Glasses have been of use to mankind from early on, be it as arrowheads for the stone age people of Corsica and the Americas, the obsidian battle axes and swords of the Aztecs, pumice scrapers for animal hides, or the tektite ornaments and fertility symbols of our ancestors. It has also been a source of fascination once its manufacturing process became understood around 2000BC in the Caucasus and has continued to amaze us when considering artifacts from the tomb of Thutmose III (1480 BC), straightened out the proper picture, it is interesting to reconsider glass from a thermodynamic viewpoint. A shard of glass, kept at fixed temperature and volume, relaxes towards lower energy. Heat is released, inducing apparent violations of all basic thermodynamic laws. The most interesting application is to use glassy or amorphous systems as a source of energy, by extracting the configurational energy in a process of melting followed by crystallization.

The glassy state: a diverging time scale

Any liquid cooled sufficiently fast will become glassy, i.e. it will lack the time to evolve into a long-range ordered crystalline array. In such glassy materials two types of processes can be distinguished: fast or $\beta$ processes, which happen on short scale and remain in thermal equilibrium, and slow or $\alpha$-processes, which are restructuring processes that involve many atoms. Somewhere during cooling they fall out of thermal equilibrium, or, more precisely, their relaxation time exceeds the time needed to reach the (sliding) equilibrium. Recently the microscopic nature of the liquid landscape that leads to these slow processes was discussed.

The relaxation time in glassy systems scales with the viscosity, which is a measure of the internal friction of a system. It has in general a strong temperature dependence varying in silica-based glasses commonly over 18 orders of magnitude in Pa.s, and is the least understood of all glass properties. Both viscosity and relaxation time will grow sufficiently rapid in a typical cooling experiment that a point is reached where equilibrium no longer exists between the thermal state of the system and the surrounding temperature. This point is called the glass transition temperature, commonly occurring in the temperature range of roughly two thirds of the melting temperature in silica based glasses.

The growth in relaxation time for so-called fragile glasses, such as toluene, glycerol, and ethanol, is built into the Vogel-Fulcher-Tammann-Hesse law $\tau_{eq} \sim \exp[B/(T - T_0)]$. Adam and Gibbs provided an intuitive explanation of this law and Parisi gave a field theoretical argument for the related behavior $\tau_{eq} \sim \exp\{(B/(T - T_0))^{d-1}\}$, where $d$ is the space...
tial dimension of the system \((d = 3\) in practice\). For so-called strong glass, such as \(\text{SiO}_2\) and \(\text{GeO}_2\), on the other hand, the relaxation time follows an Arrhenius law \(\tau_\alpha \sim \exp(A/T)\). Somewhat related expressions were proposed by Kivelson et al. [13] and by Schultz [14] to describe relaxation times for all known glasses todate.

In our studies we have benefited from exactly solving simple model systems with an Arrhenius law [12,14], or a VFTH-law [14,15]. In models such as soft-spin models [17], the spherical \(p\)-spin model [17,18], or a directed polymer model [19] partial answers can be obtained. Together this has resulted in a coherent picture that we discuss in the following.

**Breakdown of thermodynamics for the glassy state?**

Attempts for a thermodynamic interpretation of a glass phase go back to the twenties. Let us consider the experimental way to determine the entropy: one integrates \(dS = (C_p/T)dT\), where \(C_p\) is the measured heat capacity, from a sufficiently high reference temperature in the liquid phase, down to lower temperatures. The excess entropy is the thus obtained entropy minus the entropy of the crystalline state. It decreases with temperature, but will remain positive down to zero temperature, thus resulting in a residual entropy, in apparent violation with the third law.

The glass transition temperature depends on the cooling rate. Slower cooling provides the system with more time to relax, with as result that it will remain in equilibrium to lower temperatures. Kauzmann made it plausible that, for infinitely slow cooling, \(\Delta S\) goes to zero near a specific temperature, now called the Kauzmann temperature \(T_K\) [21]. It is to be expected that \(T_K\) and \(T_0\) coincide, and this indeed occurs in an exactly solvable model glass [14,15]. The ultimate vanishing of the excess entropy near this point is called the Kauzmann paradox. A thermodynamic Kauzmann transition has been found in mean field models, like the Random Energy Model [22], the spherical \(p\)-spin model [23], and a polymer model [19], but also in a model obeying a VFTH-law [14,15]. Finally, it also shows up in a mean field approach (so-called replica approach) to the glass transition in realistic models for glass [20].

