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Isothermal glass transitions in supercooled and overcompressed liquids

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We report the first calorimetric characterization of isothermal glass transitions obtained by changing the pressure at constant temperature. This isothermal glass transition is described in the case of *m*-fluoroaniline, a so-called fragile liquid. The method employed is based on Maxwell's equations and involves measurement of the heat of compression of a sample enclosed in a hydrostatic pressure cell under isothermal and reversible conditions. A discontinuity of the thermodynamic quantity αV, where α is the expansivity and V is the molar volume, defines the glass transition pressure P_g at which ergodicity is broken on the time scale of the experiments (300–1000 s) which depends on the pressure step employed. The step in αV is found initially to decrease rapidly with increasing pressure. The slope $(\partial P_g/\partial T)_\tau$ seems smaller than that determined by the usual isobaric methods, implying some distinction in the degrees of freedom involved and associated differences in defining the values of T_g. Because of the high sensitivity and stability of the calorimeter, we can also observe annealing effects in the overcompressed glass at a pressure above P_g; the slow dynamic processes associated are called entropic relaxation because it is the entropy which is measured directly. An approximate relaxation function and a model for the compression data are discussed. Keeping in mind the overall pattern of "strong and fragile" liquid behavior, isothermal pressure variations appear to offer a useful tool to connect these extremes and may constrain the glass transition of a molecular liquid in a particular range of the *P–T* diagram. The concept of Kauzmann pressure P_K is introduced, but it is noted that P_K must become less well defined the further from ambient pressure it lies due to the decrease in $\Delta\alpha V$ which is observed with increasing pressure.

I. INTRODUCTION

From the point of view of liquid state theory, the supercooling and glass formation phenomena are very interesting because, in the extended temperature–density range, a variety of new phenomena are being encountered. Of particular interest is the onset of a remarkable divergent behavior in the viscosity and in the associated relaxation times which may be measured by various techniques. Recent theoretical efforts have been made to treat the glass transition as a sort of critical phenomenon; however, in many cases their relevance remains limited to the low viscosity region well above the conventional glass transition (GT). The latter, which is commonly recognized as an ergodic-to-nonergodic-state transition, depends on the characteristic probe frequency of a given technique crossing the main structural relaxation time of the liquid. To date, the lowest frequencies are those associated with calorimetric and mechanical methods (about 10^{-3} Hz).

Following Angell's classification[1] of strong and fragile liquids, we focus our attention on the most fragile ones,[2,3] for which three temperature domains may be distinguished. These are the low viscosity regime up to 10^2 P, where the collective relaxation in a cage model of the mode coupling theory[4] may be applied; the high viscosity regime up to 10^{11}–10^{13} P, according to the definition of the T_g temperature of the glass formation,[2] where thermally activated processes become dominant,[5] and finally around and below this macroscopic T_g, where several models of cooperative dynamics analyze slow relaxation processes involved in such nonequilibrium amorphous solid.[6(a),6(b)]

The advantages of such a T_g-scaled Arrhenius plot of the viscosity lie on the one hand in the bridge connecting microscopic and macroscopic time scales of the same phenomenon, and on the other hand in the relationship established between a large variety of liquids of structurally different character; by extrapolation, it also suggests for the liquid state a possible underlying thermodynamic transition obscured by rapidly growing barriers to relaxation, which is commonly opposed to a continuous freezing process at or below T_g. Several lines of investigation in the framework of this classification are being followed by experimentalists; most of them use the technique of liquid cooling at constant pressure, viz. 1 atm. The tendencies are on the one hand to cover the enormous range of relaxation times for a given substance by applying several techniques, or on the other hand, using one technique involving one given frequency window to explore systems of different fragility. The latter approach introduces the influence of molecular shapes and the nature of the intermolecular forces.

Here we extend the study of the phenomenon by increasing the range of glass transitions observable for one given system, using one given technique, by the use of the pressure—hence the density—as an independently varying internal parameter. Keeping in mind that the temperature is an intensive variable with a twofold action on the kinetic energy and the volume, the adequacy of pure density effects should be considered by measurements which change the density at different constant temperatures. Analyzing the entropy surfaces, the slopes of these surfaces in the T

and P directions are C_p/T and $-\alpha V$, respectively,

$$dS = C_p/T \, dT - \alpha V \, dP,$$

where C_p is the heat capacity at constant P, α is the expansivity, and V is the molar volume. The method of the heat of compression[7] performed here gives the direct measurement of α or αV depending on the experimental setup. The heat flow into the system at the equilibrium temperature T corresponds to the thermodynamic entropy directly from Maxwell's equations. This opens the field for the study of "*isothermal glass transitions*" at the pressure P_g and consequently to direct study of "*entropic*" *relaxation*.

In the first section below, we describe briefly the method, apparatus, and procedure; the following section gives results and comments; a final section gives a phenomenological model for isothermal glass transition, analogous to the Narayanaswamy treatment of the isobaric glass transition, and the evolution of the entropic relaxation in the glassy state.

II. EXPERIMENT

A. Materials

The liquid chosen for this study is one of the simplest fragile glass formers *m*-fluoroaniline, a disubstituted benzene ring with the –F and –NH$_2$ groups in the 1,3 positions. It resists all attempts to crystallize it which is a great advantage for experimentation under pressure. It permits the study of liquid properties in the supercooled and over-compressed states[8] without the usual risk of premature termination of an experiment by crystallization. The initial sample, from Aldrich, was purified by repeated vitrification (with sample cracking) to degas, and vacuum distillation.

