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Nonequilibrium thermodynamics. III. Generalization of Maxwell, Clausius-Clapeyron, and response-function relations, and the Prigogine-Defay ratio for systems in internal equilibrium

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We follow the consequences of internal equilibrium in nonequilibrium systems that has been introduced recently [Gujrati, Phys. Rev. E **81**, 051130 (2010) and **85**, 041128 (2012)] to obtain the generalization of the Maxwell relation and the Clausius-Clapeyron relation that are normally given for equilibrium systems. The use of Jacobians allows for a more compact way to address the generalized Maxwell relations in the presence of internal variables. The Clausius-Clapeyron relation in the subspace of observables shows not only the nonequilibrium modification but also the modification due to internal variables that play a dominant role in glasses to which we apply the above relations. Real systems do not directly turn into glasses (GL) that are frozen structures from the supercooled liquid state L; there is an intermediate state (gL) where the internal variables are not frozen. A system possesses several kinds of glass transitions, some conventional (L→gL; gL→GL) in which the state changes continuously and the transition mimics a *continuous* or second-order transition, and some apparent (L→gL; L→GL) in which the free energies are discontinuous so that the transition appears as a *zeroth-order* transition, as discussed in the text. We evaluate the Prigogine-Defay ratio Π in the subspace of the observables at these transitions. We find that it is normally different from 1, except at the conventional transition L→gL, where $\Pi = 1$.

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I. INTRODUCTION

In recent papers [1–5], we have developed a nonequilibrium thermodynamics based on the concept of *internal equilibrium* within a macroscopic system Σ surrounded by an extremely large medium $\widetilde{\Sigma}$; the two form an isolated system Σ_0 as shown in Fig. 1. We restrict our attention to a system with energy E, volume V, and number of particles N as the observables and, for simplicity, do not allow any relative motion between the system and the medium. While it is not necessary, we will also include an extensive internal variable ξ for generality. The observables and internal variables collectively represent the *state variables* [3] of the system. In general, the fields such as the temperature $T(t)$, the pressure $P(t)$, etc., of the system are different from the corresponding temperature T_0, the pressure P_0, etc., of the medium as the system approaches equilibrium; see also Bouchbinder and Langer [6]. The differences in the fields give rise to *thermodynamic forces* driving the system toward equilibrium with the medium. Unfortunately, one such difference, the difference between $T(t)$ and T_0, is normally not accounted for in the literature in many cases, especially when dealing with glasses, where the thermal force $T(t) - T_0$ plays an important role during relaxation and entropy generation in isobaric processes [1,5]. We will overcome this shortcoming and carefully account for the consequences of this thermodynamic force in addition to following the consequences of internal equilibrium in this work as discussed below. As an application, we study glass transition, which is historically treated as a transition between a liquid and an amorphous solid. Unfortunately, it is common in the literature to overlook the important fact that the liquid and solid states are not contiguous (see below). Therefore, their free energies have a discontinuity at the transition temperature, which makes the transition a *zeroth-order transition* and not a continuous transition as is commonly believed. This, to the best of our knowledge, has not been pointed out in the glass field. Thus, our work provides a paradigm shift in the field of glass transition.

The formal similarity between the internal equilibrium and equilibrium as discussed in Ref. [3] strongly suggests that there may exist analogs of the Maxwell relations or other important relations [7] for a system that, although not in equilibrium with the medium, is in internal equilibrium; see [8–10] for other approaches. The situation is somewhat complicated as there are two distinct sets of fields and affinity related to the system and the medium, respectively, and it is not clear which set will appear in the nonequilibrium Maxwell relations if the latter exist at all.

Our aim, accordingly, is to seek the generalization of the Maxwell relations, the Clausius-Clapeyron relation, and the relations between response functions for nonequilibrium states in the presence of thermodynamic forces. These extensions will play an important role in the study of nonequilibrium systems that are nonetheless in internal equilibrium. We find *Jacobians* [11–14] to be quite useful. Therefore, we introduce Jacobians and their important properties in Appendices A–C. This discussion is somewhat technical, but we provide most of the required details so that the clarity of presentation is not compromised. An important part of this discussion is to show that the Jacobians can be manipulated in a straightforward manner even in a subspace of the variables associated with observables as discussed in Appendix C because observations require manipulating the observables and not the internal variables. Thermodynamic potentials and other useful functions for nonequilibrium states are introduced in Sec. II. We develop the generalization of the Maxwell relations in Sec. III. We discuss the generalization of the Clausius-Clapeyron relation in Sec. IV, where we also discuss the conditions

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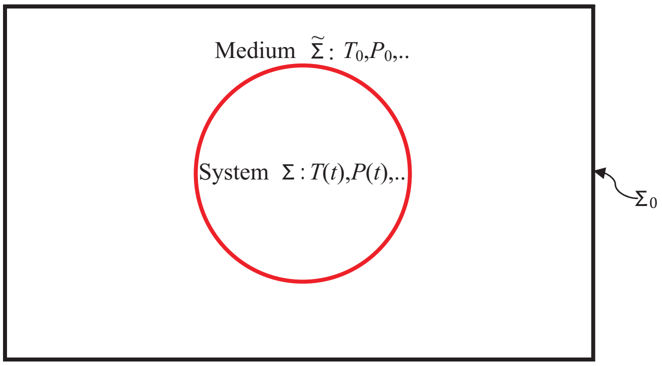

FIG. 1. (Color online) Schematic representation of a system Σ and the medium $\widetilde{\Sigma}$ surrounding it to form an isolated system Σ_0. The medium is described by its fields T_0, P_0, etc., while the system, if in internal equilibrium (see text), is characterized by $T(t), P(t)$, etc.

for phase transitions in nonequilibrium states. The response functions such as the heat capacities, compressibilities, and expansion coefficients and the various relations among them are developed in Sec. V. As an application, we study the evaluation of the Prigogine-Defay ratio in glasses in this work. Therefore, we briefly discuss what is customarily called a glass and the associated glass transition in Sec. VI. A careful discussion shows that the term does not refer to one single transition; rather, it can refer to different kinds of transitions, some of which appear similar to the conventional transitions in equilibrium, but others refer to apparent transitions where the Gibbs free energy cannot be continuous. The Prigogine-Defay ratio are evaluated at various possible glass transitions in Sec. VII. We also compare our approach with some of the existing approaches for the ratio. The last section contains a brief summary of our results.

II. INTERNAL EQUILIBRIUM THERMODYNAMICS

We will no longer exhibit the time dependence in the variables for the sake of notational simplicity. We rewrite the Gibbs fundamental relation for the system in internal equilibrium

$$dE = TdS - PdV + \mu dN - Ad\xi, \tag{1}$$

with its fields and affinity, to be collectively called fields in the following for simplicity, given by

$$\begin{aligned} \beta \equiv 1/T = \partial S/\partial E, \quad \beta P = \partial S/\partial V, \\ \beta\mu = -\partial S/\partial N, \quad \beta A = \partial S/\partial \xi, \end{aligned} \tag{2}$$

to show the thermodynamic forces and the resulting irreversible contributions explicitly

$$dE = T_0 dS - P_0 dV + (T - T_0)dS - (P - P_0)dV - Ad\xi, \tag{3}$$

that are described by the last three terms. Recall that the affinity of the medium is $A_0 = 0$ [3]. In equilibrium, the thermodynamic forces vanish and we have

$$T_0 dS_{\rm eq} = dE_{\rm eq} + P_0 dV_{\rm eq} - \mu_0 dN_{\rm eq}, \tag{4}$$

where the extensive quantities are shown by the additional subscript "eq." The following equilibrium Maxwell relations, see for example [7], follow from Eq. (4):

$$\begin{aligned} (\partial T_0/\partial V_{\rm eq})_{S_{\rm eq},N} &= -(\partial P_0/\partial S_{\rm eq})_{V_{\rm eq},N}, \\ (\partial T_0/\partial P_0)_{S_{\rm eq},N} &= (\partial V_{\rm eq}/\partial S_{\rm eq})_{P_0,N}, \\ (\partial P_0/\partial T_0)_{V_{\rm eq},N} &= (\partial S_{\rm eq}/\partial V_{\rm eq})_{T_0,N}, \\ (\partial S_{\rm eq}/\partial P_0)_{T_0,N} &= -(\partial V_{\rm eq}/\partial T_0)_{P_0,N}, \end{aligned} \tag{5}$$

and represent the equality of two partial derivatives. In the following, we will not explicitly show the additional subscript "eq" for equilibrium quantities unless clarity is needed. In equilibrium, ξ becomes a function of the observables and is not needed.