Proposals to formulate properties of the glassy state in a thermodynamic frame have remained unsuccessful till recently when we addressed this issue. The negative conclusions were not based on subtle entropy arguments, but on testing the so-called Ehrenfest relations (see the Appendix). They are relations between the smeared out discontinuities that occur around the glass formation temperature in cooling experiments at constant pressure, in the specific heat \(C_p = \partial(U + pV)/\partial T\big|_p\) and the expansivity \(\alpha = \partial \ln V/\partial T\big|_p\). One can treat them as true discontinuities, because of the small size of the smearing region. When comparing cooling experiments at different pressures one also finds discontinuities in the compressibility \(\kappa = -\partial \ln V/\partial p\big|_T\). A glass transition seems therefore to be a textbook example of a mean field second order phase transition. However, this analogy is not perfect because there is no diverging length scale, and the smaller value of the specific heat occurs in the low temperature regime.

The two Ehrenfest relations are particularly useful tests for glasses. The common notion of half a century of research is that the first relation is always violated, whereas the second relation is obeyed in most cases, though not in all [24,25]. In the most careful experiment we came across, the glass transition in atactic polystyrene with a cooling rate of 18 \(K/h\) at ambient pressure, \(\Delta C_p\) is too small by a factor 0.77 [26], while \(\Pi = 1.09 \approx 1\).

The failure of in particular the first Ehrenfest relations has led to the general belief that “thermodynamics does not work for glasses, as there is no equilibrium”. This unapplicability to glasses is unsatisfactory on two accounts. Firstly, thermodynamics should also apply to non-equilibrium systems. Secondly, in view of the large time scales, up to many years, one would hope for a universal description of the energy balance.

The negative conclusion about the applicability of thermodynamics was mainly based on the failure to understand the Ehrenfest relations and the Prigogine-Defay ratio. It should be kept in mind that, so far, the approaches leaned very much on equilibrium ideas. Well known examples are the 1953 Davies-Jones theory [27], the 1958 Gibbs-DiMarzio [28] and the 1965 Adam-Gibbs papers, while a 1981 paper by DiMarzio has title “Equilibrium theory of glasses” and a subsection “An equilibrium theory of glasses is absolutely necessary” [29]. In particular, the Gibbs-DiMarzio model has long been considered as an important theory for glass. It is our purpose to explain that the step to an equilibrium theory has been an unfortunate move.

**Thermodynamics far from equilibrium and the effective or fictive temperature**

Though a glass may reach equilibrium after many thousands of years, it will be glassy on the timescale of a few years. In such non-equilibrium systems the elapsed time \(t\), sometimes called the observation time, waiting time, or age, is an important variable for the description of the macroscopic state of the system. In realistic glass forming liquids several types of slow processes may occur. Here we shall restrict ourselves to model glasses with one type of slow process, because this already explains the basic problem. For such systems we have found that time shows up through one or two time-dependent parameters, namely the effective temperature \(T_\ast(t)\) [30], and possibly the effective pressure \(p_\ast(t)\) [14].

\(T_\ast\) was introduced phenomenologically half a century ago by Tool [31] to model the shapes of the specific heat

\(\Delta T_\ast = T_T - T_\ast\)
curves on cooling and heating through the glass transition. This effective or fictive temperature describes the relaxation of slow modes. As in a plasma, slow and fast modes will equilibrate at their own specific temperature. We have recently proposed a set of non-linear cooling and heating experiments, that should lead to system-independent shapes of the specific heat near the glass transition [3] [4].

The notion of an effective pressure in the glassy state was put forward by Goldstein [29] and Jäckle [23]. They considered glass formation under pressure. If pressure is partly released after the glass has formed, the glassy state will depend not so strong on the new pressure, but more on its formation pressure, which thus acts as a fictive pressure. In an exactly solvable model glass we found a range of parameters where such a parameter has to be introduced for a proper thermodynamic description [4,5]. The approach with two effective variables is promising, since for glass forming liquids it was found experimentally that at given $T, p$ the same volume can be reached via different histories. As these histories then lead to different histories, the glassy state of these systems cannot be coded using only one extra variable [2]. Here we shall, however, avoid the technical complications of having to deal with two effective parameters.