B. Method and apparatus

The first step is the calorimetric characterization of the isothermal glass transition and for this purpose, we use the piezothermal method introduced by Ter Minassian.[9,10] This involves the measure of the heat Q evolved from a sample upon application of a known excess pressure $\Delta P = P_{\mathrm{final}} - P_{\mathrm{initial}}$ at constant T_0,

$$\delta q = T_0 \, dS = -T_0 \left(\frac{\partial S}{\partial P} \right)_{T_0} = -\alpha V T_0 \, dP,$$

where δq is the quantity of heat liberated by one mole of substance. According to the experimental arrangement, the total quantity of heat ΔQ measured may refer to a constant effective volume V_{eff} of the vessel containing n moles of the sample

$$\Delta Q = n \delta q = \frac{V_{\mathrm{eff}}}{V} \delta q = -\alpha V_{\mathrm{eff}} T_0 \Delta P,$$

or to a constant number of moles n, defined previously from the mass of the sample $m = nM$. The quantity (αV) is then extracted as a function of T and P,

$$(\alpha V) = \frac{\Delta Q}{n T_0 \Delta P}, \quad \text{at} \quad \bar{P} = P_i \pm \frac{\Delta P}{2} \quad \text{and} \quad T_0.$$

The sample is enclosed in a flexible pressure cell made of Teflon sealed by a moving piston compressed and decompressed hydrostatically by a known liquid (*n*-pentane or a mixture of *n*-pentane + isopentane)[11] at the working temperature T_0 of the calorimeter; this technique minimizes stress gradients and allows reproducibility and reversibility better than 1% between compression and decompression data. Some additional corrections due to the sample surroundings are carefully calibrated as a function of T and P in order to be subtracted during the data processing. This procedure is different from that used in conventional studies on glasses under pressure; usually experimentalists in the field apply all pressure changes in the liquid state, then cool the sample down to the glassy domain before performing their measurements.[12,13] In this case, one cannot make comparisons with continuous compression isothermal data.

The experiments require the combination of an unusually high precision calorimeter with high pressure techniques. The calorimeter employed is based on an isothermal compensation principle; it works in a temperature range of 100–350 K and the high pressure equipment covers the range of 1–600 MPa. The complete setup is fully detailed in previous articles.[10,14]

The experimental procedure is as follows: the sample cell is set into the autoclave and the experimental working temperature is achieved after a few hours up to thermal equilibrium at atmospheric pressure. Then by discrete steps of pressure of 8–12 MPa, the mean pressure is increased until the signature of the glass transition is observed; at each step, the quantity of heat is measured between the initial and final equilibrium states. The latter is accessible after a maximum elapsed time of 1000 s in the transformation pressure range and of 300 s for pressures well above or below P_g. The waiting time Δt also depends on the pressure step magnitude, which can be decreased to a significant minimum of 0.1 MPa. The maximum Δt has been tested up to 3000 s during one run. The resulting range of compression and decompression rates ($\Delta P / \Delta t$) may be correlated to the heating or cooling rates commonly used. For all the isotherms presented, each pressure increase and its corresponding pressure decrease have been observed during the same elapsed time.

III. RESULTS AND DISCUSSION

We report in Fig. 1 αV data of three different isotherms at 171.5, 182.4, and 191.8 K for a sample of mass $m = 0.3663$ g. The glass transition temperature at atmospheric pressure is about 173 K[3] for the normal heating rate used in DSC studies. When the mean pressure increases, αV is a monotonously decreasing function until a rapid decrease occurs, which characterizes the glass transition P_g. P_g(comp) is defined by the inflexion point as determined by an *ad hoc* analytical function. On decreasing the pressure, the same αV values are observed until a sudden increase with overshoot occurs, from which P_g(decomp) is defined in the same manner. The hysteresis observed between the two thermodynamic paths is the signature of the relaxation process accompanying *the glass*
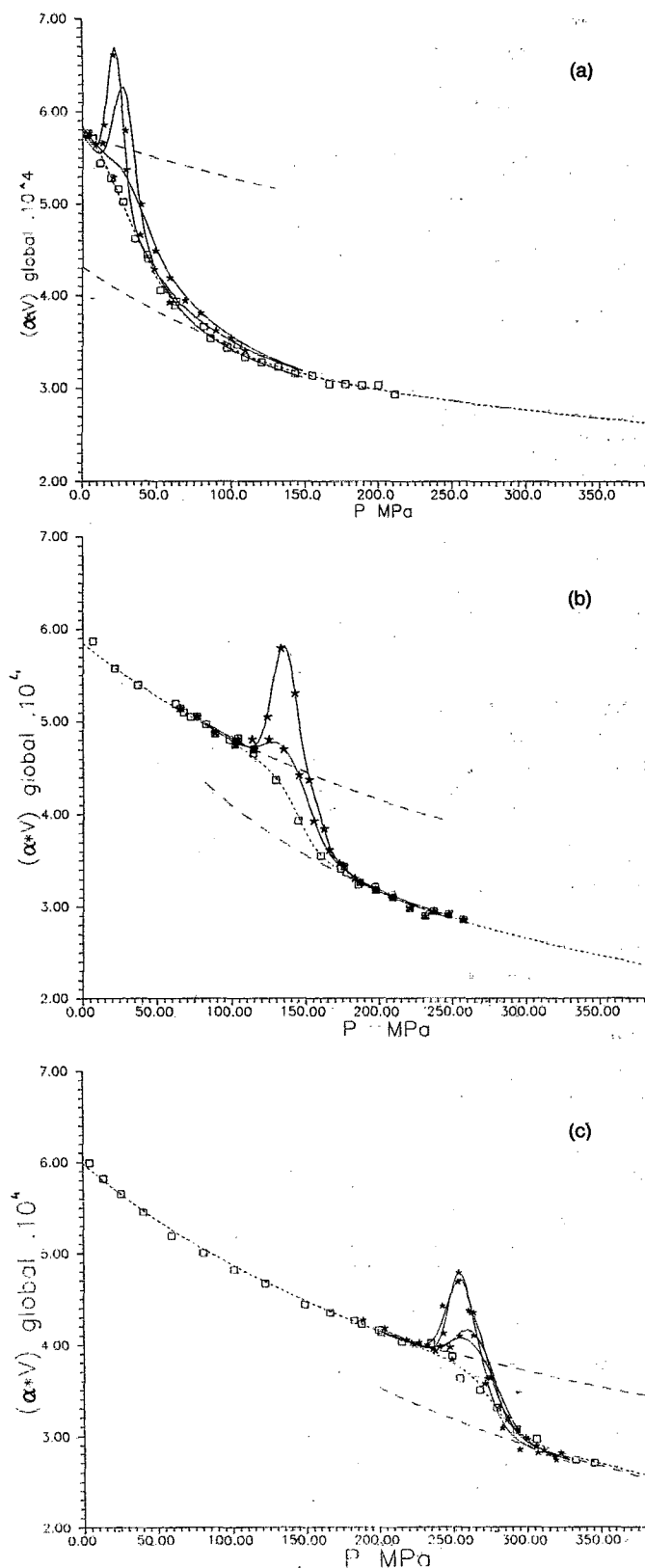
T (K)	P_g(comp) (MPa)	P_g(decomp) (MPa)	$\Delta\alpha V$	V_g (cm^{-3} M^{-1})	$\Delta\alpha$ (10^4 K^{-1})
171.5	30.5	40	1.636	85.8	5.785
182.4	137	158	0.922	82.3	3.389
191.8	275	285	0.783	78.0	3.046