It is now easy to see that

$$\begin{aligned} dH &= T_0 dS + VdP_0 + (T - T_0)dS - (P - P_0)dV - Ad\xi, \\ dF &= -SdT_0 - P_0 dV + (T - T_0)dS - (P - P_0)dV - Ad\xi, \\ dG &= -SdT_0 + VdP_0 + (T - T_0)dS - (P - P_0)dV - Ad\xi, \end{aligned} \tag{6}$$

where $H = E + P_0 V$, $F = E - T_0 S$, and $G = E - T_0 S + P_0 V$. These potentials correspond to ξ as an independent variable of the potential and have the property that they continuously decrease as the system approaches equilibrium [1]. The functions $\widehat{H} = E + PV$, $\widehat{F} = E - TS$, and $\widehat{G} = E - TS + PV$, instead, use the fields of the system but lack the latter property and cannot be identified as thermodynamic potentials. One can make a transformation of these functions to functions in which the conjugate field A_0 or A is the independent variable:

$$Q^{\rm A_0} = Q + A_0\xi, \quad \widehat{Q}^{\rm A} = Q + A\xi,$$

where $Q = E, H, F$, or G. However, as is well known, $A_0 = 0$; see for example [3]. Thus, there is no difference in the values of the two potentials Q and $Q^{\rm A_0}$. The functions $\widehat{Q}^{\rm A}$ change with A, but also do not represent potentials. In this regard, our approach is different from other nonequilibrium approaches [8–10].

III. MAXWELL RELATIONS FOR SYSTEMS IN INTERNAL EQUILIBRIUM

A. Equilibrium compact Maxwell relation

Before proceeding with our general discussion, we consider equilibrium Maxwell relations and point out a very important consequence of the use of the Jacobians. Using the Jacobians, the four Maxwell relations in Eq. (5) can be simply written as

$$\partial(T_0,S,N)/\partial(\alpha,\beta,N) = \partial(P_0,V,N)/\partial(\alpha,\beta,N), \tag{7}$$

where the pair (α,β) stands for the following *nonconjugate* pairs: $(V,S),(P_0,S),(T_0,V)$, or (P_0,T_0). All four Maxwell relations use the same numerators $\partial(T_0,S,N)$ and $\partial(P_0,V,N)$ containing *conjugate* pairs (T_0,S) and (P_0,V). Thus, they can all be combined into a single *compact* Maxwell relation containing conjugate pairs obtained by *suppressing* the common denominator on the two sides:

$$\partial(T_0,S,N) \equiv \partial(P_0,V,N). \tag{8}$$

Here, the compact relation only has a meaning if each side is divided by some common denominator such as $\partial(V,S,N), \partial(P_0,S,N), \partial(T_0,V,N)$, and $\partial(P_0,T_0,N)$ on both sides. In the following we will call a compact Maxwell relation simply as a Maxwell relation if there is no possibility of any confusion. This relation is equivalent to the following identity:

$$\partial(T_0,S,N)/\partial(P_0,V,N) \equiv 1. \tag{9}$$

From now on, we will always consider the case of a constant N, which will no longer be exhibited below for simplicity of notation.

B. Internal equilibrium Maxwell relations

The field parameters that appear in the equilibrium Maxwell relation are the fields T_0,P_0 of the medium, which because of equilibrium also represent the fields of the system. For a system in internal equilibrium, there are analogs of the Maxwell relations for systems in terms of system variables by replacing all the variables in Eq. (5) by corresponding system variables $\partial(T,S) \equiv \partial(P,V)$. In the presence of the internal variable ξ, this Maxwell relation is written as $\partial(T,S,\xi) \equiv \partial(P,V,\xi)$. However, as we establish below, there are six different compact Maxwell relations formed by the conjugate pairs $(T,S),(P,V)$, and (A,ξ). The first three are

$$\begin{aligned}&\partial(T,S,\xi) \equiv \partial(P,V,\xi), \quad \partial(T,S,V) \equiv \partial(A,\xi,V),\\ &\partial(P,V,S) \equiv -\partial(A,\xi,S);\end{aligned} \tag{10}$$

the variable common on both sides is held fixed. The remaining three relations are obtained by replacing the constant extensive variable by its conjugate system field or affinity:

$$\begin{aligned}&\partial(T,S,A) \equiv \partial(P,V,A), \quad \partial(T,S,P) \equiv \partial(A,\xi,P),\\ &\partial(P,V,T) \equiv -\partial(A,\xi,T).\end{aligned} \tag{11}$$

We can obtain all possible Maxwell relations similar to those in Eq. (7) but involving system variables by dividing each one in Eq. (10) by appropriate denominators such as $\partial(S,V,\xi)$, $\partial(T,V,\xi),\partial(S,P,\xi)$, and $\partial(T,P,\xi)$. This will become clear below. As the fields in the last three denominators correspond to the system, the resulting Maxwell relations are not very useful or interesting as the fields under our control in an experiment are those of the medium. We will show below that Maxwell relations are also found when we use fields of the medium in the denominators. Indeed, the denominators can be formed by picking any two of the *nonconjugate* variables in the set

$$\mathbf{D}: S,V,\xi,T,P,A,T_0,P_0;$$

the third variable is the one kept fixed in Eqs. (10) and (11). Note the absence of A_0.

It follows immediately from Eq. (1) and $(\partial^2E/\partial S\partial V)_\xi = (\partial^2E/\partial V\partial S)_\xi$ that

$$\partial(T,S,\xi)/\partial(S,V,\xi) = \partial(P,V,\xi)/\partial(S,V,\xi).$$

The corresponding compact Maxwell relation is $\partial(T,S,\xi) = \partial(P,V,\xi)$. The variables S,V,ξ in the denominator belong to $\mathbf{D}$ and are also the independent variables of E. It follows from the property of Jacobians that one can now divide each side by the same denominator formed from $\mathbf{D}$. One can divide by $\partial(T,V,\xi),\partial(S,P,\xi)$, and $\partial(T,P,\xi)T$, which use the natural variables of $\widehat{F},\widehat{H}$, and $\widehat{G}$ to obtain the four Maxwell relations at fixed ξ. We can also divide by $\partial(T_0,V,\xi),\partial(S,P_0,\xi)$, and $\partial(T_0,P_0,\xi)$ using the independent variables of the thermodynamic potentials F,H, and G. We will demonstrate the validity of only one of these by considering the differential dG in Eq. (6) and evaluating the cross derivative $(\partial^2G/\partial P_0\partial T_0)_\xi \equiv (\partial^2G/\partial T_0\partial P_0)_\xi$ to find $\partial(T,S,\xi)/\partial(T_0,P_0,\xi) = \partial(P,V,\xi)/\partial(T_0,P_0,\xi)$. We similarly find $\partial(T,S,\xi)/\partial(P_0,S,\xi) = \partial(P,V,\xi)/\partial(P_0,S,\xi)$ and $\partial(T,S,\xi)/\partial(T_0,V,\xi) = \partial(P,V,\xi)/\partial(T_0,V,\xi)$ using H and F, respectively. The identity

$$\partial(P,V,\xi)/\partial(T,S,\xi) = 1$$

can be converted to

$$(\partial V/\partial P)_{S,\xi} = (\partial V/\partial P)_{T,\xi} + T(\partial V/\partial T)^2_{P,\xi}\big/\overline{C}_{P,\xi},$$

where $\overline{C}_{P,\xi}$ is defined in Sec. V. It is a relation between isothermal and adiabatic compressibilities and is not treated as a standard Maxwell relation; the latter is a relation between two partial derivatives. However, we will treat the above relation as a Maxwell relation.