Let us explain how the effective temperature arises in our approach. Consider an aging experiment at fixed $(T, p)$ at some long observation time $t$. Fast modes, with relaxation time much less than $t$, will be in equilibrium with the bath temperature $T$. Modes with timescale much larger than $t$ are just quenched. The active slow modes are those that have a time scale comparable with $t$. For dynamics on this timescale one may sum out the fast processes, by calculating the restricted partition sum, i.e. the sum over the fast modes of the Boltzmann weights $\exp(-\mathcal{H}/kT)$, where $\mathcal{H}$ is the Hamiltonian, i.e. the energy of the configuration, and $k$ Boltzmann’s constant. We have worked this out in detail for a model system [4,5], but here we do not restrict ourselves to a specific system. (How to divide between fast and slow modes in realistic systems is a subject of current research). The partition sum leads to an effective Hamiltonian of the active slow modes, $\mathcal{H}_{\text{eff}}(\text{active}) = U - TS_{\text{ep}}$, where $U$ is the energy, averaged over the equilibrium processes, and $S_{\text{ep}}$ their entropy. $U$ and $S_{\text{ep}}$ depend explicitly on the actual configuration of active slow modes, but also on $T$, which results from the fast modes. The effective Hamiltonian governs the active slow dynamics, yielding the dynamical solution for $U(t)$. One may describe this result by quasi-static expressions that follow from a partition sum at an effective temperature $T_e$. It is introduced by now taking as Boltzmann factor: $\exp(-\mathcal{H}_{\text{eff}}/kT_e)$. The sum over slow modes will yield a generalized free enthalpy

$$G(T, T_e, p) = U - TS_{\text{ep}} - T_e S + pV$$ (1)

now $U$ and $S_{\text{ep}}$ have been averaged over the active slow modes, and $S$ is their configurational entropy. It is also called information entropy or complexity. $T_e(t; T, p)$ is now fixed by matching $U(T, T_e, p)$ with the dynamical value $U(t; T, p)$.

In an aging experiment at fixed $(T, p)$ both $T_e$ will be a function of time. In a cooling experiment at fixed pressure, $T$ and $T_e$ will be functions of time, so that a line in the $(T, T_e, p)$ space is singled out. For a set of smoothly related cooling experiments (e.g. having common cooling rates) at different pressures, this leads to thermodynamics confined to a surface $T_e(T, p)$ in $(T, T_e, p)$ space [3]. To cover full space many sets of cooling experiments would be needed, e.g. at different cooling rates. The results should coincide with other measurements, such as heating, compression and aging experiments.

Very recently numerical data of the (short-time) vibrational properties in the glassy phase of a binary Lennard-Jones system were observed to be governed by an effective temperature, in full harmony with our picture [3].

**The first Ehrenfest relation**

The two-temperature approach explains in one stroke the confusion about the first Ehrenfest relation, eq. (4), believed to be never satisfied. The misunderstanding arose because in the glassy state the compressibility is not a unique material parameter: this measure of the system’s response to a change in pressure depends on how the measurement is done, and basically on how much time the system is given. This fact has already severely complicated its experimental determination and interpretation. In the past, one has typically obtained $\alpha$ and $dp/\alpha dT$ from the cooling curves at fixed pressures, but determined $\kappa$ by an alternative experiment, such as the speed of sound, a procedure which normally works satisfactorily. In retrospective, this invalid approach can be traced back to a far too large trust in theories which view glass transitions as thermodynamic phase transitions [3]. In such a description a unique long-time limit of the compressibility exists, that should be measurable in various ways. McKenna has stressed that in experiments on glasses the isothermal compressibility differs from the isochoric compressibility [2]. Thus alternative experiments are not allowed, and there remains only a tautology to verify. The physical reason is that the compressibility strongly depends on the amount of time (and other details of the history) that the system has to relax. This effect immediately sets in below the glass transition. In our approach the validity of the first Ehrenfest relation can be checked explicitly [30].

**The second law and the second Ehrenfest relation**

Thermodynamics amounts to giving universal relations for the system’s state variables at nearby points in $(T,
implies together with eq. (1) and the first law \( dU = dQ + dW = dQ - pdV \), that the supplied heat is

\[
dQ = TdS_e + T_e dI
\]

The entropy terms are the same as for a cup of coffee in a room: also then there are two temperatures, the one of the room and of the cup, and there are two entropies. On top of that, the timescale for heat exchange is large, allowing maintenance of a spontaneous difference in temperatures. A very similar situation occurs in a glass. The fast modes (more precisely: fast modes combined with the bath) play the role of the bath, while the slow configurational modes play the role of the coffee.

We may decompose the change \( dS \) of the total entropy \( S = S_{e} + I \) as the sum of the externally supplied entropy \( d_{e}S = dQ/T \) and the internally produced entropy \( d_{i}S = (T - T_{e}) dI \).

\[
d_{i}S = \frac{T - T_{e}}{T} dI \tag{3}
\]

It is positive because heat flows from high to low temperatures. (At this point \( T_{e} \) plays the role of a real second temperature!) The entropy production per unit of time is \( d_{i}S/dt \).