transition and the consequent arrest of the structure on the experimental time scale. P_g(comp) and P_g(decomp) values are collected in Table I. Also tabulated are (1) $\Delta\alpha V$ is the jump measured at P_g(comp), or P_g(decomp) after an extrapolation of some adjusted equations of the liquid and glassy phases; (2) V_g is the calculated volume of the liquid at P_g, determined by an extrapolation of its expansivity[8] measured previously in the whole accessible T–P domain; and (3) $\Delta\alpha$, which is deduced from the latter two quantities at each temperature.

It is possible using the appropriate thermodynamic relations for a series of glass transitions to calculate the changes at P_g of the other thermodynamic quantities, heat capacity C_p, and isothermal compressibility κ_T, accurately along the same isothermal (or isobaric) path on equivalent time scales. Then from the Ehrenfest relations[5(b)] and the slope $(\partial T_g/\partial P)_\tau$, one may extract a value of the Prigogine–Defay ratio R,[15(a),15(b)] which reflects the number of order parameters involved in a nonthermodynamic transition. In the case of the glass transition, it is interesting to test the relevance of the concept of a number of ordering parameters at T_g or P_g, and how they evolve in a T–P diagram, and this will be done elsewhere.[10(b)]

So far we have deduced the ΔC_p jump at 171.5 K for m-fluoroaniline and have found from the first Ehrenfest relation $\Delta C_p = 103$ J M^{-1} K^{-1} compared with 78 J M^{-1} K^{-1} measured at T_g and atmospheric pressure by DSC studies.[3] This could be due to an overestimation of $\Delta\alpha$ at this temperature since the glass transformation occurs as soon as the pressure increases (see Fig. 1).

One can compare the slope $(\partial T_g/\partial P)_\tau$ obtained from data in Table I with the results of other works found in the literature, values obtained from isobaric heat/cool experiments. Our value 0.083 K MPa^{-1} is much smaller than the value 0.260 K MPa^{-1} obtained for the "fragile" liquid o-terphenyl[16] and closer to the values found for some H-bonded liquids such as benzyl alcohol (0.090 K MPa^{-1}); we note that these data depend strongly on the heating rate and on the way T_g is defined. Our value is also comparable to the value of 0.075 K MPa^{-1} of a non-H-bonded liquid 3-methyl-pentane[17] obtained by adiabatic measurements of T_g at different constant pressures.

The apparent agreement between these data hides the basic fact that along an isothermal path, the degrees of freedom being frozen out are different from those frozen out along an isobaric path. In addition, since the isothermal slope is smaller than the isobaric one, the metastable liquid range in the calorimetric time scale range is found to be extended. Besides, one does not assume that this slope should be constant at higher T and P; as shown in viscosity

FIG. 1. Total (αV) data as a function of pressure for compressing (squares) and decreasing (stars) pressure steps as explained in the text. Full curves are *ad hoc* analytical fits for different annealing times and annealing pressure; dotted curves are compressing fits and dashed lines are extrapolations of the liquid and the glassy states. The corresponding values are summarized in Tables I and III. (a) $T=171.5$ K; (b) $T=182.4$ K; (c) $T=191.8$ K.

TABLE II. Boltzmann superposition model parameters.

T (K)	P_1 (MPa)	P_2 (MPa)	τ_0 $(10^6\,s)$	$\Delta V^{\neq}$ $(cm^3\,M^{-1})$	x	β	P_{g_c} (MPa)	$\Delta V^{\neq}/RT$ (GPa^{-1})
171.5	1	91	2151	477.75	0.79	0.14	30.5	335.0
182.4	80	190	10.5	132.6	0.91	0.56	137	87.4
191.8	200	326	0.8	79.7	0.96	0.88	275	50.0

measurements of glycerol under pressure, the $T_g(P)$ line is curvilinear above 1 GPa.[18]

Finally, Fig. 1 and Table I highlight a crucial point. When temperature increases, in consequence the glass transition occurs at higher pressure, the magnitude of the discontinuity is lowered, and P_g and the ΔP width of the transition increases. Therefore, we may ask whether at sufficiently high temperature and pressure the calorimetric signature of the GT tends to disappear completely. In any case, it appears that a system which is fragile at atmospheric pressure may behave thermodynamically like a stronger liquid at high pressure. The same is suggested by volumetric measurements on polymers,[13] and by adiabatic measurements of ΔC_p of Suga et al.[17] Recent isothermal measurements of the viscosity in a higher pressure range made by Herbst et al.[18] also seem to be in accord with these findings.