By evaluating the cross derivatives $(\partial^2E/\partial S\partial\xi)_V$ and $(\partial^2E/\partial V\partial\xi)_S$, we obtain

$$\frac{\partial(T,S,V)}{\partial(\xi,S,V)} = \frac{\partial(A,\xi,V)}{\partial(\xi,S,V)}, \quad \frac{\partial(P,V,S)}{\partial(\xi,V,S)} = -\frac{\partial(A,\xi,S)}{\partial(\xi,V,S)},$$

from which we are able to establish the existence of the Maxwell relations $\partial(T,S,V) = \partial(A,\xi,V)$ and $\partial(P,V,S) = -\partial(A,\xi,S)$. By evaluating $(\partial^2\widehat{E}^{\mathrm{A}}/\partial V\partial S)_A$, we find the identity $\partial(T,S,A)/\partial(S,V,A) = \partial(P,V,A)/\partial(S,V,A)$ with V,S belonging to $\mathbf{D}$ and V,S,A the natural variables of $\widehat{E}^{\mathrm{A}}$. This establishes the Maxwell relation $\partial(T,S,A) \equiv \partial(P,V,A)$ listed in Eq. (11). Other Maxwell relations can be similarly established.

In the compact Maxwell relations above, the fields are the instantaneous fields of the system. Using instead the fields of the medium does not give a Maxwell relation. We demonstrate this explicitly by evaluating $(\partial^2F/\partial\xi\partial V)_{T_0}$ and $(\partial^2G/\partial\xi\partial T_0)_{P_0}$. A simple calculation yields in terms of the Jacobians

$$\begin{aligned}\partial(A,\xi,T_0) &= -\partial(P,V,T_0) + \partial(T,S,T_0),\\ \partial(A,\xi,P_0) &= -\partial(P,V,P_0) + \partial(T,S,P_0).\end{aligned}$$

These relations are not of the Maxwell relation type in Eq. (11).

In conclusion, *the compact Maxwell relations contain only the conjugate pairs of the system from*T,P,S,V,A,*or*ξ; the third system variable is kept *fixed*.

IV. CLAUSIUS-CLAPEYRON RELATION

It is possible for the system to exist in two distinct phases that have the same Gibbs free energy at some instant. Such a nonequilibrium phase transition will arise, for example, when an isotropic supercooled liquid can turn into a liquid crystal phase. This is not a novel idea as there are several attempts in the literature [15–18], and references therein] where such nonequilibrium phase transitions have been investigated. We now consider the possibility of the system being in two different phases at some time. As experiments are carried out by varying the fields of the medium, it is important to consider thermodynamic quantities as a function of E, Vor T_0,P_0 only.

In particular, the Clausius-Clapeyron relation is obtained in the T_0-P_0 plane, a subspace.

We denote the two phases involved in the transition by 1 and 2, and use subscripts 1 and 2 to refer to the quantities in the two phases. The instantaneous entropy S is a function of instantaneous averages E, V,ξ along with the fixed number of particles N. It is important to include N in our consideration as the two phases will contain number of particles N_1 and N_2 that are not constant. Obviously, $E = E_1 + E_2$, $V = V_1 + V_2$, $\xi = \xi_1 + \xi_2$, $N = N_1 + N_2$. The entropy of the system is a sum over the two phases:

$$S(E,V,\xi,N) = S_1(E_1,V_1,\xi_1,N_1) + S_2(E_2,V_2,\xi_2,N_2),$$

which takes its maximum possible value in internal equilibrium. This can only happen if

$$T_1 = T_2 = T, \quad P_1 = P_2 = P, \quad \mu_1 = \mu_2 = \mu,$$
$$A_1 = A_2 = A$$

at that instant in the two phases. We will only consider the two pure phases below, and not a mixture of the two. The Gibbs free energies of the two pure phases ($N_1 = N$ and $N_2 = N$) must be equal at the coexistence. As the numbers of particles in the two pure phases are constant, we will no longer consider them in the discussion. Since the Gibbs free energy is continuous along the transition line in the T_0-P_0 plane, its difference

$$\Delta G(T_0,P_0(T_0)) = 0$$

along the coexistence; here $P_0(T_0)$ is the pressure along the transition line. It follows that

$$dT_0/dP_0|_{\text{coex}}\Delta(\partial G/\partial T_0)_{P_0} + \Delta(\partial G/\partial P_0)_{T_0} = 0 \tag{12}$$

along the coexistence. Using dG from Eq. (6) to evaluate $\Delta(\partial G/\partial T_0)_{P_0}$ and $\Delta(\partial G/\partial P_0)_{T_0}$ finally gives us the following Clausius-Clapeyron equation along the coexistence

$$\left.\frac{dT_0}{dP_0}\right|_{\text{coex}} = \frac{\Delta V + (T - T_0)\Delta(\partial S/\partial P_0)_{T_0} - (P - P_0)\Delta(\partial V/\partial P_0)_{T_0} - A\Delta(\partial \xi/\partial P_0)_{T_0}}{\Delta S - (T - T_0)\Delta(\partial S/\partial T_0)_{P_0} + (P - P_0)\Delta(\partial V/\partial T_0)_{P_0} + A\Delta(\partial \xi/\partial T_0)_{P_0}}; \tag{13}$$

compare with Ref. [10]. We express $(\partial S/\partial P_0)_{T_0}$ in terms of $(\partial V/\partial T_0)_{P_0}$ by using the Maxwell relation $\partial(P,V) = \partial(T,S)$ and Eq. (C1) ($F \to S$, $K \to V$, $x \to P_0$, and $y \to T_0$) as follows:

$$\left(\frac{\partial S}{\partial P_0}\right)_{T_0} = -\frac{(\partial P/\partial P_0)_V}{(\partial T/\partial T_0)_S}\left(\frac{\partial V}{\partial T_0}\right)_{P_0}, \tag{14}$$

which can be used in the Clausius-Clapeyron equation. In equilibrium, $T = T_0$, $P = P_0$, and $A = 0$, so that the above equation reduces to the well-known version

$$dT_0/dP_0|^{\text{eq}}_{\text{coex}} = \Delta V/\Delta S. \tag{15}$$

V. RESPONSE FUNCTIONS IN INTERNAL EQUILIBRIUM

We consider some quantity Q as a function of T,V, and ξ or of T_0,P_0, and ξ so that

$$dQ = \frac{\partial Q}{\partial T}dT + \frac{\partial Q}{\partial V}dV + \frac{\partial Q}{\partial \xi}d\xi, \tag{16}$$

$$dQ = \frac{\partial Q}{\partial T_0}dT_0 + \frac{\partial Q}{\partial P_0}dP_0 + \frac{\partial Q}{\partial \xi}d\xi. \tag{17}$$

A. $\bar{C}_P$ and $\bar{C}_V$

The heat capacities with respect to the system temperature at fixed P or V are

$$\bar{C}_{P,\xi} = T(\partial S/\partial T)_{P,\xi}, \quad \bar{C}_{V,\xi} = T(\partial S/\partial T)_{V,\xi},$$
$$\bar{C}_P = T(\partial S/\partial T)_P, \quad \bar{C}_V = T(\partial S/\partial T)_V.$$

Using Eq. (16) to evaluate the derivative $(\partial S/\partial T)_{P,\xi}$ we obtain

$$\overline{C}_{P,\xi} = \overline{C}_{V,\xi} + T(\partial S/\partial V)_{T,\xi}(\partial V/\partial T)_{P,\xi}. \tag{18}$$

The identity is not useful from a practical point of view. We need to transform various derivatives to the derivatives with respect to T_0 at fixed P_0 or V. However, the identities still contain $\bar{C}_{P,\xi}$ and $\bar{C}_{V,\xi}$, which are defined with respect to T, and not with respect to T_0.