Within a set of smoothly related cooling experiments one is confined to a surface \( T_{e} = T_{e}(T, p), p_{e} = p_{e}(T, p) \). This implies that \( G \) has a discontinuous slope at the glass transition. This difference in slope was first emphasized by spin glasses \[3, 30\]. Since its naive explanation as being caused by a latent heat does not apply, since that has typically not been observed, we were motivated to find the physical background, which turned out to be the two-temperature approach, discussed here. The difference in slopes implies for the Maxwell relation

\[
U' + pV' + TV = (T_{e} - TT_{e})' I' + TT_{e}'
\]

where we denoted \( \partial / \partial T|_{p} \) by a dot and \( \partial / \partial p|_{T} \) by a prime. In equilibrium (\( T_{e} = T \)) the right hand side vanishes, but out of equilibrium there is no reason why it should. The second Ehrenfest relation is also modified, since it employs this Maxwell relation. It now becomes

\[
\frac{\Delta C_{p}}{TV} = \Delta \alpha \frac{dp}{dT} + \frac{1 - T_{e}}{T} \frac{dI}{dT}
\]

where \( d/dT = \partial / \partial T + (dp_{e}/dT) \partial / \partial p \) yields the total change along the glass transition line. The last two terms are new, but would vanish in equilibrium. The violation of the second Ehrenfest relation thus gives information about the configurational entropy.

For atactic polystyrene Rehage and Oels report a value \( \Pi = 1.09 \approx 1 \). Having realized that these authors used a short-time value for the compressibility in the glass, we have taken the theoretical value from the first Ehrenfest relation, and obtained \( \Pi = 0.77 \). This can be described by eq. \[\text{[4]}\]. Values \( \Pi < 1 \) also occur in the exact dynamical solution of a toy model \[\text{[2]}\].

In the past it was proven that \( \Pi \geq 1 \) is needed for mechanical stability \[\text{[22]}\]. The starting point was the assumption that at the glass transition unspecified order parameters undergo a thermodynamic phase transition. It was even shown that the same assumptions implied the equality \( \Pi = 1 \). Since experiments mostly yielded \( 2 < \Pi < 5 \), this remained a field of confusion. It is now clear that the assumption of a thermodynamic transition is false: the above theoretical framework does not involve it, and the Rehage-Oels experiment has \( \Pi < 1 \).

A phase diagram of amorphous ice was presented recently \[\text{[4]}\]. This approach, however, employs equilibrium thermodynamics. In particular, it assumes the validity of the Clausius-Clapeyron relation at the first order transition from low density amorphous ice to high density amorphous ice. However, for first order transitions to a glassy state the Clausius-Clapeyron relation will be modified \[\text{[30]}\].

\[
\Delta V \frac{dp_{e}}{dT} = \frac{\Delta U + p\Delta V}{T} + (1 - \frac{dT_{e}(T, p_{e}(T))}{dT}) I_{g}
\]

It would be interesting to test this for amorphous ice.

**Apparent violations of the laws of thermodynamics**

The basis of our approach has been to show that glassy systems respect the fundamental laws of thermodynamics. However, if one “forgets” that the material is in a non-equilibrium state, glass addresses practically all thermodynamic paradoxes that have been discussed in the past.

Take a piece of natural or volcanic glass and keep it at room temperature for extremely long time. The material is in an excited, non-equilibrium state. In the course of time it will slowly evolve towards the equilibrium crystalline state. In doing so it will go to a state of lower energy and configurational entropy. As is well known, see e.g. \[\text{[27]}\], and described by eq. \[\text{[3]}\], this will generate heat. There will be no true violation of the first and second law: after the glass has reached equilibrium, such processes are impossible.

The released heat can be used in several ways:

*Energy out of “nothing”: glass as a source of energy*

An efficient way to extract all configurational energy of a glass is as follows. One first brings it into its liquid state by heating; then one lets it carefully go into the crystalline state. This process allows to extract the configurational energy in a reasonable time. The energy needed for heating can in principle be regained upon cooling. On top of that, one obtains the crystallization heat \( \Delta U \) (also called relaxation heat or latent heat), corrected for the difference in specific heats of glass and crystal.
For metallic glasses this principle is well known to material scientist [1], and it equally holds for glasses and other amorphous materials, such as glassy volcanic rocks. In analogy with metal alloys we can estimate the configurational energy as some 10 kJ/mole atoms. This is some 30 times less than the conventional gain of energy from combustion of oil and stone coal. This principle may also be applied to extract the energy due to stresses in polycrystalline rocks. Though these mechanisms are presently not attractive, they may be relevant for traveling or living in outer space, or perhaps for the mining of asteroids [2].

