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# Thermal expansion and the glass transition

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Melting is well understood in terms of the Lindemann criterion, which essentially states that crystalline materials melt when the thermal vibrations of their atoms become so vigorous that they shake themselves free of the binding forces. This picture does not necessarily have to hold for glasses, where the nature of the solid–liquid cross-over is highly debated. The Lindemann criterion implies that the thermal expansion coefficients of crystals are inversely proportional to their melting temperatures. Here we find that, in contrast, the thermal expansion coefficient of glasses decreases more strongly with increasing glass temperature, which marks the liquid–solid cross-over in this material class. However, this proportionality returns when the thermal expansion coefficient is scaled by the fragility, a measure of particle cooperativity. Therefore, for a glass to become liquid, it is not sufficient to simply overcome the interparticle binding energies. Instead, more energy must be invested to break up the typical cooperative particle network that is common to glassy materials. The thermal expansion coefficient of the liquid phase reveals similar anomalous behaviour and is universally enhanced by a constant factor of approximately 3. These universalities allow the estimation of glass temperatures from thermal expansion and vice versa.

Many materials in technology and nature are glasses, that is, disordered materials that are solid but lack the periodicity of a crystalline lattice[1,2]. This includes not only the common silica-based transparent materials used for windows, glass fibres, etc. but also many polymers and bio-derived materials, various solid-state electrolytes, supercooled molecular liquids and even amorphous metals. This state of matter is usually prepared by cooling a liquid sufficiently fast to avoid crystallization[1–3]. Below the melting temperature $T_m$, a so-called supercooled liquid is formed first, before the material becomes a glass below the glass temperature $T_g < T_m$. The latter marks the boundary between liquid and solid, which usually is defined at a viscosity value of $10^{12}$ Pa s. However, in contrast to crystallization, the solidification at $T_g$ occurs smoothly, that is, without a discontinuous jump of the viscosity. Below $T_g$, most physical quantities of a glass-former exhibit a cross-over to weaker temperature dependence, that is, a jump in their derivatives, at first glance reminiscent of a second-order phase transition. This is also the case for the volume (Fig. 1a) as well as the thermal expansion, which is considered in the present work.

Although humans have used supercooling to prepare glasses for millennia, there is no consensus on the true nature of the glass transition[1–5]. The temperature of the mentioned cross-over depends on the cooling rate, clearly excluding a canonical phase transition. Instead, it is commonly assumed that the liquid falls out of thermodynamic equilibrium at the glass transition, which happens just at $T_g$ for a typical cooling rate of 10 K min$^{-1}$. Nevertheless, various competing theoretical approaches assume that an underlying, 'hidden' phase transition at a temperature above or below $T_g$ may in fact govern the cross-over between liquid and glass[2,4,6,7]. Alternatively, it could simply be a purely kinetic phenomenon[4,8,9].