B. C_P and C_V

We now introduce the heat capacities

$$C_P \equiv T(\partial S/\partial T_0)_{P_0}, \quad C_V \equiv T(\partial S/\partial T_0)_V, \tag{19}$$

$$C_{P,\xi} \equiv T(\partial S/\partial T_0)_{P_0,\,\xi}, \quad C_{V,\xi} \equiv T(\partial S/\partial T_0)_{V,\xi}, \tag{20}$$

and the expansion coefficient

$$\alpha_P \equiv (\partial V/\partial T_0)_{P_0}/V, \quad \alpha_{P,\xi} \equiv (\partial V/\partial T_0)_{P_0,\xi}/V \tag{21}$$

obtained as a derivative with respect to T_0. We easily find that

$$C_P/\alpha_P = TV(\partial S/\partial V)_{P_0}, \quad C_{P,\xi}/\alpha_{P,\xi} = TV(\partial S/\partial V)_{P_0,\xi}.$$

Let us now consider the relation between $C_{P,\xi}$ and $C_{V,\xi}$ and between C_P and C_V. It follows from Eq. (16)

$$(\partial S/\partial T_0)_{P_0,\xi} = (\partial S/\partial T)_{V,\xi}(\partial T/\partial T_0)_{P_0,\xi}$$
$$+ (\partial S/\partial V)_{T,\xi}(\partial V/\partial T_0)_{P_0,\xi},$$

which gives the desired relation between $C_{P,\xi}$ and $C_{V,\xi}$

$$C_{P,\xi}(\partial T/\partial T_0)_{V,\xi} = C_{V,\xi}(\partial T/\partial T_0)_{P_0,\xi}$$
$$+ T(\partial P/\partial T_0)_{V,\xi}(\partial V/\partial T_0)_{P_0,\xi}. \tag{22}$$

This relation generalizes the following standard equilibrium relation:

$$C_P^{\text{eq}} = C_V^{\text{eq}} + T_0(\partial P_0/\partial T_0)_V(\partial V/\partial T_0)_{P_0}.$$

A standard form of Eq. (22) is given by

$$C_{P,\xi} = C_{V,\xi} + T(\partial S/\partial V)_{T_0,\xi}(\partial V/\partial T_0)_{P_0,\xi}, \tag{23}$$

which is an extension of Eq. (18). Although tedious, it is straightforward to show that the two relations are identical. One needs to use the permutation property given in Eq. (B1). In a similar fashion, we find that

$$C_P = C_V + T(\partial S/\partial V)_{T_0}(\partial V/\partial T_0)_{P_0}. \tag{24}$$

We now relate C_P with $C_{P,\xi}$ and C_V with $C_{V,\xi}$. For this, it is convenient to consider the differential dS using Eq. (17). We finally find that

$$\begin{aligned} C_P &= C_{P,\xi} + T(\partial S/\partial \xi)_{T_0,P_0}(\partial \xi/\partial T_0)_{P_0},\\ C_V &= C_{V,\xi} + T(\partial S/\partial \xi)_{P_0,V}(\partial \xi/\partial T_0)_{V}. \end{aligned} \tag{25}$$

C. K_T and K_S

The isothermal and adiabatic compressibilities are given by

$$\begin{aligned} K_T &\equiv -(\partial V/\partial P_0)_{T_0}/V, \quad K_{T,\xi} \equiv -(\partial V/\partial P_0)_{T_0,\xi}/V,\\ K_S &\equiv -(\partial V/\partial P_0)_{S}/V, \quad K_{S,\xi} \equiv -(\partial V/\partial P_0)_{S,\xi}/V. \end{aligned}$$

The isothermal compressibility and the expansion coefficient are related by $K_T/\alpha_P = (\partial T_0/\partial P_0)_V, K_{T,\xi}/\alpha_{P,\xi} = (\partial T_0/\partial P_0)_{V,\xi}$.

By treating V as a function of T_0, P_0, and ξ and of S, P_0, and ξ, respectively, we find

$$\begin{aligned} K_T &= K_{T,\xi} - (\partial V/\partial \xi)_{T_0,P_0}(\partial \xi/\partial P_0)_{T_0}/V,\\ K_S &= K_{S,\xi} - (\partial V/\partial \xi)_{S,P_0}(\partial \xi/\partial P_0)_{S}/V. \end{aligned} \tag{26}$$

We similarly find that

$$\alpha_P = \alpha_{P,\xi} - (\partial V/\partial \xi)_{T_0,P_0}(\partial \xi/\partial T_0)_{P_0}/V. \tag{27}$$

Using

$$\begin{aligned} (\partial V/\partial P_0)_{T_0,\xi} &= (\partial V/\partial P_0)_{S,\xi} C_{P,\xi}/C_{V,\xi},\\ (\partial V/\partial P_0)_{T_0} &= (\partial V/\partial P_0)_{S} C_P/C_V, \end{aligned}$$

we find

$$\frac{C_{P,\xi}}{C_{V,\xi}} \equiv \frac{K_{T,\xi}}{K_{S,\xi}}, \quad \frac{C_P}{C_V} \equiv \frac{K_T}{K_S}. \tag{28}$$

The adiabatic and isothermal compressibilities are related by

$$\begin{aligned} K_{T,\xi} &\equiv K_{S,\xi} - (\partial S/\partial P_0)_{T_0,\xi}(\partial V/\partial S)_{P_0,\xi}/V,\\ K_T &= K_S - (\partial V/\partial P_0)_{T_0}(\partial V/\partial S)_{P_0}/V. \end{aligned} \tag{29}$$

VI. CONVENTIONAL AND APPARENT GLASS TRANSITIONS

A. Vitrification and continuity of states

We will apply the above nonequilibrium results to an isobaric glass [8–10,19–24] at the cooling rate r; see Figs. 2 and 3. The supercooled liquid L shown by ABF is a time-independent metastable state [21], which we treat as an equilibrium state (by not allowing the crystalline state into consideration); at $T_{0\mathrm{g}}(P_0)$, it turns into a *time-dependent* metastable liquid gL along BD, the *transition region*. At $T_{0\mathrm{G}}(P_0)$, BD turns into a glass GL shown by DE [9,20]. The L-gL transition at B is a *precursory* glass transition. The *actual* glass transition or simply the glass transition at D is not a L→GL transition as envisioned normally [20,22–24], but a gL→GL transition. The state changes *continuously* at B and D, which is highly *reproducible* for a given r or the observation time τ_{obs}. Both B and D can be taken as well-defined and unique nonequilibrium glass transitions at temperatures $T_{0\mathrm{g}}(P_0)$ and $T_{0\mathrm{G}}(P_0)$, respectively, for a given history. Here, not only the Gibbs free energy, see Fig. 3, but also its derivatives are *continuous*. We will collectively call them *conventional transitions* but caution the reader that neither represents the glass transition L→GL [20,22–24]. The dynamical aspect of the glass transition is more complex than the above discussion [19]. Here, we will be content with the above simple picture for our application.

