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The Connection Between the Measured Glass Transition Temperature and the Time Dependent Order Parameter Description of the Glass Transition

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Summary

The time dependent order parameter concept of the glass transition is used in a description of the relaxation behaviour of the glassforming material. The connection between the macroscopic theory and the measured glass transition temperature has been determined. It has been found that in a case when the Prigogine-Defay ratio is greater than unity, different values of the relaxation functions of entropy and volume obtained by different experiments (e.g., isobaric dilatometry and isothermal compression) should be used in order to obtain the identical T_g. The Prigogine-Defay ratio is found to be a decreasing function of the observation time reaching values between unity in the limit of infinite time and a limit which corresponds to extremely short experiments.

Introduction

Recent progress in the macroscopic description of glass transition has been made possible by applying the order parameter concept and by treating the glass transition as a freezing-in process. Quasistatic approximation brough a finding that, when the Prigogine-Defay ratio

$$\Pi \equiv \Delta\beta\Delta C_p/TV(\Delta\alpha)^2 > 1 \qquad (1)$$

(where $\Delta\alpha$, $\Delta\beta$ and ΔC_p are discontinuities in the temperature expansion coefficient, isothermal compressibility and isobaric heat capacity and T and V respectively are the temperature and volume at the glass transition), then it holds that (i) the number of independent order parameters $n > 1$ (DAVIES and JONES 1953), (ii) excess entropy ΔS and excess volume ΔV are non-zero along the transition line (GOLDSTEIN 1975), but ΔV differs from zero more importantly than ΔS (HAVLÍČEK 1981), and (iii) surfaces of the Gibbs free energy of glass G_g and of liquid G_e are not tangent over an area (GUPTA and MOYNIHAN 1976) and their deviations are quadratic in the first approximation in T and P (HAVLÍČEK 1981).

In the region of linear relaxation, a set of order parameters can always be transformed into a new set in which separately each Z_i relaxes exponentially with a relaxation time τ_i (BERG and COOPER 1978, MOYNIHAN and GUPTA 1978). In this representation relationships have been found for the relaxation functions of entropy and volume, in the case of constant T and P (MOYNIHAN and GUPTA 1978) and in a general case (BERG and COOPER 1978). ROE proved in 1977 that the temperature and pressure experiments do not give the same relaxation time. Also, the relaxation spectra of the S(T), V(P) and V(T) experiments differ for $\Pi > 1$, while the V(T) and S(P) experiments give identical spectra (BERG and COOPER 1978, MOYNIHAN and GUPTA 1978). Relationships between positive functions of the relaxation times and their average values in these experiments were derived and summarized by MOYNIHAN and GUPTA 1978, and by LESIKAR and MOYNIHAN 1980).

In this contribution the findings reported above are correlated with the glass transition temperature determined at a certain experimental time.

Theory

Let Q designate the volume or entropy of a system which can undergo the glass transition. Q is a function of some applied force X (temperature T, pressure P and the like) and of the set of order parameters Z_i

$$Q = Q[X, Z_1(X,t), \ \ldots \ , Z_n(X,t)] \qquad (2)$$

The order parameters are assumed to include the whole time (relaxation) dependence of the property Q.

Let it be that at a time t = 0,X changes jumpwise by ΔX for a brief moment; then for a change ΔQ of the property Q it can be written, while limiting oneself to the first term of the Taylor expansion, that

$$\Delta Q_o(\Delta X) = \sum_i \frac{\partial Q}{\partial Z_i} \Delta Z_{io}(\Delta X) \qquad (3)$$

for t = 0, where $\Delta Z_{io}(\Delta X) = (\partial Z_i/\partial X)\Delta X$ is the deviation of Z_i from equilibrium immediately following the jump in the applied force X, and

$$\Delta Q(\Delta X, t) = \sum_i \frac{\partial Q}{\partial Z_i} \Delta Z_i(\Delta X, t) \qquad (4)$$

for t > 0.

The time dependence of Q tending towards new equilibrium is expressed in terms of the relaxation function

$$\phi_{QX}(t) = \Delta Q(\Delta X, t)/\Delta Q_o(\Delta X) \tag{5}$$

In the approximation of the linear relaxation of order parameters, we have for the relaxation function (BERG and COOPER 1978, MOYNIHAN and GUPTA 1978)

$$\phi_{QX}(t) = \sum_i w^i_{QX} \exp(-t/\tau_i) \tag{6}$$

where w^i_{QX} is the relaxation spectrum corresponding to the QX experiment.