IV. ENTROPIC RELAXATION AND THE PHENOMENOLOGICAL MODEL FOR THE GLASS TRANSITION

A. Formalism of the model and departure from equilibrium

In order to understand how a liquid moves further and further away from metastable equilibrium, i.e., how structural relaxation is arrested in the course of the compressing process, we have adapted a purely empirical model first developed by Narayanaswamy,[19] Moynihan,[20] and Hodge[21] for polymers, and more recently by Bezot et al.[22] for 5-phenyl–4-ether. It is based on the Boltzmann superposition principle of nonexponential responses to the pressure steps. The distribution of relaxation times is incorporated in the model via the decay function $\phi(t)$, which is for convenience supposed to be of the Kohlrausch–Williams–Watts form

$$\phi(t) = \exp[-(t/\tau_m)^\beta],$$

where $0 < \beta \leqslant 1$ determines the degree of nonexponentiality and τ_m is the mean relaxation time at a given pressure and temperature.

To take into account the nonequilibrium nature of the GT, the notion of fictive pressure is introduced and defined as the pressure at which the observed entropy variation would be the equilibrium value. Like the fictive temperature, the fictive pressure measures the relaxational component of the entropy and may differ for each property considered;[19(b)] the decay of the fictive pressure towards P, dP_{fic}/dP, expresses only the variation of the properties of a glass obtained by this method and it depends strongly on

its thermal history. For handling nonlinearity and the departure from equilibrium, we have used a method comparable to that of Narayanaswamy and Gordon[19(a)] and expressed τ_m with an Arrhenius relaxation time–pressure dependence

$$\tau_{m,i} = \tau_0 \exp\left\{\frac{\Delta V^{\neq}}{RT_0}\left[xP_i + (1-x)P_{f,i-1}\right]\right\}$$

for the ith step,

where R is the ideal gas constant, τ_0 is a characteristic relaxation time, x is a dimensionless parameter $0 < x \leqslant 1$, $\Delta V^{\neq}$ a so-called activation volume, and T_0 the working temperature. These expressions are valid only in the transformation range defined by P_1 and P_2 in Table II for each isotherm. When linear kinetics are recovered, then $x = 1$ and $P = P_{fictive}$.

The fictive pressure is expressed as follows:

$$P_{f,i} = P_0 + \sum_{m=1}^{i} \Delta P_m \left(1 - \exp\left\{-\left[\sum_{j=m}^{i}(\Delta t_j/\tau_j)^\beta\right]\right\}\right),$$

where P_0 is an equilibrium starting pressure above P_g.

The experimental data used for the best fit evaluations are $\alpha V^{(N)}(P)$ and dP_{fict}/dP,

$$\alpha V^{(N)}(P) = \frac{(\alpha V)_{mes} - (\alpha V)_{liq}}{(\alpha V)_{liq} - (\alpha V)_{glass}} = \frac{dP_{fict}}{dP}.$$

The index (N) stands for normalized because this quantity is zero in the glassy state and equal to unity in the liquid state. The quantities (Δt and ΔP) are associated to each $\alpha V^{(N)}$ data for a given P and T; they occur as input data and depend on the experimental procedure chosen as described in the Experimental section. The quantities $(\alpha V)_{glass}$ and $(\alpha V)_{liquid}$ were previously fitted and extrapolated below and above P_g for the normalization. For a given temperature τ_0, $\Delta V^{\neq}$, x, and β are fitting parameters (they are collected in Table II). The resulting analytical curves are shown in Fig. 2, where they are compared with the experimental data in their original form and seen to agree to within 2% at all pressures. Caution with values collected in Table II must be exercised because of correlations between the parameters. In particular for the lowest isotherm, the parameters may be affected by the small range of pressure before the transition.

This analysis of the data leads to several points of discussion.

The first point concerns the stretching parameter β—no pressure dependence of β is necessary to improve the fit. Instead the exponent is strongly temperature depen-
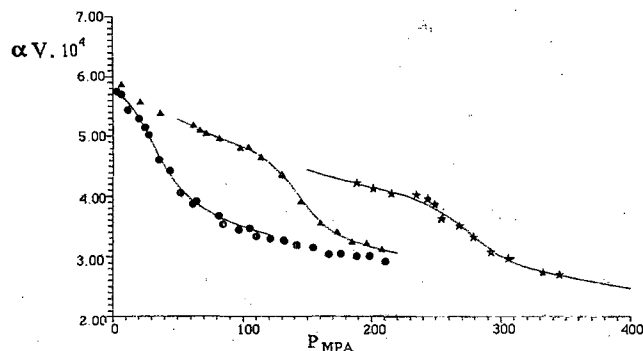
FIG. 2. A fit of the compressing (αV) data at the three temperatures $T_1=171.5$ K (circles); $T_2=182.4$ K (triangles); $T_3=191.8$ K (stars) according to the four parameters of Table II.