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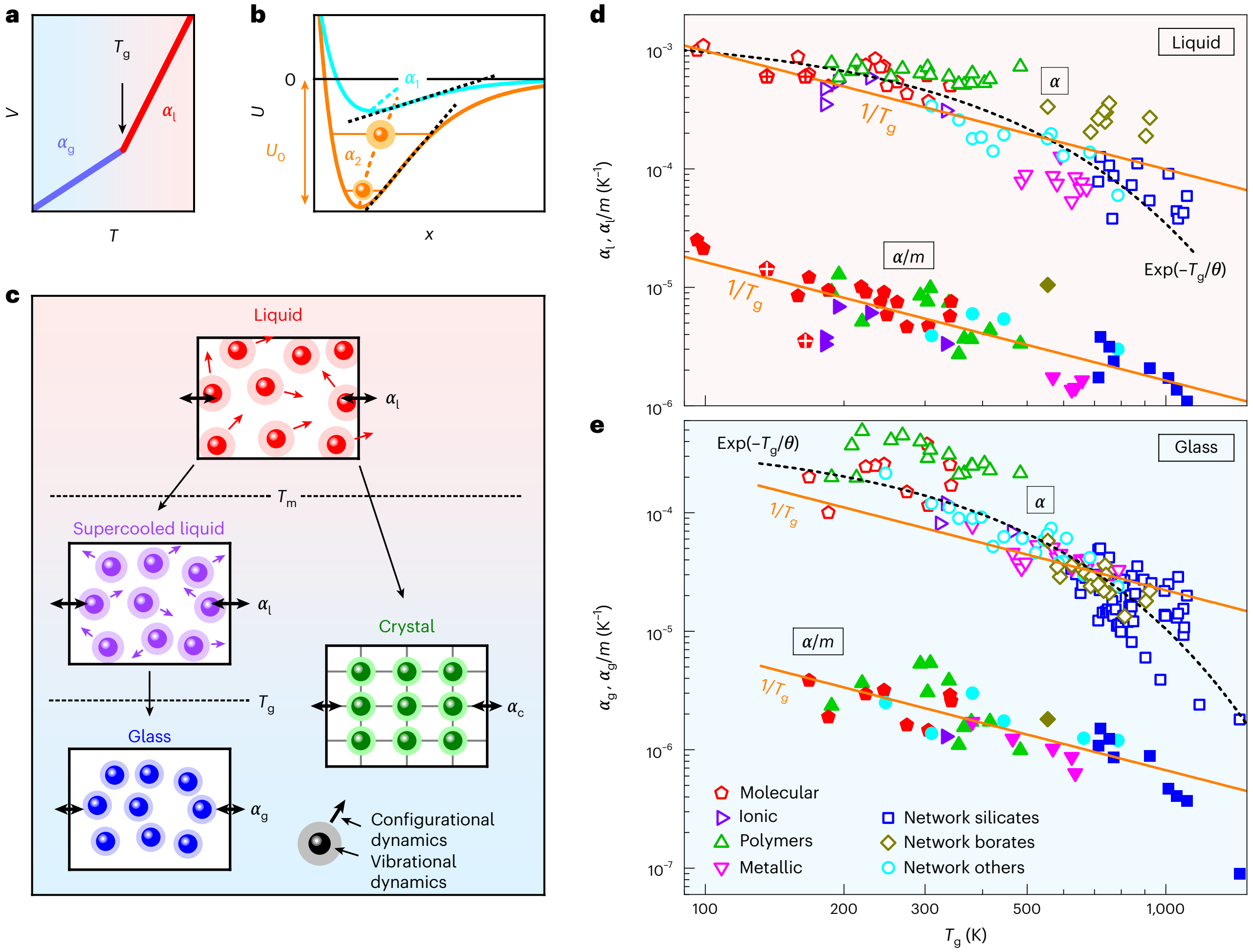

**Fig. 1 | Contributions to the thermal expansion and its correlations with the glass temperature. a**, Schematic of the temperature variation of the volume around the glass transition (blue line, glass state; red line, liquid). **b**, Schematic of the asymmetric pair potential giving rise to thermal expansion in a solid. Two potentials for two different binding energies (depths of minima) are shown (orange and cyan solid lines: potential for high and low binding energies, respectively). The dotted black lines show the slopes at the attractive parts of the potentials, which are smaller for lower binding energy. The dashed lines (orange, high binding energy; cyan, low binding energy) indicate the average location of the particle, which shifts to the right (larger interparticle distance) for higher temperature, leading to thermal expansion. For the deeper potential, the particle position is shown for two temperatures. **c**, Schematic of the different contributions to the thermal expansion of liquids, glasses and crystals: the vibrational dynamics is indicated by the shaded areas around the spheres, representing the atoms or molecules of the material. The additional configurational dynamics in the liquid phases is indicated by single-headed arrows. The double-headed arrows illustrate the resulting thermal expansion. **d**,**e**, Double-logarithmic plot of the experimentally determined thermal volume-expansion coefficients $\alpha_g$ in the glass phase (**e**) and of $\alpha_l$ in the liquid phase (**d**) versus the glass temperature $T_g$ for a large variety of glass-formers belonging to different material classes (see Supplementary Table 1 for detailed information on all the materials and values and the corresponding references; for water, shown by the crossed pentagons, two glass-transition scenarios were considered; see Supplementary Note 5). In addition to the bare expansion coefficients (open symbols), the figure also provides the $\alpha$ values divided by the fragility parameter $m$ (filled symbols), being a measure of cooperative dynamics. The solid orange lines show linear fits with a slope of −1, based on all data points for each phase, except for $\alpha_l$ of the borates and of water and except for $\alpha_g$ of $SiO_2$. The dashed lines represent fits with $\alpha \propto \exp(-T_g/\theta)$ with the same $\theta \approx 270$ K for both data sets. Note that the ordinates of **d** and **e** have been adjusted to achieve the same decades per centimetre ratio. In **a** and **c**–**e**, bluish and reddish backgrounds indicate solid- and liquid-like states, respectively.