Heat out of “nothing”: an isolated piece of glass heats itself slowly up

When the glass is kept in an isolated container (dQ = 0), the heat will be absorbed by the fast processes of the glass. As they determine the temperature, the glass will slowly heat up. Eq. (2) says that \( T \dot{S}_{\text{ep}} + T \dot{I} = 0 \). In the equilibration process \( T_e \) will go down, but \( T \), the temperature that can be read off from a thermometer, will enhance.

An analogous manifestation is the fact that most of the earth’s interior is fluid due to radioactive decay. Indeed, the radioactive content, with its decay time of several billion years, is a slow and thus “configurational” process. The generated heat is absorbed by the “fast” geological processes, which maintain the fluid nature.

The quantum glass as an almost ideal motor

A quantum glass in a bath at very low temperature, or a realistic glass in outer space with its 3 Kelvin background temperature, can have a high effective temperature, but basically have vanishing bath temperature. The efficiency for transforming the dynamically released heat into work, \( \eta = 1 - T/T_e \), can be arbitrarily close to unity, at the verge of violating the second law.

Work out of “nothing”: a “perpetuum mobile of the third kind”

The heat released by the glass can also be used to perform work by a suitable machine. We thus have a mobile that performs work as long as the glass is not in equilibrium. From geology it is known that, at least for Si-rich glasses, this period may be astronomical [1]. We may therefore call the non-equilibrium glass, combined with some apparatus that performs the work, a “perpetuum mobile of the third kind”. Indeed, work \( dW = -dQ \) is performed at the cost of configurational entropy, which, according to the third law, should have been much closer to zero, in particular in cases where the glass formation temperature is much larger than the room temperature.

It should be admitted that for a small piece of glass such a mobile is merely an academic object. In the above terrestrial analog, the heat released by radioactive decay finally performs work by moving of the earth crust.

The third law and the residual entropy

It is long known that on realistic time scales the zero temperature entropy of glass does not vanish. It is equal to the configurational entropy of slow modes \( I \).

The zeroeth law and the effective temperature

The configurational modes of a window glass “live” at an effective temperature. During the glass formation process they got essentially stuck after the glass transition, which for window glass occurs at some 1000 K. As they did not relax very much since then, the effective temperature \( T_e \) of these modes is still close to, but below, the glass transition temperature. It is thus not proper to say that a glass has a single, constant temperature: the one related to its slow modes is very different from room temperature, and will be measured when performing experiments on long enough timescales.

APPENDIX: THE EHRENFEST RELATIONS

At a first order phase transition from phase A to phase B, the slope of the transition line is given by the Clausius-Clapeyron relation. It derives from continuity of the free enthalpy \( G = U + pV - TS \). The difference \( \Delta G = G_A - G_B \) vanishes along the transition line. Differentiating \( \Delta G(T, p_g(T)) = 0 \) one obtains

\[
\frac{\Delta U + p \Delta V}{T} = \Delta V \frac{dp_g}{dT} \tag{7}
\]

For second order phase transitions of classical type one can differentiate \( \Delta V = 0 \), which yields the first Ehrenfest relation

\[
\Delta \alpha = \Delta \kappa \frac{dp_g}{dT} \tag{8}
\]

It is said to be violated in glasses, but we shall argue against that.

By considering \( \Delta U = 0 \) one obtains the second Ehrenfest relation

\[
\frac{\Delta C_p}{TV} = \Delta \alpha \frac{dp_g}{dT} \tag{9}
\]

It is believed to be often satisfied for glasses, though not in all cases. We shall show that in principle it is violated.

The information of both Ehrenfest relations is often coded in the so-called Prigogine-Defay ratio

\[
\frac{\Delta C_p}{TV} = \frac{\Delta U}{T^2} \frac{dp_g}{dT} \tag{10}
\]
\[ \Pi = \frac{\Delta C_p \Delta \kappa}{TV(\Delta \alpha)^2} \] (10)

Using eq. (8) and (9) it seen to equal to unity in equilibrium. For glasses it is reported to lie typically between 2 and 5. We shall stress that also values below unity are possible, and actually already have been measured.

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FIG. 1. Data of the glass transition for cooling atactic polystyrene with 18 K/h, taken from Rehage and Oels (1976): specific volume \( V (cm^3/g) \) versus temperature \( T (K) \) at various pressures \( p (kbar) \). The data in the liquid essentially lie on a smooth surface, and so do the data in the glass. The first Ehrenfest relation describes no more than the intersection of these surfaces, and is thus automatically satisfied. The values for the compressibility that follow from these data will generally differ from results obtained via other experiments.