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A Simple Phenomenological Model for the Order Parameter Description of Glass Transition

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Summary

Glass transition has been investigated as a freezing-in process by using a simple form of the Gibbs free energy with two order parameters. Two cases are examined: that of a single freezing-in line (transition line) and that involving two different lines on which the individual order parameter freeze-in gradually. The latter case is a simple, but adequate description of the diffusivity of glass transition. The effect is discussed of the mutual position of freezing-in lines and of the Prigogine-Defay ratio on the dependence of the behaviour of material on the thermodynamic history of glass transition.

Introduction

Glass transition depends on the velocity of changes in thermodynamic variables, i.e. temperature T or pressure P. A study of the extreme cases of velocity of these changes is useful. A freezing-in model based on the description of glass transition by means of order parameters (DAVIES and JONES 1953a) approximates very fast changes in which time effects can be neglected. Freezing-in of the order parameters is related to jumps of those quantities which are directly connected with the second derivatives of the Gibbs free energy, i.e. with the jump in the isobaric heat capacity, ΔC_p, in the coefficient of the volume temperature expansion $\Delta\alpha$, and in isothermal compressibility $\Delta\beta$. These coefficients allow us to construct the Prigogine-Defay ratio

$$\pi = \Delta C_p \Delta\beta / TV(\Delta\alpha)^2 \qquad (1)$$

(V being the volume) which for the second-order phase transitions is always unity. For glass transition, however, the experiment suggests that $\pi>1$ (DAVIES and JONES 1953b, O'REILLY 1962, GUPTA and MOYNIHAN 1976). Most authors (DAVIES and JONES 1953a, GOLDSTEIN 1975, GUPTA and MOYNIHAN 1976, ROE 1977, BERG and COOPER 1978) agree that experimental findings just mentioned and theory are not at variance, if one admits that in the liquid-glass transition more than one order parameter freeze-in. On the other hand, however, DIMARZIO (1974, 1977a,b) proves that, if the experiment shows $\pi\neq1$, the freezing-in concept of order parameters cannot be applied to the given material.

Now it seems useful to discuss the concrete form of the dependence of the Gibbs free energy on order parameters,

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temperature and pressure. The form of the Gibbs free energy suggested by GOLDSTEIN (1980) though it adequately describes, in the most general features, the difference between the second-order phase transtion and glass transition, do not, however, explain why $\pi>1$. A certain limitaion of the theory also consists in that the author leaves unnoticed pressure dependences.

Our approach is a phenomenological one, being the continuation of a study by GOLDSTEIN (1980). We attempt to demonstrate that the analytically very simple form of the Gibbs free energy may adequately describe the essential properties of glass transition, at least in the close vicinity of a certain point or region where the liquid becomes glass, A view forwarded by ROE (1977) that the diffusivity of glass transition is a consequence of the gradual freezing-in of the individual order parameters, is also dealt with in some detail.

Theory

Basic relations

The Gibbs free energy of a glass-forming system suggested by GOLDSTEIN (1980) is generalized to a form containing two order parameters η_1 and η_2

$$G = G_o + \sum_{i=1,2} (A_i\eta_i + B_i\eta_i^2/2) \qquad (2)$$

Let it be assumed, for the sake of simplicity, that only coefficients A_i are temperature- and pressure-dependent, while B_i are nonzero constants. In the state of thermodynamic equilibrium,

$$(\partial G/\partial\eta_i)_{T,P} = 0 \qquad i = 1,2 \qquad (3)$$

so that the equilibrium values of order parameters (i.e. in the liquid) become

$$\eta_i^e = -A_i(T,P)/B_i \qquad i = 1,2 \qquad (4)$$

Let it also be assumed that in the liquid-glass transition, a freezing-in line exists for each order parameter

$$T = f_i(P) \qquad i = 1,2 \qquad (5)$$

on which for the order parameters we have

$$\eta_i^e[f_i(P),P] = \eta_i^g(P) \qquad (6)$$

In agreement with the freezing-in model, for $T \le f_i(P)$ the order parameters are constant (frozen-in). Let the parameter η_i freeze-in in the point $[T_{oi}, P_{oi}]$ which satisfies (5); then in this point, according to (4) and (6),