In contrast, the transition between the liquid and solid states via crystallization and melting is much better understood[10], in particular in terms of the basic ideas behind the Lindemann criterion[11,12]. The latter predicts that melting occurs when the r.m.s. displacement of particles due to thermal vibrations exceeds a certain percentage of the interparticle spacing[12], often reported to be roughly on the order of 10% (refs. [13–15]). It is nowadays well established that these vibrations take place within potential wells whose asymmetry gives rise to thermal expansion. There are arguments (Supplementary Note 1 and ref. [16]) that, for higher melting temperatures, associated with deeper wells, the slope of the attractive part of the potential should be steeper (Fig. 1b). As this slope $s$ is related to the thermal expansion coefficient $\alpha_c$ of a crystalline material, one can expect less expansion for materials with higher $T_m$. Making the reasonable approximations that $T_m \propto U_0$ (with $U_0$ the depth of the well) and that $1/\alpha_c \propto s \propto U_0$ (ref. [16]; see Supplementary Note 1 for a more detailed discussion), one arrives at:

$$\alpha_c T_m = \text{const.} \tag{1}$$

Here, $\alpha_c$ is defined as the relative volume change at constant pressure $p$, namely, $\alpha_c = 1/V(\partial V/\partial T)_p$. Indeed, such a relation was suggested to be directly related to the Lindemann criterion[14,17] (see also Supplementary Note 1).

In crystalline solids, the ordered structure melts at the melting temperature, and in glasses, the rigid disordered structure dissolves above the glass temperature. Thus, it seems natural that these two phenomena should have a common basis, specifically bearing in mind that, for many glasses, the relation $T_g \approx 2/3T_m$ holds[18–22] (although exceptions are also reported[23]). In light of a possible Lindemann-like criterion for the glass–liquid transition considered, for example, in refs. [4,21,22,24–28], in analogy to crystals, one may thus expect the relation:

$$\alpha_g T_g = \text{const.} \tag{2}$$

In general, the thermal expansion is of fundamental importance, defining universal quantities such as the Grüneisen parameter or the Prigogine–Defay ratio[1,12,29]. It also reflects the occurrence of different dynamic processes in glasses[30]. The change of slope of $V(T)$ at $T_g$ (Fig. 1a) is one of the most paradigmatic characteristics of the glass transition[18,31,32]. The thermal expansion coefficient in liquids, $\alpha_l$, is higher by about a factor of 1.5–4 than in solids[32–35]. It is well established that $\alpha_l$ contains two contributions: a vibrational one, also present in the solid state, and an additional configurational one, being caused by the translational motions of the particles that also give rise to the viscous flow defining a liquid[22,33,34,36] (see the schematic representation in Fig. 1c). The vibrational contribution arises from the anharmonic interparticle potential and dominates the thermal expansions of crystals and glasses, which mostly are of similar magnitude.