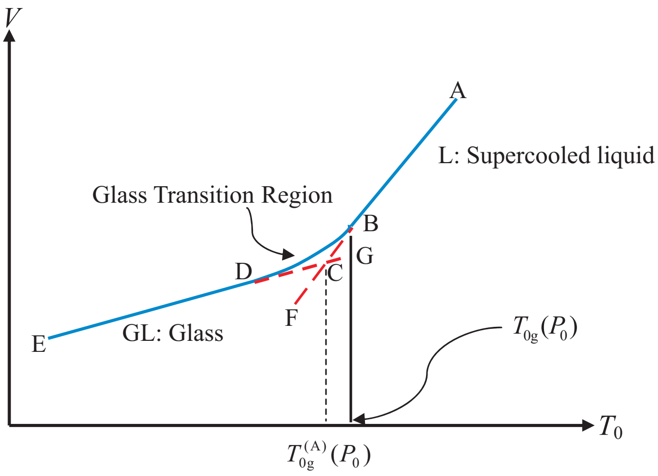

FIG. 2. (Color online) Schematic form of isobaric (constant P_0) volume $V(T_0)$ for a given cooling rate r.

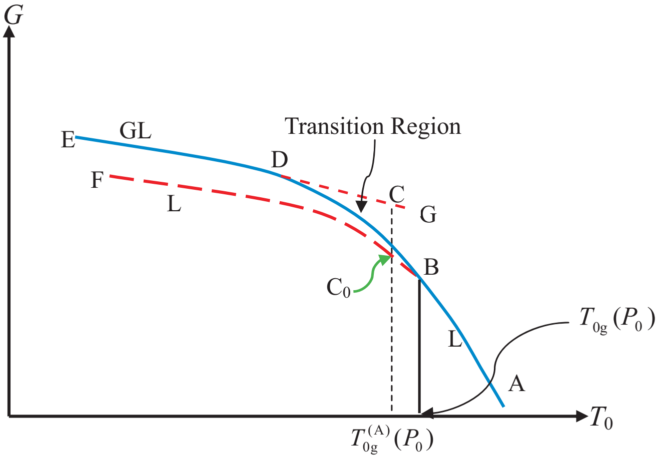

FIG. 3. (Color online) Schematic form of the isobaric Gibbs free energy $G(T_0)$.

B. Traditional glass transitions and thermodynamic discontinuities

It is common to assume that over the glassy region DE, ξ is frozen at its value ξ_G at D, even though it continues to change over BD. Over AB, ξ is not an independent variable. A common practice in the field is to take a point somewhere between BD as a transition point obtained by electing some well-defined rules for some chosen thermodynamic quantity such as the volume of the system, see for example [20], and introduce an *apparent* glass transition temperature $T_{0g}^{(A)}(P_0)$ by the crossing C in Fig. 2 of the *equilibrium continuation* BCF of AB and the *extrapolation* (based on the *specific rules*) DCG of DE; see for example [24] for a good discussion of various ways of identifying the glass transition temperature. The state of the glass following Tool and Narayanaswamy [25,26] is then traditionally identified with C. However, there is no theoretical justification for C to represent any real glass [27]. In particular, ξ will have a discontinuity at C, contrary to the normal expectation. Moreover, the extrapolation does not even have to satisfy nonequilibrium thermodynamics; the latter is valid only along the physical path DB. The "glass" at $T_{0g}^{(A)}(P_0)$ must be described by the point on DB at $T_{0g}^{(A)}(P_0)$, if we insist on employing nonequilibrium thermodynamics. But this state is most certainly not a glass as it is not frozen. To be sure, one can find a slower enough cooling rate than the one used to obtain gL at B so that the point B actually coincides with the point C on ABF. However, the gL that will emerge at C for the slower cooling rate has nothing to do with the extrapolated state C on DCG. Because of the continuity of the state, the gL at the slower rate at C will have its $A = 0$ and $\xi = \xi_{eq}$ and will have its Gibbs free energy continuous. Moreover, the new gL will follow a curve that will be strictly below BDE. These aspects make the new gL different from the extrapolated GL at C. Taking the point C on CD to represent the glass will be an approximation, which we will avoid in this work, as our interest is to apply thermodynamics in the study of glasses. Therefore, we will use the extrapolation to only determine $T_{0g}^{(A)}(P_0)$, but the unfrozen "glass" and the liquid are determined by BD and BCF, respectively. The discussion above shows how our glass transition concept differs from the traditional glass transition; see [24] for more details.

The value of $T_{0g}^{(A)}(P_0)$ depends on the property being extrapolated such as the entropy or the enthalpy. To call one of these temperatures as a transition temperature is a misnomer for another reason. None of the apparent glass transition temperatures represent a "nonequilibrium" thermodynamic transition for the simple reason that the two branches DCG and BC$_0$F do not have a common Gibbs free energy at $T_{0g}^{(A)}(P_0)$ as is clearly seen in Fig. 3. The extrapolation DCG in Fig. 2 corresponds to the extrapolated segment DCG in Fig. 3. The extrapolated Gibbs free energy of the glass is given by the point C, while that of L by the point C$_0$. The same *discontinuity* will also appear in other thermodynamic extensive quantities except the one used to locate C. The discontinuity also occurs between the glass at D and the corresponding L at $T_{0G}(P_0)$. This represents yet another apparent glass transition that has also been traditionally investigated [24]. Due to the discontinuity in G at $T_{0G}(P_0)$ and $T_{0g}^{(A)}(P_0)$, the apparent glass transitions represent a *zeroth-order* transition.

TABLE I. Various states.

	Apparent T_{0G}	Apparent $T_{0g}^{(A)}$	Conventional T_{0g}	Conventional T_{0G}
I	GL	gL	gL	GL
II	L	L	L	gL

VII. PRIGOGINE-DEFAY RATIO IN INTERNAL EQUILIBRIUM

A. Prigogine-Defay ratio and rapid quench

The magnitude of the Prigogine-Defay ratio [10,22,28–34] is considered a reflection of nonequilibrium effects. Therefore, we can apply our nonequilibrium results to determine its values at various glass transitions shown in Figs. 2 and 3; see Table I. In this ratio, two states are compared at the same T_0, P_0. The original ratio was first introduced for glasses [22] using Simon's model [23,24]. In the classic approach adopted by Simon, the range $(T_{0gG}(P_0), T_{0g}(P_0))$ is shrunk to a point, either by considering the apparent glass transition at $T_{0g}^{(A)}(P_0)$ or by comparing the GL at D with L at B. The latter amounts to neglecting the segment BD altogether from consideration. This is easily done in the laboratory by a rapid quench from B to D so that the segment BD disappears from consideration. It is this rapid quench that is discussed by Prigogine and Defay in their celebrated book [22] connecting $A_0 = 0$ L with frozen $\xi = \xi_{eq}$ GL; here ξ_{eq} denotes the equilibrium value in L that has been quenched in GL at time $t = 0$ when the quench occurs. The *equality* of ξ in the two states then allows Prigogine and Defay to identify, for example, the second term in their Eq. (19.24) with the difference in the isothermal compressibility ΔK_T in the two states. They are very careful in their discussion by pointing out just below this equation that "... the pressure must be applied so rapidly that the composition of the system does not have time to change...." Thus, their identification works only at the instant $t = 0$ of a rapid quench. With time, there would be structural relaxation so that ξ will no longer equal ξ_{eq} at later times. Then the second term above will no longer represent the difference ΔK_T in the two states at time t unless relaxation is completely neglected. Unfortunately, this point seems to have been overlooked by several workers in the field.

We will not consider the rapid quench studied by Prigogine and Defay in this work since GL at D and L at B have different T_0's. This will lead to an ambiguity in the definition of the Prigogine-Defay ratio in Eq. (31). The only possible scenario where Simon's approach is meaningful is that of the *ideal glass transition* [21], and references therein], in the limit the cooling rate $r \to 0$. In this limiting case, the crossover region BD disappears and the ideal glass IGL emerges directly out of the L at the ideal glass transition temperature T_{0IG}. This is a conventional continuous transition between the two stationary states IGL and L, both of which remain in equilibrium with the medium at T_0, P_0. There is no need to invoke any internal variable ξ to describe the ideal glass.

