Affinity and Internal Parameter of Glass Transition and Full Relaxation

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A non-equilibrium glass-forming system differs from an equilibrium one by having excessive volume and negative pressure. We show that excessive volume is affinity to glass transition while negative pressure is an internal parameter of the system.

Introduction

In an equilibrium thermodynamic system the temperature, T, external pressure, P and volume, V completely define all of its functions of the state, such as Gibbs free energy, G, Helmholtz free energy, F and other:

$$dG = -SdT + VdP \qquad (1)$$

$$dF = -SdT - PdV \qquad (2)$$

Correspondingly:

$$(\partial G/\partial T)_P = -S; \quad (\partial G/\partial P)_T = V; \quad (\partial F/\partial T)_V = -S; \quad (\partial F/\partial V)_T = -P$$

If a chemical reaction takes place in a system, it can be characterized, according to [i], by an additional internal parameter, ξ, and a function of the state, A. Parameter ξ characterizes a degree of completion of a chemical reaction, and function A, called affinity, characterizes an ability of a system to enter a chemical reaction:

$$dG = -SdT + VdP - Ad\xi \qquad (1a)$$

$$dF = -SdT - PdV - Ad\xi \qquad (2a)$$

$$A = -(\partial G/\partial \xi)_{P,T} = -(\partial F/\partial \xi)_{V,T} \qquad (3)$$

Physical meaning of affinity and internal parameter of glass transition and relaxation

Cooper [ii] used the ideas of affinity and internal parameter in a description of a non-equilibrium glass-forming system, for which he defined two specific states: (1) that of a non-equilibrium liquid with $A \neq 0$ and $d\xi \neq 0$, therefore relaxation can be observed in it; (2) of a solid body with $A \neq 0$ and $d\xi = 0$, therefore relaxation processes in it are frozen. These definitions (or criteria) are insufficient to define which characteristics of a glass-forming system should be used as affinity to relaxation and glass transition, and as an internal parameter that would adequately describe the completeness of these processes.

In general, A and ξ should meet several criteria:

1. Equilibrium criterion. In equilibrium state, $A = 0$ and $\xi = 0$. This means that out of all characteristics of a system, the one with maximum relaxation time should be chosen as ξ.
2. Dimension criterion. Component $Ad\xi$ must be measured in energy units, therefore A and ξ can not be chosen independently from each other.
3. Cooper's criterion. In solid glass ξ = const., $Ad\xi = 0$.
4. Negativity criterion. Considering the signs in Equations 1a and 2a, and the physical meaning of G and F, in a process of fast cooling, when a system becomes more non-equilibrium, $Ad\xi < 0$, so both G and F increase.
5. Positivity criterion. In a process of relaxation $Ad\xi > 0$, so both G and F decrease.

Application of the theory of affinity to the glass-forming systems

There are two important characteristics of a non-equilibrium system that meet all of the above criteria, as it is shown in [iii] and [iv]: internal negative pressure in the system, called configurational pressure, P_C , and its excessive volume, δV. Let us demonstrate that excessive volume can be considered as affinity of the system to relaxation and glass transition, and negative pressure – as its internal parameter, in other words, that $A = \delta V$ and $\xi = P_C$.

It is also shown in [3,4] that fast cooling of a glass-forming liquid within the glass transition interval from T_a to T_b is an isochoric process, that is, it occurs at V = const. Therefore, at temperature $T < T_a$ a non-equilibrium glass-forming system has excessive volume and negative pressure that can be given as:

$$\delta V = \alpha V(T_a - T) > 0 \qquad (4)$$

$$P_C = (\alpha/\beta)\,(T - T_a) < 0 \qquad (5)$$

where α and β are coefficients of thermal expansion and isobaric compression of a liquid, correspondingly.

In a solid glass, that is, when $T \le T_b$, excessive volume, δV, and negative pressure, P_C , have the following constant values:

$$\delta V^{\text{glass}} = \alpha V\,(T_a - T_b) > 0 \qquad (4a)$$

$$P_C^{\text{glass}} = (\alpha/\beta)\,(T_a - T_b) < 0 \qquad (5a)$$

In a process of isothermal relaxation of a glass-forming system at a certain constant temperature, T, with $T_a < T < T_b$, $\delta V \rightarrow 0$ from the side of positive values, while P_C "increases to zero", that is $P_C \rightarrow 0$ from the side of negative values:

$$(\delta V)^{\mathrm{relax}} > 0 \tag{6}$$

$$dP_C^{\mathrm{relax}} > 0 \tag{7}$$

In a process of fast cooling of such system, at $V = \mathrm{const}$, $dT < 0$, its volume increases with a decrease in temperature, and a change in P_C is negative:

$$\delta V^{\mathrm{cool}} = \alpha V(T_a - T) > 0 \tag{8}$$

$$dP_C^{\mathrm{cool}} = (\alpha/\beta)\ dT < 0 \tag{9}$$

Thus, it follows from Equations 6 and 7 that

$$(\delta V^{\mathrm{relax}})\ (dP_C^{\mathrm{relax}}) > 0 \tag{10}$$

and from Equations 8 and 9 – that

$$(\delta V^{\mathrm{cool}})\ (dP_C^{\mathrm{cool}}) < 0 \tag{11}$$

Sum total of Equations 4 -11 confirm that δV and P_C do meet all the criteria for A and ξ.

For a system in equilibrium, that is at $T \geq T_a$, or after completion of relaxation, $\delta V = 0$ and $P_C = 0$, therefore the 1st criterion – Equilibrium criterion, is fulfilled. Apparently, the second – Dimension criterion, is fulfilled, since $(\delta V dP_C)$ is measured in energy units. As follows from Equations 4a and 5a, in a solid glass Cooper's criterion is fulfilled: $\delta V \neq 0$ and $dP_C = 0$, hence $(\delta V dP_C) = 0$ and $P_C = \mathrm{const}$. Equations 10 and 11 prove that δV and P_C also meet both Negativity and Positivity criteria.

Conclusion

In a non-equilibrium glass-forming system, the excessive volume is its affinity to relaxation and glass transition, and negative pressure is an internal coefficient of full relaxation.

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[i] De Donder, Th., *Thermodynamic theory of affinity* (Stanford University Press, London, 1936), p. 142.

[ii] Cooper, A. in *4th International Conference on the Physics of Non-Cryst. Solids,* 1976, edited by G. Frischat, (Transtech, Aedermansdorf, 1977), p. 384.

[iii] Landa, L., Landa, K. in *Fundamentals of glass science and technology,* 1977, edited by , (Glafo, Vaxjo, 1977), p. 591.

[iv] Landa, L. and Landa, K., Glastechnische Ber. Glass Sci. Technol **73**, p. 441 (2000).