dent in this T domain. In the initial tests of the model for the normal glass transition,[20,21] no T dependence of β was introduced and, as Nagel et al.[23] have clearly demonstrated in their work on specific heat spectroscopy, this approximation is unrealistic. While the value $\beta=0.14$ for the lowest temperature should not be taken seriously as pointed out before, the trend to lower β at lower temperature is probably reliable and supports the notion that β may tend to zero at a temperature T_K (Ref. 23) below T_g. The existence of an underlying phase transition remains an open question; it is an attractive concept[24(a)] and could be regarded as an intrinsic limit of metastability,[24(b)] but it is accessible only on time scales of the lifetime of the universe. From the experimental point of view around T_g, only a continuous solidification process is observed. However, the value of 0.14 found for β, even with an error of 10% in its evaluation, is still lower than the predictions of two-thirds from the free volume theory[25] and of one-third by more recent predictions of Campbell et al.[26] used by several authors for the purpose of the mode coupling theory predictions.[27]

The second point concerns the increasing value of the activation volume $\Delta V^{\neq}$ when the temperature decreases, as well as the activation enthalpy increases for several increased isobars. The lowering of the interstitial volume, without changes in the relative molecular arrangements, involves increasing barriers to reorientation at higher densities. An extrapolation of such a quantity up to a higher value at lower temperature is once again useless. It could be related only to an increase in short-range order. The order of magnitude of the quantity $\Delta V^{\neq}/RT$ is in good agreement with other works[22(a),22(b)] done by high pressure Brillouin scattering.

The third point concerns the nonlinearity parameter x; it increases to unity as the temperature increases. Thus the nonlinearity tends to vanish as for strong liquids as P_g increases, in accord with the strengthening tendency of the liquid behavior observed already from the decreasing jump of $\Delta\alpha$ at P_g.

The fourth point concerns the preexponential factor τ_0 of the mean relaxation time τ_m—it increases when T decreases. Except for the lowest temperature, its values are
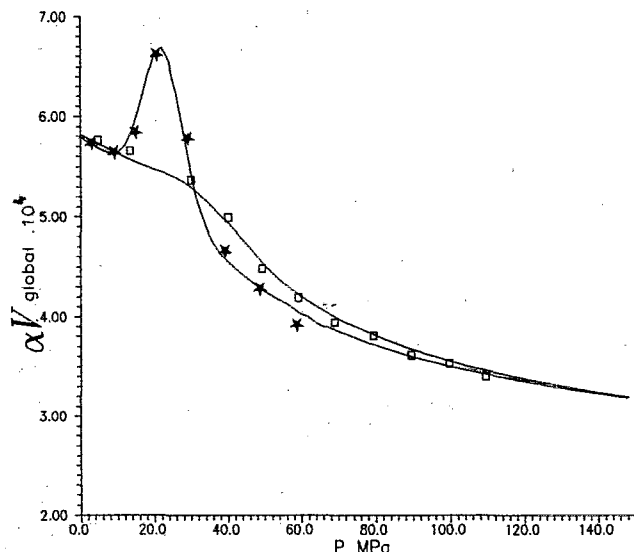
(a)
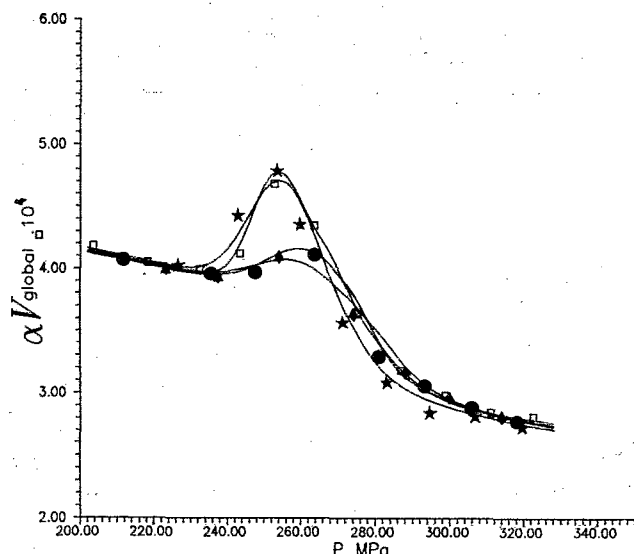
(b)

FIG. 3. Enlargement of the isotherms 1 and 3 from the Fig. 1 around P_g reflecting the annealing effects summarized in Table III. (a) $T=171.5$ K (stars), $P_a=64$ MPa; (squares) $P_a=115$ MPa; (b) $T=191.8$ K; (diamonds) $t_a=1$ h (rings); $t_a=19$ h; (squares) $t_a=32$ h; (stars) $t_a=67$ h.

compatible with viscosities of 10^5 to 10^9 P at ambient pressure, which are estimated from a shear modulus at infinite frequency G_∞ of 10^{10}–10^{11} erg cm^{-3} at atmospheric pressure in this temperature domain. This consistency enhances the reliability of the calculations.

B. Very slow dynamics and entropic relaxation

Another aspect illustrated in Fig. 1 and detailed in Fig. 3 and Table III is the "entropic relaxation." The recovery of the entropy lost during annealing at pressure above P_g is manifested by an increase of the area under the peak of αV and by a change of the P_g(decomp). Annealing experiments affect the dynamical properties of a glass, although the variations in structure remain quite negligible; it also

TABLE III. Annealing effects.