From the discussion in Sec. VI, we know that the Gibbs free energies, volumes, and entropies exhibit discontinuities at the apparent transitions, but not at the conventional transitions.

Let us introduce the difference

$$\Delta Q \equiv Q_{\mathrm{I}} - Q_{\mathrm{II}} \tag{30}$$

for any quantity Q at a given T_0,P_0 in the two possible states I and II. These states are summarized in Table I.

In terms of the discontinuities $\Delta C_P,\Delta K_T$, and $\Delta\alpha_P$, the Prigogine-Defay ratio [22] is traditionally defined as [9,10,22, 27–32,34]

$$\Pi^{\mathrm{trad}} \equiv \Delta C_P \Delta K_T / V T_0 (\Delta\alpha_P)^2,$$

where it is assumed that the volume is the same in both states at T_0,P_0. Since the volume may not be continuous at apparent glass transitions, used in most experimental and theoretical analyses of the glass transition, we need to allow for this possibility. We will consider the following equivalent definition of the Prigogine-Defay ratio in this work:

$$\Pi \equiv \Delta C_P \Delta K_T / T_0 (\Delta V \alpha_P)(\Delta\alpha_P), \tag{31}$$

where we have absorbed V in one of the $\Delta\alpha_P$ factors. It is clear that Π is not different from Π^{trad} when the volume is the same as happens for conventional transitions.

We will evaluate Π in the T_0-P_0 plane. We will consider a single internal variable; however, the general case of several internal variables $\xi_k, k=1,2,\ldots,n$, causes no complications. All we need to do is to make the change $A d\xi \to \mathbf{A}\cdot d\boldsymbol{\xi}$.

B. Conventional transitions at $T_{0\mathrm{g}}$ and $T_{0\mathrm{G}}$

Let us first consider the transition at B, where gL and L are in equilibrium with the medium ($T=T_0, P=P_0$, and $\mathbf{A}=\mathbf{A}_0=0$ for both states). There is no need to consider $\boldsymbol{\xi}$. As $V=(\partial G/\partial P_0)_{T_0}$ and $S=-(\partial G/\partial T_0)_{P_0}$, G and its derivatives are continuous at B but the second derivatives need not be. The glass transition occurs along a curve $T_{0\mathrm{g}}(P_0)$ in the T_0-P_0 plane.

For the transition at D, GL and gL are out of equilibrium but have the same temperature T and pressure P, different from T_0,P_0, respectively, at the transition. Similarly, $\mathbf{A}\neq 0$ is the same in both states. We now follow the consequences of the continuity of states.

1. Continuity of volume

From the continuity of the volume, we have

$$\begin{aligned} d\Delta_{\mathrm{g}} \ln V = {} & \Delta_{\mathrm{g}}(\partial \ln V/\partial T_0)_{P_0} dT_0 \\ & + \Delta_{\mathrm{g}}(\partial \ln V/\partial P_0)_{T_0} dP_0 = 0 \end{aligned} \tag{32}$$

at the transition points $T_{0\mathrm{g}}$ or $T_{0\mathrm{G}}$, where the derivatives are evaluated. At the transition

$$dT_0/dP_0|_{\mathrm{tr}} = \Delta_{\mathrm{g}} K_T / \Delta_{\mathrm{g}}\alpha_P, \tag{33}$$

K_T and α_P are given in Eqs. (19) and (21), respectively, and can be expressed in terms of the derivatives of the internal variable $\boldsymbol{\xi}$, such as given in Eqs. (26) and (27) by replacing ξ by $\boldsymbol{\xi}$.

2. Continuity of entropy

From the continuity of the entropy at $T_{0\mathrm{g}}$, we similarly have

$$d\Delta_{\mathrm{g}} S = \Delta_{\mathrm{g}}(\partial S/\partial T_0)_{P_0} dT_0 + \Delta_{\mathrm{g}}(\partial S/\partial P_0)_{T_{0\mathrm{g}}} dP_0 = 0, \tag{34}$$

from which we obtain at the precursory glass transition at B

$$dT_{0\mathrm{g}}/dP_0|_{\mathrm{tr}} = V_{\mathrm{g}} T_0 \Delta_{\mathrm{g}}\alpha_P / \Delta_{\mathrm{g}} C_P, \tag{35}$$

where we have used the equilibrium Maxwell relation $(\partial S/\partial P_0)_{T_0} = -(\partial V/\partial T_0)_{P_0} = V\alpha_P$; see Eq. (5) or (14) applied to this case. Here V_{g} is the common volume of gL and L at B and has been taken out of $\Delta_{\mathrm{g}}(V\alpha_P)$. Accordingly, $\Pi_{\mathrm{g}} \equiv \Delta_{\mathrm{g}} C_P \Delta_{\mathrm{g}} K_T / V_{\mathrm{g}} T_0 (\Delta_{\mathrm{g}}\alpha_P)^2 = 1$, as expected for equilibrium states. It is a consequence of the glass transition being a continuous transition between equilibrium states at B. As we will see below, it is not merely a consequence of the continuity of volume and entropy simultaneously.

Let us now consider the glass transition at $T_{0\mathrm{G}}$. It follows from Eq. (19) that $\Delta_{\mathrm{g}}(\partial S/\partial T_0)_{P_0} = \Delta_{\mathrm{g}} C_P/T$. In conjunction with Eq. (14), we find that

$$dT_{0\mathrm{G}}/dP_0|_{\mathrm{tr}} = (V_{\mathrm{G}} T \Delta_{\mathrm{g}}\alpha_P/\Delta_{\mathrm{g}} C_P)(\partial P/\partial P_0)_V/(\partial T/\partial T_0)_S,$$

where V_{G} is the common volume of gL and GL at D. We finally obtain

$$\Pi_{\mathrm{G}} = T(\partial P/\partial P_0)_V / T_0 (\partial T/\partial T_0)_S \neq 1 \tag{36}$$

for the conventional glass transition at D. The deviation of Π_{G} from unity is independent of the number of internal variables. It will be different from unity even if we have no internal variables, a conclusion also found in Ref. [1].

C. Apparent glass transitions at $T_{0\mathrm{g}}^{(\mathrm{A})}$ and $T_{0\mathrm{G}}$

Unfortunately, it is not a common practice to determine the Prigogine-Defay ratio at the conventional transitions. In experiments, one determines the ratio at apparent glass transitions at C and D. As the extrapolated GL at C cannot be described by nonequilibrium thermodynamics, we only consider the apparent transition at $T_{0\mathrm{g}}^{(\mathrm{A})}(P_0)$ and at $T_{0\mathrm{G}}$. It is known that the volume and entropy in gL and GL are higher than their respective values in L and relax toward the latter.