Interestingly, Stillinger and co-workers suggested a Lindemann-like freezing criterion for liquids[37–39]. On the basis of molecular dynamics simulations, they found that melts freeze if the r.m.s. particle displacement falls below about one-half of the interparticle spacing. In analogy to equations (1) and (2), related to the Lindemann melting criterion, one could thus naively expect that:

$$\alpha_l T_g = \text{const.} \tag{3}$$

with $\alpha_l$ as the expansion coefficient of the liquid. However, $\alpha_l$ is believed to be governed by additional configurational motions instead of the vibrations exclusively considered in the Lindemann scenario. Therefore, deviations from such a correlation, if present at all, may be expected. Nevertheless, in ref. [40], such a relation was predicted, on the basis of theoretical considerations. Moreover, within the framework of the recently developed Krausser–Samwer–Zaccone model[41], equation (3) should also be approximately valid and consistent with a correlation of the repulsive part of the interparticle potential and the fragility index $m$ (refs. [42,43]) that was recently found for a variety of glass-formers[44] (see Supplementary Note 2 for details).

In literature, there are some reports on, partly contradicting, correlations of $T_g$ with the thermal expansion or with $\Delta\alpha$, the jump of $\alpha$ at $T_g$, namely, $\Delta\alpha T_g = \text{const.}$ (refs. [45,46]), $\Delta\alpha T_g \propto T_g$ (ref. [47]), $\alpha_g T_g^2 = \text{const.}$ (ref. [20]) and $\alpha_l T_g = \text{const.}$ (refs. [40,45]) (equation (3)). However, they all were found for specific classes of glass-formers only, and the overall data base was limited. In contrast, in the present work, using data on more than 200 materials from literature (Supplementary Table 1), we check for such correlations across very different classes of glass-formers.

If equation (2) or (3) or alternative universal relations hold, $\alpha$ measured in a glass or liquid would allow one to predict glass temperatures, without any knowledge of microscopic pair potential parameters. At the same time, one could gain insight into the universality of configurational contributions to the thermal expansion at $T > T_g$ and concerning the relevance of a Lindemann-like mechanism for the glass transition. In any case, the explanation of a possible universal relationship of $\alpha$ and $T_g$ would represent a severe benchmark for any model of the glass transition.

## Experimental data and analysis

The values of $\alpha_g$, $\alpha_l$ and $T_g$ used in the present work are listed in Supplementary Table 1, and details on their selection and reliability are provided in Supplementary Notes 3 and 4. The included materials can be classified as molecular glass-formers (alcohols, van der Waals-bonded and other systems), polymers, ionic glass-formers (including ionic liquids and melts), metallic systems (so-called bulk metallic glasses and others) and network glass-formers (including silicates, borates, phosphates, chalcogenides and halogenides, whose networks are mainly formed by covalent bonds, in contrast to hydrogen-bonded materials such as water or alcohols, which also can form molecular networks). Their interparticle bond types vary from covalent, hydrogen, ionic, metallic to van der Waals. Their glass temperatures cover about one decade, and their thermal expansion coefficients vary by approximately 2.5 and 1.5 decades in the glass and liquid phase, respectively. In general, the available data basis is broader for the glass state than for the liquid phase.

The open symbols in Fig. 1d,e show the complete $\alpha(T_g)$ data sets for the liquid and glass states, respectively, using a double-logarithmic representation. The first conclusion from these figures is a clear correlation of the thermal expansion with the glass temperature, namely, a decrease of $\alpha_g$ and $\alpha_l$ with increasing $T_g$. Notably, this correlation holds across very diverse material classes (indicated by different symbols in the figures) with different bond types and drastically varying glass temperatures. The scatter of the data certainly partly signals the fact that $\alpha$ was often measured employing very different techniques applied by various experimental groups during the last century. It probably also arises from variations in the width and separation from $T_g$ of the temperature regime where the thermal expansion was determined (see also Supplementary Notes 3 and 4). Figure 1d also includes data for water (crossed pentagons), whose glass transition is highly controversial. When considering the ambiguities in the determination of its $\alpha$ and $T_g$, for both proposed glass-transition scenarios (with or without assuming a liquid–liquid transition and with different $T_g$ values; see Supplementary Note 5 for more details), its values reasonably match the suggested correlation.

