The Role of Negative Pressure in Glass Formation and Glass Transition

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Internal negative, or configurational pressure, P_C, originates in a glass-forming liquid as a result of its fast cooling within the glass transition interval, $T_b < T < T_a$. An equilibrium phase – crystal – is not formed under negative pressure, so at $T = T_b$ a non-equilibrium liquid transforms into a non-equilibrium phase – glass. Also, at $T = T_b$, the entropy of a glass-forming liquid decreases down to its critical level at which liquid state does not exist.

Introduction

It is known that a liquid transforms into glass at fast cooling [1] and also at an isothermal increase of the external pressure [2]. It is also known[2] that an intermediate state – the so-called non-equilibrium liquid – precedes the formation of solid glass not only at fast cooling but with an increase of the external pressure as well. Thus, in any event a liquid transforms into a non-equilibrium state before solidification. The fact of relaxation of a glass-forming system proves that it is non-equilibrium, since relaxation is a transition from a non-equilibrium state to equilibrium one.

The most important feature of a non-equilibrium liquid is its excessive volume. Therefore relaxation of a glass-forming system is accompanied by a decrease in volume ($dV<0$), and it can be easily observed in a process of isothermal relaxation. Excessive volume appears as during transition from liquid to glass upon fast cooling, so with an increase in the external pressure[2]. For example, at $T = 333$ K and after a change in pressure from 864 to 1152 atmospheres, relaxation of the volume in phenol-formaldehyde tar occurred in 16 minutes. In the process of isothermal relaxation the volume of the tar decreased by 0.3% with an instrumental error 0.0065%.

The fact of a decrease in volume of a glass-forming system during its isothermal relaxation proves that negative pressure exists in the system, that is, the system is self-compressible. In [3] negative pressure was called configurational.

Negative pressure and relaxation of volume

According to the principles of thermodynamics, if irreversible processes occur in a body at constant temperature, Helmholtz free energy, F, of this body decreases ($dF < 0$).

Pressure inside a thermodynamic system is given by:

$$P = -(\Delta F/\Delta V)_T \qquad (1)$$

hence with identical signs for a change in V and F, $P < 0$.

The existence of negative pressure in non-equilibrium glass-forming systems explains the fundamental contradiction between the relaxation theory of glass transition on the one hand, and the theory of relaxation in physical kinetics and statistical physics on the other hand.

The relation between the changes in volume and entropy of a system is given by:

$$\Delta S = (P/T)\,\Delta V \qquad (2)$$

The relaxation theory of glass transition (see, for example [4] and [5]) does not take into account the existence of negative pressure in non-equilibrium glass-forming systems and, based on Equation 2, draws a conclusion that the entropy of a glass-forming system decreases during relaxation[5]. Relaxation, however, is a transition of a system from a non-equilibrium state to equilibrium. Since the latter state has the highest probability of existence, it also has maximum entropy. In Landau's statistical physics [6] it is emphasized that at $P<0$ the entropy of a system increases on compression. It also follows from Equation 2.

Negative pressure as thermodynamical cause of amorphous solidification of a liquid

As it was shown before [3], negative pressure, P_C, appears on cooling of a glass-forming liquid. Within the glass transition interval P_C can be defined as follows:

$$P_C = (\alpha/\beta)\,(T - T_a) < 0 \qquad (3)$$

and in solid glass as:

$$P_C = (\alpha/\beta)\,(T_b - T_a) < 0 \qquad (4)$$

where T_a and T_b are the upper and lower boundaries of the glass transition interval, and α and β – coefficients of thermal expansion and compression of a liquid, correspondingly. In solid glass P_C reaches hundreds and even thousands atmospheres, for example, in boron trioxide, B_2O_3 , $P_C \approx 1500$ atmospheres. It is also stated in [6] that negative pressure does not exist in stable systems. The opposite is also true: a stable system or structure, for example an equilibrium crystal, can not be formed under negative pressure, therefore the system remains amorphous.

On cooling of a glass-forming system, its entropy decreases due to a decrease in temperature. At a high cooling rate there is an additional decrease in entropy due to the rise of negative pressure that is expressed as [3]:

$$\Delta S\,(P_C) = (\alpha^2/\beta)\,V\,(T - T_a) \qquad (5)$$

When a system reaches a certain critical entropy value, it can no longer exist as a liquid, therefore it solidifies at $T = T_b$.

In a process of structural relaxation at constant temperature the entropy of a glass-forming liquid increases:

$$\Delta S^R = (\alpha^2/\beta)\,V\,(T_a - T) > 0 \qquad (6)$$

Since the entropy of a crystal is lower than the entropy of a non-equilibrium liquid, it is obvious that, in a process of relaxation, a glass-forming system approaches to the state of a metastable liquid that would have been formed at infinitely slow cooling, rather than to the state of a crystal.

Conclusions

1. Within the glass transition interval, negative pressure is a thermodynamic factor that is responsible for amorphous solidification of a liquid.

2. In a process of isothermal relaxation of a glass-forming system an increase of its entropy and "an increase to zero" of negative pressure take place.

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