$T_K=191.8$ K	t_a (h)	1	19.5	32.5	67
$P_a=326$ MPa	P_g(decomp) (MPa)	285	279.5	276.3	272.1
$T_K=171.5$ K	P_a (MPa)	115	64		
$t_a=93$ h	P_g(decomp) (MPa)	38.5	28.5		

depends strongly on the thermal history. The decompressing runs detailed in Fig. 3 were made in all cases using the same compressing rate; we observe that P_g(decomp) decreases when the annealing times t_a increases at a given annealing pressure P_a; P_g(decomp) also decreases when P_a decreases for a given t_a. This behavior is equivalent to that observed with different annealing temperatures at atmospheric pressure.[28]

From the preceding phenomenological model applied to the third isotherm at 191.8 K, we estimate the value of the structural relaxation time τ_m and the fictive pressure associated to the compressing experiments up to a given annealing pressure $P_a=326$ MPa above P_g(comp)$=275$ MPa. With a β exponent of 0.884, independent of the pressure, the calculated τ_m was 47.6 h and $P_{\text{fictive}}=271.8$ MPa at the experimental P_a. At this pressure and temperature, the sample was kept isothermally and isobarically during several annealing times t_a listed in Table III; after the time t_a, the sample is decompressed down to an equilibrium pressure $P_i=235$ MPa in an equilibrium region of the liquid.

For each run, the area of the curve αV was calculated from P_a to P_i. It represents the entropy release $\Delta S(t)$ over this pressure range for each given period t_a at a given P_a and T_0 according to

$$S_a(t)=\Delta S(t)=-\int_{P_i}^{P_a}(\alpha V)dP, \quad \text{at } T_0.$$

These data are plotted against t_a in Fig. 4(a).

Now we introduce the relaxation function $\phi_S(t)$ following Brawer[29]

$$\Delta S(t)=-\{\alpha V_0+(\alpha V_\infty-\alpha V_0)[1-\phi_S(t)]\}\Delta P,$$

where

$$(\alpha V)_\infty=(\alpha V)_{\text{glass}}=\lim_{\Delta P\to 0}\left(\frac{\Delta S_g}{\Delta P}\right)$$

corresponding to the instantaneous glass-like change of ΔS from the initial equilibrium value after a single pressure step ΔP, and

$$(\alpha V)_0=(\alpha V)_{\text{liq}}=\lim_{\Delta P\to 0}\left(\frac{\Delta S_{\text{liq}}}{\Delta P}\right)$$

corresponding to the totally relaxed entropy of the metastable liquid.

The entropic relaxation function $\phi_S(t)$ is then written as follows:

$$\phi_S(t)=\frac{\Delta S(t)-\Delta S_{\text{liq}}}{\Delta S_{\text{glass}}-\Delta S_{\text{liq}}}=\exp[-(t/\tau_m)^\beta].$$
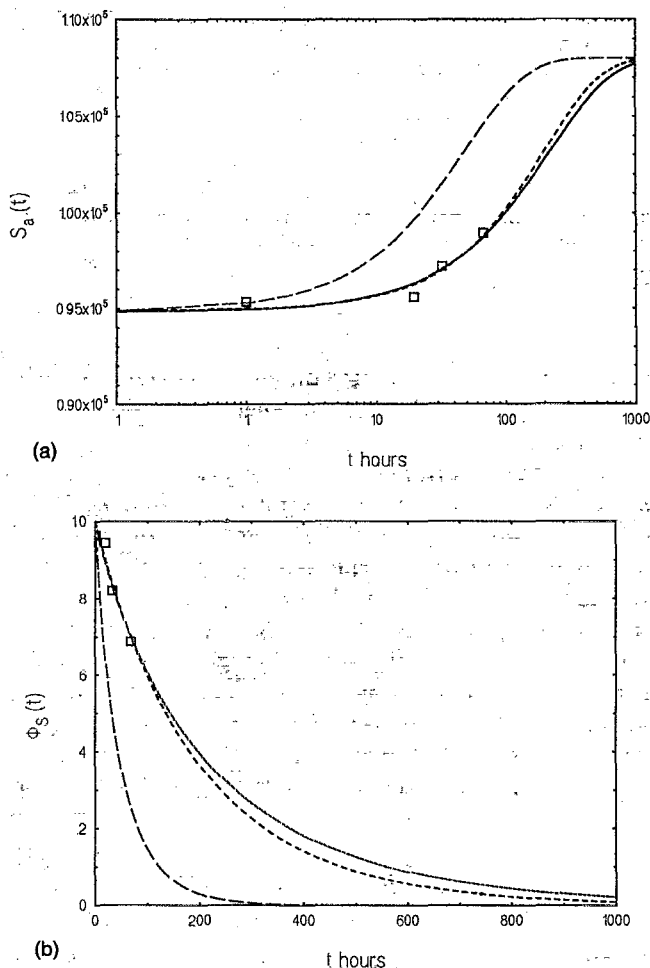

(a)

(b)

FIG. 4. (a) Entropic release $S_a(t)$ at $T=191.8$ K between $P_a=326$ MPa and $P_0=235$ MPa and (b) entropic relaxation function $\phi_S(t)$ vs annealing time t_a in hours; the full curve is the best fit of a simple stretched exponential function with the parameters 2 in Table IV; the dashed curve uses the parameters of the Boltzmann superposition principle model (set 1) and the dotted curve uses set 3 in Table IV.

$\phi_s(t)$ is plotted in Fig. 4(b) and varies between 1 and 0 in semilogarithmic plot of time t_a. We have only few experimental data of $\Delta S(t)$ and the input quantities ΔS_{liquid} and ΔS_{glass} depend strongly on the extrapolations which were made on both sides of P_g in the liquid and in the glassy regions. In putting the value of $\beta=0.884$ from the earlier analysis, the best fit to the annealing data yields $\tau_m=218.3$ h. This value obtained from measurements as ergodicity is regained and is quite different from the value of 47.6 h deduced from the preceding model (set 1 in Table IV) based on the analysis of behavior during pressurization (losing ergodicity). It is also different from the data of the set 3, in which τ_m and β are free parameters.