$$-A_i(T_{oi}, P_{oi})/B_i = \eta_i^g(P_{oi}) \qquad (7)$$

If A_i is expanded into a series as a function of T,P in the vicinity of the point $[T_{oi}, P_{oi}]$, we obtain in the first approximation

$$-A_i(T,P;T_{oi},P_{oi}) = B_i\eta_i^g(P_{oi}) + a_i(T - T_{oi}) - b_i(P - P_{oi}) \qquad (8)$$

where a_i, b_i are regarded as constants. Using Eqs (4), (6) and (8), it may be written for lines (5) in the first approximation that

$$a_i(T - T_{oi}) = [B_i(\partial\eta_i^g/\partial P)_{P=P_{oi}} + b_i](P - P_{oi}) \qquad (9)$$

These assuptions allow us to investigate the behaviour of the model of glass-forming material in the vicinity of the point $[T_{oi}, P_{oi}]$ (i=1,2).

Liquid-glass transition

First, let it be assumed that both order parameters freeze-in on the same line ($f_1 = f_2 = f$) and that the liquid is transformed into glass in the point $T_o = f(P_o)$. For the volume and entropy near the point $[T_o, P_o]$,

$$V_L(T,P) = V_g(T,P) - [(T-T_o)\Sigma a_ib_i/B_i - (P-P_o)\Sigma b_i^2/B_i] \qquad (10)$$

$$S_L(T,P) = S_g(T,P) - [(T-T_o)\Sigma a_i^2/B_i - (P-P_o)\Sigma a_ib_i/B_i] \qquad (11)$$

where the indices "L" and "g" denote the liquid and glass respectively. Eqs (10) and (11) show that in the point $[T_o,P_o]$ the quantities appearing in the Prigogine-Defay ratio (11) assume the values

$$C_p = \Sigma a_i^2/B_iT_o \qquad \Delta\alpha = V_o\Sigma a_ib_i/B_i \qquad \Delta\beta = V_o\Sigma b_i^2/B_i \qquad (12)$$

where $V_o = V_L(T_o,P_o) = V_g(T_o,P_o)$. It is easy to see that if, and only if

$$a_1b_2 \neq a_2b_1 \qquad (13)$$

we have $\pi(T_o,P_o)>1$. If (13) is satisfied, the lines $V_L - V_g = 0$ and $S_L - S_g = 0$ in the T,P plot do not coincide, in agreement with the results obtained by GUPTA and MOYNIHAN (1976).

Let us now examine a case which, it seems, is closer to reality, where the freezing-in lines of various order parameters do not coincide, and let us assume that $f_1(P)>f_2(P)$ within the whole range of accessible pressures. In the liquid-glass transition the path of the system states first crosses the line f_1 in the point $[T_{o1}, P_{o1}]$ where η_1 freezes-in, and partially frozen-in glass is formed. Only after f_2 has been crossed in the point $[T_{o2}, P_{o2}]$ the whole system freezes-in. It is easy to demonstrate that in points $[T_{o1}, P_{o1}]$ and $[T_{o2}, P_{o2}]$ the corresponding π´s are unity. The two-parameter model is regarded as a simplified model of the diffuse transition, in which in fact many parameters may gradually become frozen-in. In the experimentally investigated diffuse transition, no jump of C_p, α and β occurs in any of the points; if an extrapolated jump is mentioned, such as that of C_p, for instance, then what is meant is the difference between the C_p value in the point at the onset of transition and the C_p value in the point at the end of it (which similarly holds for the other quantities). Under such circumstances, the Prigogine-Defay ratio cannot be used as stated in the Introduction, because this ratio has been defined for a point transition. Let therefore the Prigogine-Defay ratio for the diffuse transition be generalized by

$$\pi_d = \Delta(\bar{C}_p/T)\Delta\bar{\beta}/(\Delta\bar{\alpha})^2 \tag{14}$$

where

$$\Delta(\bar{C}_p/T) = (\partial\bar{S}_L/\partial T) - (\partial\bar{S}_g/\partial T) \tag{15}$$