As discussed above, in principle, a decrease of $\alpha$ with increasing $T_g$, as demonstrated in Fig. 1d,e, is expected if a Lindemann-like scenario would apply for the glass–liquid transition, too. However, when assuming the validity of equations (2) and (3), such double-logarithmic plots of $\alpha$ versus $T_g$ (open symbols) should lead to approximately linear behaviour with a slope of −1. Instead, both data sets depend much more strongly on $T_g$, as becomes obvious from a comparison with the upper solid lines, indicating a slope of −1, that is $\alpha \propto 1/T_g$. At best, only part of the liquid data, especially at $T_g < 400$ K, are roughly consistent with equation (3). We find that an exponential $T_g$-dependent variation, $\alpha_i = \alpha_{0,i}\exp(-T_g/\theta_i)$ (with $i$ = 'g' or 'l' for glass or liquid, respectively), as indicated by the dashed lines in Fig. 1d,e, provides a much better formal description of the experimental data than the dependence $\alpha_i \propto 1/T_g$ suggested by equations (2) and (3). Indeed, both data sets can be quite well linearized within a semi-logarithmic representation, plotting the logarithm of $\alpha_i$ versus $T_g$ (Supplementary Fig. 1). The only exception are the values for the borates in the liquid state, whose thermal expansion seems to represent a special case. Indeed, exceptional thermal expansion properties of the borate glasses were identified earlier[19,48,49] They are believed to be due to their specific network structure involving triangular-shaped $BO_3$ basic units, instead of the tetrahedral units prevailing in most other network glass-formers (Supplementary Fig. 1, circles and squares) in this high $T_g$ range. Moreover, temperature- and composition-dependent structural rearrangements also may play a role[50,51].

The very similar $\alpha$–$T_g$ correlations for the liquid and glass state are astonishing, bearing in mind that the thermal expansion in the supercooled liquid includes vibrational as well as configurational contributions, while in the glass it should be dominated by vibrational contributions only. Moreover, we find an approximately identical exponential factor $\theta_l = \theta_g \approx 270$ K for both glasses and liquids. This implies a fixed ratio $\alpha_l/\alpha_g = \alpha_{0,l}/\alpha_{0,g}$. Using $\alpha_{0,l} \approx 1.4 \times 10^{-3}$ K$^{-1}$ and $\alpha_{0,g} \approx 4.3 \times 10^{-4}$ K$^{-1}$, obtained from the fits, this ratio is approximately 3, which should be universally valid for all glass-formers. To check this prediction, Fig. 2 shows $\alpha_l/\alpha_g$ versus $T_g$ for those materials where both expansion

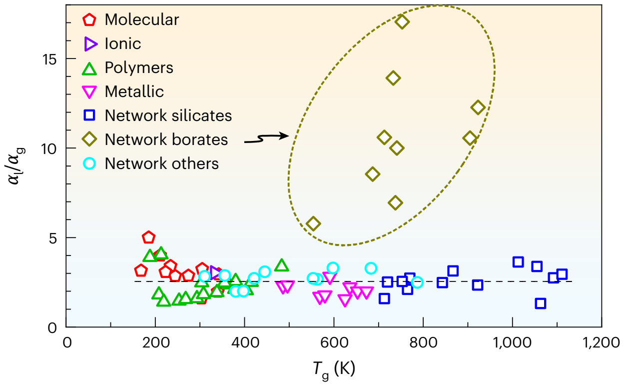

**Fig. 2 | Ratio of the thermal expansion coefficients measured in the liquid and glass phases.** Leaving the borate glasses aside, this ratio is essentially independent of the glass temperature and on the order of 3 for all systems (the horizontal dashed line indicates the average value of 2.6).

coefficients are available. Indeed, this ratio is close to 3 for a large variety of glass-formers belonging to different material classes. Only the borate glasses reveal much larger ratios, in accord with their known anomalous expansion behaviour[19,48,49].