The difference between all these fitting curves is shown in the linear plot of $\phi_S(t)$ in the long time domain of Fig. 4(b). In particular, it explains why it was not possible to recover the decompressing data and the overshoot of αV according to the Boltzmann model after a given compression. However, this discrepancy also shows how a simple fit such as this one is ambiguous, without a better knowledge of the very long time relaxing processes in condensed

TABLE IV. Normalized entropic relaxation function at $T = 191.8$ K and $P_a = 326$ MPa.

	τ_m	β
Set 1	47.6[a]	0.884[a]
Set 2	218.3[b]	0.884[a]
Set 3	197.9[b]	0.960[b]

[a]Fixed parameters deduced from the Boltzmann superposition principle model.
[b]Free adjusted parameters.

matter as was already pointed out by Bouchaud[30] and Vincent[31] in their studies of the magnetization relaxation in spin glasses.

Using the data from this work, one can also calculate a possible Kauzmann pressure P_K for fragile liquids, P_K being the pressure at which the entropy of the overcompressed liquid becomes equivalent to that of the corresponding crystal. As in the Adam and Gibbs theory,[32] the excess entropy of the liquid is considered as purely configurational. The schematic diagram (Fig. 5) shows the isothermal behavior of the liquid and crystal entropies as a function of P with respect to particular points—P_m the melting pressure, P_g the glass transition pressure, and P_K the extrapolated Kauzmann pressure. P_K is deduced from the following equation:

$$\Delta S_m = \int_{P_{\text{atm}}}^{P_K} \Delta(\alpha V) dP, \quad \text{at constant } T,$$

where

$$\Delta(\alpha V) = (\alpha V)_{\text{overcompressed liquid}} - \alpha(V)_{\text{crystal}}.$$

If any second order phase transition[24,32] exists at higher densities below the glass transition, i.e., at $P > P_g(T)$—or $T < T_g(P)$—then a single line should describe it in a P–T diagram. In this case, isobaric measurements of the heat capacity C_p at several constant pressures will provide the pressure dependence of the Kauzmann temperature $T_K(P)$ equivalent to $P_K(T)$ determined by our experiments. These data should be complemented by viscosity measurements under high pressure to provide an alternative set of limiting variables $T_0(P)$ or $P_0(T)$ from the well-known Vogel–Tammann–Fulcher equation. For
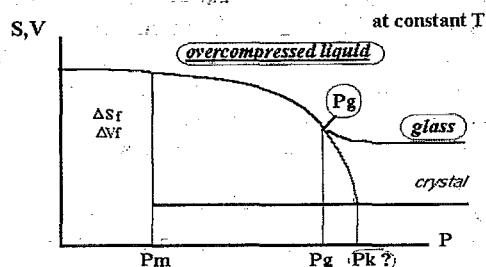
this study, m-fluoroaniline will not be suitable because it does not crystallize, and glycerol should be a more appropriate substance. Experiments in this direction are currently in progress.

V. CONCLUSIONS

In this study, we have presented a new concept of vitrification and opened the field of isothermal glass transitions, showing how the range of data for a given system using a given technique can be greatly extended and how the influences of density and temperature on the transition can be separated. Because the expansivity α reflects the covariance of volume and entropy fluctuations, its T and P dependencies are good qualitative indicators of cooperative phenomena associated with the glass transitions.

More experiments must be done in order to define more precisely the $(\partial P_g / \partial T)$ slope, the Prigogine–Defay ratio, and the kinetics controlling the structural relaxation in the transformation range around P_g at several temperatures. Long relaxation time processes in overcompressed glasses will be analyzed for different compression rates, changing the pressure increment ΔP and the waiting time Δt in the framework of the Boltzmann superposition principle. Annealing experiments above P_g are also necessary. Moreover, the time dependence—or frequency dependence—of the expansivity suggests its conceptualization as a susceptibility with a reactive and a dissipative part as a function of P and T like the heat capacity or the adiabatic compressibility.

Isothermal pressure variations on a very viscous liquid should provide important aids to clarifying the relation between strong and fragile behavior in liquids, at least from the thermodynamic point of view. The apparent decrease of the αV steps at $T_g(P)$ or $P_g(T)$ suggest decreasing fragility with increasing pressure.

Available theories such as mode-coupling theory should now be tested in terms of density in temperature range around the critical point defined at 1 atm; the possible existence of an equivalent critical pressure and density in a P–T diagram would therefore limit application of the theory if the strengthening tendency of a molecular liquid is confirmed since MCT only applies well to fragile liquids.

FIG. 5. A schematic representation of the isothermal behavior of the entropy—or the volume—as a function of P, where P_m is the melting pressure, P_g is the glass transition pressure, and P_K is the Kauzmann pressure.

[1] C. A. Angell, *Relaxations in Complex Systems*, edited by K. Ngai and G. B. Wright (N. T. I. S., U.S. Department of Commerce, Springfield, VA, 1985); J. Non-Crystalline Solids **102**, 205 (1988); J. Phys. Chem. Solids **49**, 863 (1988).
[2] C. Alba, L. Busse, and C. A. Angell, J. Chem. Phys. **92**, 617 (1990).
[3] C. Alba-Simionesco, J. Fan, and C. A. Angell, J. Chem. Phys. (to be published).
[4] W. Goetze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1990), and references quoted therein; W. Goetze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[5] (a) M. Goldstein, J. Chem. Phys. 51, 3728 (1969); (b) 39, 3369 (1963); J. Phys. Chem. 77, 667 (1973).

[6] (a) *Slow Dynamics in Condensed Matter*, AIP Conference Proc. 256, Fukuoka, Japan (1991), and references therein. (b) F. Mauch and J. Jäckle, J. Non-Cryst. Solids (in press).