$\bar{S}_L$ and $\bar{S}_g$ respectively are the specific entropies of liquid and glass, and the temperature derivatives are taken in the points where the isobar crosses the line f_1, f_2 respectively, $\Delta\bar{\alpha}$ and $\Delta\bar{\beta}$ are defined similarly. In our case we have

$$\pi_d = (\Sigma a_i^2/B_i)(\Sigma b_i^2/B_i)/(\Sigma a_i b_i/B_i)^2 \tag{16}$$

It can be seen that, similarly to the case of a single transition line, also $\pi_d>1$ then and only then, if (13) is valid. Generally, π_d may depend on the chosen isobaric and isothermal paths. To avoid ambiguity, a certain convention must be agreed upon (e.g., that both paths pass through the point $[T_{o1}, P_{o2}]$).

Glass-liquid transition

Let it be assumed that if the glass-liquid transition proceeds along the same path as the formation of glass from the liquid, the freezing-in parameters defreeze in the same points in which they froze-in during the glass formation. If the glass-liquid transition proceeds along a different path, the dependence of the system on its thermodynamic history may come into play. Studies published so far (GOLDSTEIN 1976, HAVLÍČEK 1981) have been based on the hypothesis (A): the order parameters defreeze on the lines $f_i(P)$ irrespective of conditions under which they froze-in. The model just mentioned allows us to analyze another extreme hypothesis (B): the order parameters defreeze on lines $\eta_i^e(T,P) - \eta_i^g(P_{oi}) = 0$. Let us now examine consequences reached by applying the hypotheses (A) and (B) to the model described above, if the system passes, e.g., along the following path: glass was formed by isobaric cooling at P_o, in the glass state the pressure was changed to P', and at the latter pressure transition back to the liquid was effected by isobaric heating. We shall examine the behaviour of the system during the transition from glass to liquid at P'.

Let it first be taken that $f_1 = f_2 = f$. $\pi = 1$ holds for the system, then the lines given by equations

$$V_L - V_g = 0 \tag{17}$$

$$S_L - S_g = 0 \tag{18}$$

$$\eta_i^e(T,P) - \eta_i^g(P_o) = 0 \tag{19}$$

coincide with each other, and it can be demonstrated that they are identical with the line f(P). The order parameters assume a constant value along the line f(P); the paths from the liquid