The discontinuity of volume $\Delta_{\mathrm{g}}^{(\mathrm{A})} V$ ($\neq 0$) causes a modification of Eq. (32) at $T_{0\mathrm{g}}^{(\mathrm{A})}$ or $T_{0\mathrm{G}}$:

$$\begin{aligned} dT_0/dP_0|_{\mathrm{tr}} &= \left(\delta \ln V_P^{(\mathrm{A})} + \Delta_{\mathrm{g}}^{(\mathrm{A})} K_T\right)/\Delta_{\mathrm{g}}^{(\mathrm{A})}\alpha_P \\ &= \Delta_{\mathrm{g}}^{(\mathrm{A})} K_T\left(1+\delta_{\mathrm{g}}^{(\mathrm{A})} V_P\right)/\Delta_{\mathrm{g}}^{(\mathrm{A})}\alpha_P, \end{aligned} \tag{37}$$

where $\delta \ln V_P^{(\mathrm{A})} \equiv d\Delta_{\mathrm{g}}^{(\mathrm{A})} \ln V/dP_0|_{\mathrm{tr}}$ is the variation of $\Delta_{\mathrm{g}}^{(\mathrm{A})} \ln V = \ln V_{\mathrm{I}}(T_0,P_0) - \ln V_{\mathrm{II}}(T_0,P_0)$ with P_0 along the transition curve $T_{0\mathrm{g}}^{(\mathrm{A})}(P_0)$ or $T_{0\mathrm{G}}(P_0)$, and can be found experimentally by recognizing that

$$\delta \ln V_P^{(\mathrm{A})} = (1/V_{\mathrm{I}}) dV_{\mathrm{I}}(P_0)/dP_0|_{\mathrm{tr}} - (1/V_{\mathrm{II}}) dV_{\mathrm{II}}(P_0)/dP_0|_{\mathrm{tr}}. \tag{38}$$

The three $\Delta_{\mathrm{g}}^{(\mathrm{A})}$'s represent the difference Δ in Eq. (30) evaluated at $T_{0\mathrm{g}}^{(\mathrm{A})}$ or $T_{0\mathrm{G}}$, and the new quantity $\delta_{\mathrm{g}}^{(\mathrm{A})} V_P$ has an obvious definition $\delta_{\mathrm{g}}^{(\mathrm{A})} V_P = \delta \ln V_P^{(\mathrm{A})}/\Delta_{\mathrm{g}}^{(\mathrm{A})} K_T$ at the appropriate temperature. This contribution vanishes under the approximation $\Delta_{\mathrm{g}}^{(\mathrm{A})} \ln V \simeq 0$, or $\delta \ln V_P^{(\mathrm{A})} \simeq 0$. We can use Eqs. (26) and (27) to express the slope in terms of $\Delta_{\mathrm{g}} K_{T,\xi}$ and

$\Delta_{\rm g}\alpha_{P,\xi}$:

$$dT_0/dP_0|_{\rm tr} = \big(\delta\ln V_P^{\rm (A)} + \Delta_{\rm g}^{\rm (A)}K_{T,\xi} - V_{\xi,{\rm I}}\partial\xi/\partial P_0|_{\rm tr}/V_{\rm I}\big) \big/\big(\Delta_{\rm g}^{\rm (A)}\alpha_{P,\xi} - V_{\xi,{\rm I}}\partial\xi/\partial T_0|_{\rm tr}/V_{\rm I}\big), \tag{39}$$

where $V_{\xi,{\rm G}}$ represents the derivative $(\partial V_{\rm I}/\partial\xi)_{T_0,P_0}$, and $V_{\rm I}$ is the GL volume at $T_{0{\rm G}}$ or the gL volume at $T_{0{\rm g}}^{\rm (A)}$. The ξ contribution from the L state is absent due to the vanishing of the affinity A_0 in the L.

A similar calculation for the entropy difference yields

$$dT_0/dP_0|_{\rm tr} = \big[\delta S_P^{\rm (A)} - \Delta_{\rm g}^{\rm (A)}(\partial S/\partial P_0)_{T_0}\big]\big/\Delta_{\rm g}^{\rm (A)}(\partial S/\partial T_0)_{P_0}, \tag{40}$$

with $\delta S_P^{\rm (A)} \equiv d\Delta_{\rm g}^{\rm (A)}S/dP_0|_{\rm tr} = dS_{\rm I}(P_0)/dP_0|_{\rm tr} - dS_{\rm II}(P_0)/dP_0|_{\rm tr}$ representing the rate of variation of the entropy discontinuity $\Delta_{\rm g}^{\rm (A)}S = S_{\rm I}(T_0,P_0) - S_{\rm II}(T_0,P_0)$ along apparent glass transition curves. The derivative $(\partial S_{\rm I}/\partial P_0)_{T_0}$ in Eq. (40) can be manipulated as in Eq. (14) to give

$$\begin{aligned}(\partial S_{\rm I}/\partial P_0)_{T_0} &= -(\partial V_{\rm I}/\partial T_0)_{P_0}\big(1+\delta S_{VS}^{\rm I}\big)\\ &= -V_{\rm I}\big(1+\delta S_{VS}^{\rm I}\big)\alpha_P^{\rm I}.\end{aligned}$$

For the supercooled liquid, we evidently have ($S_{\rm II}\equiv S_{\rm L}$)

$$(\partial S_{\rm L}/\partial P_0)_{T_0} = -(\partial V_{\rm L}/\partial T_0)_{P_0} = -V_{\rm L}\alpha_P^{\rm L},$$

so that

$$\Delta_{\rm g}^{\rm (A)}(\partial S/\partial P_0)_{T_0} = -\Delta_{\rm g}^{\rm (A)}(V\alpha_P) - V_{\rm I}\alpha_P^{\rm I}\delta S_{VS}^{\rm I}.$$

We now turn to the denominator in Eq. (40). For L, we have $(\partial S_{\rm L}/\partial T_0)_{P_0} = C_P^{\rm L}/T_0$. For the glass at T, we have

$$(\partial S_{\rm I}/\partial T_0)_{P_0} = C_P^{\rm I}/T \equiv (1+\delta T^{\rm I})C_P^{\rm I}/T_0,$$

where we have introduced a correction parameter $\delta T^{\rm I} \equiv T_{0{\rm g,G}}^{\rm (A)}/T - 1$, with $T_{0{\rm g,G}}^{\rm (A)}$ denoting $T_{0{\rm g}}^{\rm (A)}$ or $T_{0{\rm G}}$ as the case may be. Again, this modification term vanishes when $T = T_0$. We thus find that

$$T_0\Delta_{\rm g}^{\rm (A)}(\partial S/\partial T_0)_{P_0} = \Delta_{\rm g}^{\rm (A)}C_P + C_P^{\rm I}\delta T^{\rm I}.$$

Equating the two different versions of the slope in Eqs. (37) and (40), we finally find that the Prigogine-Defay ratio is given by

$$\Pi_{\rm gA} = \frac{1+\big(V_{\rm I}\alpha_P^{\rm I}\delta S_{VS}^{\rm I} + \delta S_P^{\rm (A)}\big)\big/\Delta_{\rm g}^{\rm (A)}(V\alpha_P)}{\big(1+C_P^{\rm I}\delta T^{\rm I}/\Delta_{\rm g}^{\rm (A)}C_P\big)\big(1+\delta_{\rm g}^{\rm (A)}V_P\big)}. \tag{41}$$

It should be obvious that the Prigogine-Defay ratio is itself a function of time as it depends on time-dependent quantities such as $\Delta_{\rm g}^{\rm (A)}S$, $\delta T^{\rm I}$, etc.

1. *Approximation A*

Let us assume that the discontinuities in the volume and entropy are negligible or that the contributions $\delta\ln V_P^{\rm (A)}$ and $\delta S_P^{\rm (A)}$ are negligible. In that case, the Prigogine-Defay ratio reduces to

$$\Pi_{\rm gA} \simeq \frac{1+V_{\rm I}\alpha_P^{\rm I}\delta S_{VS}^{\rm I}\big/\Delta_{\rm g}^{\rm (A)}(V\alpha_P)}{1+C_P^{\rm I}\delta T^{\rm I}\big/\Delta_{\rm g}^{\rm (A)}C_P},$$

and will have a value different than 1. Thus, the continuity of volume and entropy alone is not sufficient to yield $\Pi_{\rm gA} = 1$, as noted above. If we further approximate $T \simeq T_0$ and $P \simeq P_0$, then $\delta S_{VS}^{\rm I} \simeq 0$ and $\delta T^{\rm I} \simeq 0$, and we obtain $\Pi_{\rm gA} \simeq 1$. This is expected as the approximations change the apparent glass transition into a continuous transition. If, however, we only assume $P \simeq P_0$, but allow T to be different from T_0, then

$$\delta S_{VS}^{\rm I} \simeq \frac{1}{(\partial T/\partial T_0)_{S_{\rm I}}} - 1,$$

and we still have $\Pi_{\rm gA} \neq 1$.