The shape of the time dependence (6) guarantees that at sufficiently long times Q sufficiently approaches the new equilibrium value. On the other hand, however, the real experiments proceed in finite time intervals, let it be said Δt. At the end of the experiment, two limiting cases may be met:

$$\phi_{QX}(\Delta t) \cong \begin{cases} 0 & (7a) \\ 1 & (7b) \end{cases}$$

(7a) obviously refers to an equilibrium liquid, while (7b) corresponds to glass. The range of ϕ_{QX} values between the two extremes represents the glass transition. The sign ≅ in equations (7) is related to the accuracy with which we want or are able to distinguish the respective state. In practical determinations, a graphically significant value $0 < \phi^g_{QX} < 1$ is usually chosen which implicitly defines the glass transition temperature T_g:

$$\phi^g_{QX} = \sum_i w^i_{QX}(T_g) \exp[-\Delta t/\tau_i(T_g)] \tag{8}$$

Obviously, if two different experiments QX and $\overline{QX}$ are performed (e.g., ST and VP or VT) so that $w^i_{QX} \neq w^i_{\overline{QX}}$ (i.e. $\Pi > 1$) and we want to obtain the same glass transition value ($T_{gQX} = T_{g\overline{QX}}$), it must hold that $\phi^g_{QX} \neq \phi^g_{\overline{QX}}$.

Let us now search for the connection between concrete ϕ^g_{QX}. At T_g, it can be written that

$$\begin{aligned} \Delta V(\Delta T,\Delta t) &= - V_g\Delta\alpha(\Delta t)\Delta T \\ \Delta V(\Delta P,\Delta t) &= V_g\Delta\beta(\Delta t)\Delta P \\ \Delta S(\Delta T,\Delta t) &= - \Delta C_p(\Delta t)\Delta T/T_g \\ \Delta S(\Delta P,\Delta t) &= V_g\Delta\alpha(\Delta t)\Delta P \end{aligned} \tag{9}$$

Hence, Eq(5) gives

$$\phi^g_{VT} = \phi^g_{SP} = \Delta\alpha(\Delta t)/\Delta\alpha_o$$

$$\phi^{g}_{VT} = \Delta\beta(\Delta t)/\Delta\beta_o \qquad (10)$$
$$\phi^{g}_{ST} = \Delta C_p(\Delta t)/\Delta C_{po}$$

where $\Delta\alpha_o$, $\Delta\beta_o$ and ΔC_{po} are related to $\Delta t = 0$. By combining Eq.(10) we obtain that

$$\frac{\phi^{g}_{VT}\,\phi^{g}_{SP}}{\phi^{g}_{VP}\,\phi^{g}_{ST}} = \frac{\pi_o}{\pi(\Delta t)} \qquad (11)$$

where π_o is the Prigogine-Defay ratio at $\Delta t = 0$. The Prigogine-Defay ratio $\pi(\Delta t)$ corresponding to $\Delta t > 0$ is a monotonically decreasing function of Δt

$$1 \leq (\Delta t) \leq \pi_o \qquad (12)$$

Since the left-hand side of Eq.(11) approaches π_o for $\Delta t \rightarrow \infty$, equality appears, in this case, on the left-hand side of relation (12).

Discussion

In the case of genuine phase transition the stability criteria in the transition point hold for all the phases present. Unlike this, the glassforming liquid meets the stability criteria only in the range of its equilibrium; in the glass region some degrees of freedom (e.g., translational, rotational etc.) are frozen and the system remains deviated from the state of thermodynamic equilibrium which in this case too would be given by the stability criterion of the liquid phase. The relaxation times required by glass for the attainment of equilibrium are incomparably longer than the time available in the observation. Under such circumstances it becomes difficult, if not impossible, to define the point or the range of glass transition otherwise than by means the experiment used in its determination. Practical determinations of the glass transition temperature are usually based on some kind of graphic approximation, e.g., on the inflexion in the course of the temperature dependence of C_p or α. The choice of a certain graphic method for one of the ϕ^g values is rather arbitrary, and T_g is then implicitly defined by Eq.(8). If, however, we want to obtain the same T_g by employing the other two independent methods, the remaining two ϕ^g are given unequivocally and their magnitude is predicted by Eqs (10). According to Eq.(11), the differences between ϕ^g increase with increasing Δt.

Already the approximation $\Delta t \rightarrow 0$ has demonstrated the extraordinary position occupied by the Prigogine-

Defay ratio for glassforming materials as aids in distinguishing two completely different cases, i.e. $\pi_0 = 1$ and $\pi_0 > 1$ (DAVIES and JONES 1953, GOLDSTEIN 1975, GUPTA and MOYNIHAN 1976, HAVLÍČEK 1981). This paper shows that the results of the approximation $\Delta t \to 0$ can be applied also to the results of experiments carried out on a real time scale. Inequality (12) also shows that the experimentally determined $\pi(\Delta t)$ is smaller than the theoretical criterion π_0. If experience shows (cf., e.g., GUPTA and MOYNIHAN 1976, HAVLÍČEK et al., 1980) that $\pi(\Delta t) > 1$, the more so $\pi_0 > 1$.

The sense of this study consists in providing a closer connection between the theoretical and experimental results. The introduction of a certain (experimental) time interval Δt leads to a new Prigogine-Defay ratio and to Eq.(11) describing the mutual relation between the relaxation functions, more general than similar equations obtained by BERG and COOPER 1978 and MOYNIHAN and GUPTA 1978.

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