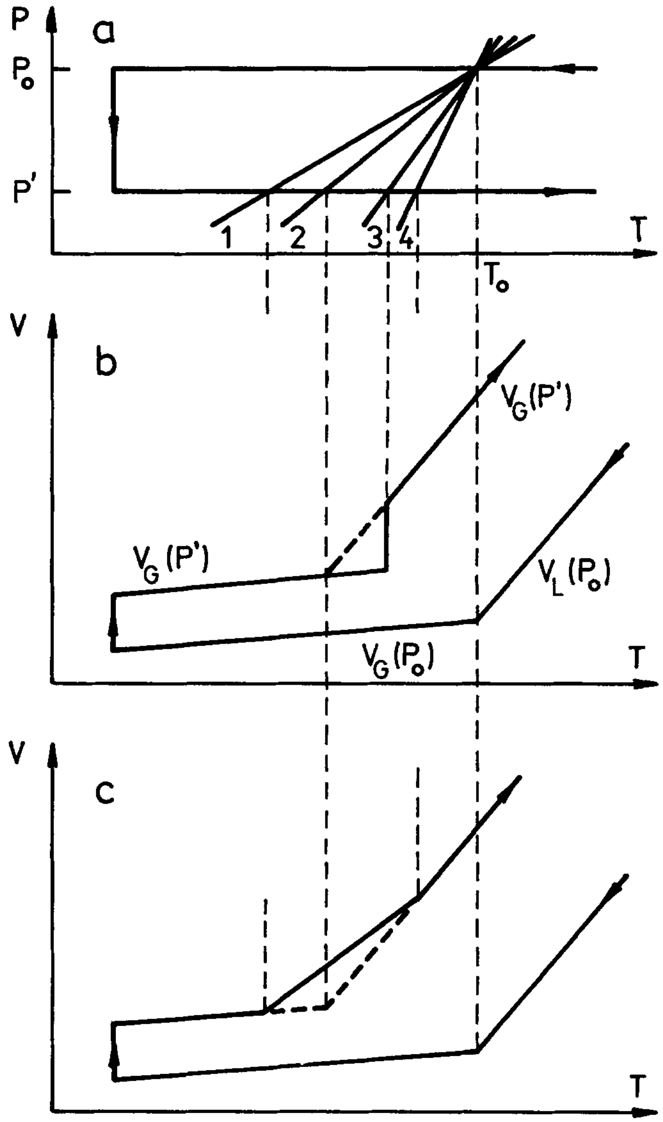

Fig.1 Schematically represented dependences of the system on thermodynamic history
(a) Temperature and pressure régime. Designation of lines: 1: $\eta_1^e(T,P) - \eta_1^g(T_o,P_o) = 0$, 2: $V_L - V_g = 0$, 3: $T = f(P)$, 4: $\eta_2^e(T,P) - \eta_2^g(T_o,P_o) = 0$
(b) Behaviour of the volume according to the hypothesis (A)
(c) Behaviour of the volume according to the hypothesis (B)

into glass and vice versa do not differ, irrespective of the chosen path, and the system is independent of its thermodynamic history. If, however, $\pi>1$, the lines given by Eqs (17)-(19) differ from each other. The use of hypothesis (A) leads to a prediction of discontinuities in the volume and entropy (cf. GOLDSTEIN 1976, HAVLÍČEK 1981). The hypothesis (B) does not predict any jumps, both the volume and entropy vary continuously and monotonically, and material, when heated, passes through the state of partly frozen-in glass when only one order parameter is frozen-in. Both these possibilities are schematically illustrated by Fig.1.

If the lines $T = f_i(P)$ are different, but parallel to each other, the situation is similar. At $\pi_d = 1$ the lines given by Eq. (19) coincide with the lines f_i and the system is independent of thermodynamic history. If $\pi_d>1$, at least one of the lines given by Eq. (19) has a slope different from that of f_i, and either the hypothesis (A) or (B) may be applied to the system. According to the hypothesis (A), a jump in the volume and entropy occurs on that line f_i which differs from the respective line given by Eq. (19). The hypothesis (B) leads to the prediction of a continuous and monotonic transition of glass into liquid through the state of partly frozen glass. At the same time, both the volume and entropy of partly frozen glass and the discontinuities (if any) depend on the thermodynamic history of the system.

If the lines f_i are not parallel, but $a_1b_2 = a_2b_1$, then according to inequality (13) is $\pi_d = 1$; in spite of this, however, according to the hypothesis (A) jumps occur in the volume and entropy, and in any case material depends on the thermodynamic history in the glass-liquid transition. A case may also arise, however, where $\pi_d>1$ and the lines given by Eq. (19) coincide with the corresponding f_i. Then both hypotheses represent the same, and the system is independent of thermodynamic history, because according to Eq. (9), lines given by Eq. (19) are lines of constant η_i^g irrespective of the points of transition.

It can be said, in conclusion, that assuming the existence of a single line of the glass-liquid transition, our model of such transition is in accordance with the results obtained earlier (DAVIES and JONES 1953a, GUPTA and MOYNIHAN 1976, GOLDSTEIN 1975, ROE 1977, BERG and COOPER 1978). Although in this case the liquid-glass transition is "sharp", we indicate the possibility of a diffuse character of the glass-liquid transition, if the latter proceeds along a path different from that of glass formation.

It seems more realistic to assume that the order parameters freeze-in gradually. Such a gradual freezing-in models the diffusivity of glass transition. Under such circumstances, the Prigogine-Defay ratio should be defined in a more general manner, and the quantities ΔC_p, $\Delta\alpha$ and $\Delta\beta$ should not be related to a single point, but to values at the beginning and end of the transition.

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