[7] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[8] C. Alba-Simionesco, in *Hydrogen Bonded Liquids*, edited by J. Dore and J. Teixera (Kluwer, Dordrecht, 1991), pp. 81–88.

[9] J. C. Petit and L. Ter Minassian, J. Chem. Thermodyn. 6, 1139 (1974); 51, 1123 (1979).

[10] (a) C. Alba, L. Ter Minassian, A. Denis, and A. Soulard, J. Chem. Phys. 82, 384 (1985); L. Ter Minassian, K. Bouzar, and C. Alba, J. Phys. Chem. 92, 487 (1988); (b) C. Alba-Simionesco (unpublished).

[11] J. D. Barnett and C. D. Bosco, J. Appl. Phys. 40, 3144 (1969) G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. 44, 5377 (1973).

[12] O. Sandberg, P. Andersson, and G. Bäckström Proc. Symp. Theromphys. Prop. 7, 181 (1977); J. Polymer Sci. 18, 2123 (1980); G. P. Johari and E. Whalley, Faraday Symp. Chem. Soc. 6, 23 (1972); C. A. Angell, L. J. Pollard, and W. Strauss, J. Chem. Phys. 50, 2694 (1969).

[13] A. Quach and R. Simha, J. Phys. Chem. 76, 416 (1972), J. Appl. Phys. 42, 4592 (1971).

[14] L. Ter Minassian and F. Milliou, J. Phys. E. 16, 450 (1983).

[15] (a) R. O. Davies and G. O. Jones, Adv. Phys. 2, 370 (1953); (b) J. Jäckle, J. Phys. Condensed Matter 1, 1267 (1989).

[16] T. Atake and C. A. Angell, J. Phys. Chem. 83, 3218 (1979); E. Williams and C. A. Angell, *ibid* 81, 232 (1977).

[17] H. Suga *et al.*, 27th Symposium of Japanese Calorimetric Society, Kyoto, 1991.

[18] C. Herbst, R. L. Cook, and H. E. King, Jr, Nature 361, 518 (1993).

[19] (a) O. S. Narayanaswamy and R. Gordon, J. Am. Ceram. Soc. 53, 380 (1970); 54, 491 (1971); N. O. Gonchukova, Sov. J. Glass Phys. 7, 217 (1981).

[20] C. Moynihan *et al.* Ann. N. Y. Acad. Sci. 279, 15 (1976).

[21] I. Hodge and H. Berensh, Macromolecules 16, 371 (1983); 16, 898 (1983); 15, 762 (1982); 20, 2897 (1987).

[22] (a) P. Bezot and C. Hesse-Bezot, J. Appl. Phys. 65, 2814 (1989); J. Non-Cryst. Solids 122, 160 (1990); (b) W. F. Oliver, C. A. Herbst, S. M. Lindsay, and G. H. Wolf, Phys. Rev. Lett. 67, 2795 (1991).

[23] N. Birge and S. Nagel, Phys. Rev. Lett. 54, 2674 (1985); P. Dixon and S. Nagel, *ibid*, 61, 341 (1988); 65, 1108 (1990).

[24] (a) W. Kauzmann, Chem. Rev. 43, 219 (1948); J. Gibbs, E. Dimarzio, and J. Jäckle, Rep. Prog. Phys. 49, 171 (1986); J. Jäckle, Philos. Mag. B 56, 113 (1987); J. Souletie, J. Phys. France 51, 883 (1990); D. Kivelson, W. Steffen, Q. G. Meier, and A. Patkowski, J. Chem. Phys. 93, 1943 (1991); J. P. Sethna, J. D. Shore, and M. Huang, Phys. Rev. B 44, 4943 (1991); (b) M. Descamps, J. F. Willart, and O. Delcourt, AIP Conference Proc. 256, 71 (1991); V. Legrand, C. Alba-Simionesco, M. Descamps, and O. Delcourt (unpublished).

[25] M. H. Cohen, and G. S. Grest, Phys. Rev. B 24, 4091 (1981).

[26] I. A. Campbell, J. M. Flesselles, R. Jullien, and R. Botet, Phys. Rev. B 37, 3825 (1988); J. M. Flesselles, Ph.D. thesis, Orsay, 1989. The 1/3 value of β calculated in the preceding article cannot be considered as a definitive one at T_g; it is due mainly to the reduced number of spins allowed for the calculations and may change with another set of N spins. In the case, the zero value represents the limit of the validity of the theory [J.M. Flesselles (private communication)].

[27] G. Li, W. M. Du, A. Sakai, H. Z. Cummins, Phys. Rev. A 46, 3343 (1992); L. M. Torrel, L. Börgesson, and M. J. Elmroth, J. Condensed Matter 3, 207 (1991).

[28] M. A. DeBolt, A. J. Easteal, P. B. Macedo and C. T. Moynihan, J. Am. Ceram. Soc. 59, 16 (1976).

[29] S. Brawer, in *Relaxation in Viscous Liquids and Glasses* (New York American Ceramic Society, New York, 1983).

[30] J. P. Bouchaud, J. Phys. (France) 2, 1705 (1992).

[31] J. P. Bouchaud, E. Vincent, J. Hammann, and M. Ocio (unpublished).

[32] G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965); J. H. Gibbs, in *Modern Aspects of the Vitreous State*, edited by E. J. MacKenzie (Butterworths, London, 1960, Vol. 19); J. H. Gibbs and E. A. Dimarzio, J. Chem. Phys. 43, 139 (1965); K. L. Ngai, R. W. Rendell, and D. J. Plazek, *ibid* 94, 3018 (1991).