## Discussion and concluding remarks

We have shown that the thermal expansion data of about 200 glass-formers reveal a clear correlation with the glass temperature, which holds across vastly different material classes. However, the data are clearly inconsistent with $\alpha T_g$ = const., expected when assuming a Lindemann-like scenario for the glass transition. This expectation is met neither for the glass, nor for the liquid phase, where it was theoretically predicted[40,41,44]. Instead, we find a much stronger decrease of $\alpha$ with $T_g$ for both states. This only becomes obvious when considering data covering a broad range of glass temperatures and thermal expansion coefficients.

The invalidity of equation (2) implies that at least one of the intuitive proportionalities $T_g \propto U_0$ and $1/\alpha_g \propto U_0$ (analogous to the crystal case; see the introduction and Supplementary Note 1) must be invalid for glasses. A clue is given when considering that $U_0$, the depth of the pair potential, essentially corresponds to the interparticle binding strength. As materials with very weak (van der Waals) and strong (covalent) bonds are included here, it should vary by about two or three decades. This is in accordance with the observed variation of $\alpha_g$ (Fig. 1e), that is, consistent with $1/\alpha_g \propto U_0$. In contrast, $T_g$ varies by 1.2 decades only, and thus, $T_g \propto U_0$ should be invalid. Therefore, we conclude that the transition temperature from glass to liquid depends much more weakly on the microscopic quantity $U_0$ than for the crystal–liquid transition for which $T_m \propto U_0$. This marked difference seems somehow to reflect the fact that the glass transition differs qualitatively from crystal melting. This can be rationalized as follows:

Notably, the systems with small $T_g$ and high $\alpha$, lying in the upper left part of Fig. 1e (for example, the polymers and molecular materials), generally exhibit higher fragility index $m$ than those with high $T_g$ and small $\alpha$ such as the metallic or network systems[52] (Supplementary Table 1 and Supplementary Fig. 2). $m$ is a quantitative measure of the deviation of a material's viscosity $\eta$ from the Arrhenius temperature dependence, $\eta \propto \exp[E/(k_B T)]$ (where $k_B$ is the Boltzmann constant), expected when assuming canonical thermally activated particle dynamics with a well-defined energy barrier $E$ (refs. [42,43]). Such deviations are a hallmark feature of glass-forming liquids and strongly material dependent, being most pronounced, for example, in many polymers and molecular liquids[1,4,43]. They are often ascribed to an increase of the effective energy barrier with decreasing temperature, caused by the cooperative motion of ever larger numbers of molecules upon cooling a liquid towards its glass transition[2,3,53]. Within this framework, higher $m$ values (characterizing so-called fragile glass-formers[1,4,43]) mean that this increase is stronger than for small $m$ values ('strong' glass-formers).

The stronger $T_g$ dependence of $\alpha_g$ compared with equation (2), observed in the present work, then could be due to this effective energy barrier enhancement. The glass temperatures of the more fragile materials in the upper left part of Fig. 1e are larger than expected from their pair potential depth alone, because, to liquify these glasses, more energy has to be invested to break up their cooperatively rearranging regions. Within this scenario, $T_g \propto mU_0$ instead of $T_g \propto U_0$ may be tentatively assumed. In contrast, the relation $\alpha_g \propto 1/U_0$ should be unaffected by cooperativity as the thermal expansion in a solid glass is governed by vibrational motions within the local pair potential only (Fig. 1b), for which cooperative motions play no role. Therefore, the proportionality $\alpha_g \propto 1/T_g$ should be invalid, in accordance with experimental observation (Fig. 1e) and, instead, the quantity $\alpha_g/m$ should be proportional to $1/T_g$. This expectation indeed is well fulfilled, as demonstrated by the filled symbols in Fig. 1e, showing $\alpha_g/m$ versus $T_g$ for those systems where $m$ is known (Supplementary Table 1). This finding corroborates the correctness of the assumption $T_g \propto mU_0$ mentioned above. The only clear exception is the data point for pure $SiO_2$, which is also exceptional by having the highest $T_g$ and smallest $\alpha_g$ of all systems and an anomaly in its temperature-dependent density[54] similar to water.

