ultrasonic time scale). On the scale of this plot, an isothermal value κ_T for glycerol is indistinguishable from the κ_S datum at the same T . References for the data are given in the legend after each symbol identification and are included in numerical order at the end of the reference section. Data for two other liquids that fall in the already crowded portion of this figure have been omitted for clarity.

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