Notably, a corresponding cooperativity correction also is able to linearize the thermal expansion coefficients of the liquid state (Fig. 1d, filled symbols). That is, we find $\alpha_l/m \propto 1/T_g$. Thus, equations (2) and (3) should be replaced by:

$$(\alpha_i/m)T_g = \text{const.} \quad (i = \text{g, l}). \tag{4}$$

Interestingly, a similar relation is an outcome of the free volume model, assuming that $\alpha$ is the thermal expansion coefficient due to free volume[55]. Notably, the above-mentioned ratio $T_g \approx 2/3T_m$ is incompatible with the simultaneous validity of equations (1) and (4), considering that $\alpha_g \approx \alpha_c$. As this ratio is quite well established[18–22], some doubts about the validity of equation (1) may arise. It certainly would be interesting to check this relation for a similarly broad data base as in the present work.

Finally, it is remarkable that $\alpha_l$ and $\alpha_g$ (or $\alpha_l/m$ and $\alpha_g/m$) exhibit the same dependence on glass temperature and are related by a universal factor of about 3, characterizing the increase of the thermal expansion when crossing the glass transition upon heating. A factor of 2–4 was occasionally quoted in literature[33,34], and here we document a factor close to 3 that is valid for the complete universe of glass-forming materials, leaving the borates aside. As discussed above, it is reasonable that the vibrational contributions to the thermal expansion are essentially the same in the glass and liquid states (Fig. 1c), ascribing the observed higher $\alpha_l$ to additional configurational contributions arising above $T_g$ (refs. [33,34]). Then, $\alpha_l/\alpha_g \approx 3$ implies that the configurational part is universally two times higher than the vibrational one, which seems surprising when considering their different physical origins. It is reasonable that the thermal expansion is related to the maximum possible displacement of a particle during the corresponding motion (either vibrational and/or configurational). If one expands the third derivative of the pair potential versus distance (the thermal expansion coefficient) from one to three dimensions, assuming still the same local process, and adds the configurational (many body) motions, one can rationalize the detected factor of 3 (see Supplementary Note 6 for details). Thus, the enhancement of $\alpha$ above $T_g$ essentially seems to be a dimensionality effect. Locally, we propose here the cross-over from a two-body interaction (vibrations on the picosecond time scale) to an additional many-body process (configurational changes on a much longer time scale).

The found universal correlation of $\alpha_g$ and $T_g$, involving the degree of cooperativity of particle motion in different material classes, quantified by the fragility $m$, obviously is a typical, so far unnoticed, property of glasses. It markedly differs from the much simpler behaviour of crystalline systems, which can be explained in terms of the Lindemann criterion. This and the unexpected universal factor relating $\alpha$ in the glass to that in the liquid put severe constraints on existing and future models of the glass transition. Finally, the present results have predictive power for engineering glassy materials by design: one will be able to predict $T_g$ in a bottom-up way based on interatomic/intermolecular parameters and to deduce it from a simple thermal expansion measurement. Conversely, a simple $T_g$ measurement will yield a wealth of information about atomic-scale composition and thermal properties.

## Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-022-01920-5.

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## Data availability

The data that support the findings of this study are available in Supplementary Table 1.

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## Author contributions

K.S. initiated this work. P.L. and B.R. collected the experimental data. P.L. analysed the data and prepared the figures. A.L., P.L., K.S. and A.Z. wrote the manuscript. All authors discussed the results and commented on the manuscript.

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## Competing interests

The authors declare no competing interests.

## Additional information

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