2. *Approximation B*

We make no assumption about $\delta\ln V_P^{\rm (A)}$ and $\delta S_P^{\rm (A)}$, but approximate $T \simeq T_0$ and $P \simeq P_0$. In this case, $\delta S_{VS}^{\rm I} \simeq 0$ and $\delta T^{\rm I} \simeq 0$, and we obtain

$$\Pi_{\rm gA} \simeq \frac{1+\delta S_P^{\rm (A)}\big/\Delta_{\rm g}^{\rm (A)}(V\alpha_P)}{1+\delta_{\rm g}^{\rm (A)}V_P}.$$

If, however, the approximation $T \simeq T_0$ is not valid, we have

$$\Pi_{\rm gA} \simeq \frac{1+\delta S_P^{\rm (A)}\big/\Delta_{\rm g}^{\rm (A)}(V\alpha_P)}{\big(1+C_P^{\rm I}\delta T^{\rm G}\big/\Delta_{\rm g}^{\rm (A)}C_P\big)\big(1+\delta_{\rm g}^{\rm (A)}V_P\big)}.$$

In both cases, $\Pi_{\rm gA} \neq 1$.

D. Comparison with other attempts for Π

As far as we know, almost all previous attempts [8–10,22,27–32] for the evaluation of Π are based on some sort of approximation. The following three versions of the glass transition have been investigated in which the glass structure is taken to be *frozen* so that $\xi_{\rm GL}$ remains constant:

(1) The glass transition is treated as a *hypothetical* transition from L to the extrapolated GL at C; see Figs. 2 and 3. There will be a discontinuity between the values of the internal variable ξ at C: the equilibrium value $\xi_{\rm C}^{\rm eq}$ in L and a nonequilibrium value $\xi_{\rm C}^{\rm extra} \neq \xi_{\rm C}^{\rm eq}$ obtained along DC. Similarly, $A_{\rm L} = A_0 = 0$ in L, while $A_{\rm GL}^{\rm extra} = A_{\rm C} \neq 0$ in the extrapolated GL at C. If C is obtained by matching the volumes (entropies, etc.), the volume (entropy, etc.) remains continuous, but there is no reason to believe that the entropy, etc. (volume), or the energy will remain continuous in this transition. The Gibbs free energy obviously remains discontinuous in this transition. This makes this version of the glass transition a zeroth-order glass transition. It is not a continuous transition as is commonly believed to be.

(2) Instead of extrapolating the volume, one can extrapolate GL by keeping the internal variable frozen at $\xi_{\rm GL}$ until the extrapolation meets L. This kind of approach is used in the Simon model [24,32]. The glass transition is similar to the above, except that the volumes, energies, etc., do not have to be the same in the two states. This creates the problem of which volume is going to be used in $\Pi^{\rm trad}$.

(3) The glass transition is treated as a transition between L and GL at D. Again, there is a discontinuity in the state similar to the one discussed above and the transition is a zeroth-order glass transition.

Despite the discontinuities between the states, one normally overlooks the discontinuity in ξ so that the evaluation of Π in several calculations is based on identifying the second term in Eq. (19.24) of Prigogine and Defay [22] with the configurational contribution to the isothermal compressibility, and similarly for the expansivity and the heat capacity; see their Eq. (19.27). It is obvious from the above that this is an approximation. In other calculations, one takes the volume and/or the entropy (or energy) to be continuous at the transition. This is also an approximation. All these calculations do not distinguish the instantaneous temperature and pressure of the system from those of the medium. An exception is the work in Ref. [10] where an effective temperature is introduced but not an effective pressure. As discussed earlier by us [1], this effective temperature is very different from our $T(t)$. The work, however, is based on the continuity of volume and energy at the transition.

We have been careful in treating this transition as an apparent transition for the simple reason that there is no guarantee that the branch DC can be described by vitrification thermodynamics at the constant cooling rate r. To treat this transition as a conventional transition requires some approximations, which we have avoided. Indeed, we have not made any approximation in the general part of our work.

VIII. CONCLUSIONS

We have followed the consequences of internal equilibrium and the existence of thermodynamic forces to derive generalizations of equilibrium thermodynamic relations such as the Maxwell relations, Clausius-Clapeyron relation, relations between response functions (heat capacities, compressibilities, etc.) to nonequilibrium systems. Nonequilibrium states are described not only by instantaneous thermodynamic forces due to fields (temperature, pressure, etc.) that are different from those of the medium, but also described by internal variables or corresponding affinities that cannot be controlled by the observer. The generalization of Maxwell relations are no longer relations between two partial derivatives; rather they become relations between two Jacobians; the numerators in these relations give rise to compact Maxwell relations. The compact Maxwell relations (the numerators) only contain the variables of the system and not the fields of the medium; however, when divided, the denominators can contain the fields of the medium. We discuss various response functions and obtain the relationship between them in nonequilibriums states. Surprisingly, many of these relations look similar in form to those found in equilibrium thermodynamics, even when expressed in terms of the fields of the medium. As the observer can only control the observables, we have discussed the nonequilibrium thermodynamics in the subspace of the observables or their associated fields only.

As glasses are a prime example of nonequilibrium states, we have applied these relations to glasses. We find that there is no one unique nonequilibrium transition. We introduce four of the most conceptually useful transitions. At the two conventional glass transitions, the Gibbs free energies and the states are continuous. Thus, they are the nonequilibrium analogs of the conventional continuous or second-order transition between equilibrium states. At the two apparent glass transitions, not only the states but also the Gibbs free energies are discontinuous. Because of this, these transitions are examples of a zeroth-order transition where the free energy is discontinuous. These transitions merely relate two distinct states at the same $T_0,P_0.$ We evaluate the Prigogine-Defay ratio at the four possible glass transitions. We consider the general case of any number of internal variables including no internal variable. We find that the ratio is normally different than 1, except at the conventional glass transition at the highest temperature, where it is always equal to 1, regardless of the number of internal variables. We also find that the continuity of volume and entropy is not a guarantee for $\Pi = 1$.

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APPENDIX A: PROPERTIES OF JACOBIANS

Jacobians [11] will be found extremely useful in this work just as they are found useful in equilibrium thermodynamics [7]; see also [12–14]. The Jacobian of $u_1,u_2,\cdots u_n$ with respect to $x_1,x_2,\cdots x_n$ is the determinant of the matrix formed by $\partial u_k/\partial x_l$. It is clear from the properties of the determinant that

(1) The Jacobian vanishes if any two u's are identical

$$\frac{\partial(u_1,u_2,\cdots u_i,u_i\cdots u_n)}{\partial(x_1,x_2,\cdots x_i,x_{i+1}\cdots x_n)}=0.$$

(2) If u_i and u_{i+1} interchange their order, the Jacobian changes its sign

$$\frac{\partial(u_1,u_2,\cdots u_{i+1},u_i\cdots u_n)}{\partial(x_1,x_2,\cdots x_i,x_{i+1}\cdots x_n)}=-\frac{\partial(u_1,u_2,\cdots u_i,u_{i+1}\cdots u_n)}{\partial(x_1,x_2,\cdots x_i,x_{i+1}\cdots x_n)}.$$

(3) If any u_i is equal to x_i, the nth-order Jacobian reduces to a $(n-1)$th-order Jacobian formed by derivatives at fixed x_i. For example, for $n=2$, we have

$$\partial(u_1,x_2)/\partial(x_1,x_2)=(\partial u_1/\partial x_1)_{x_2}.$$

(4) When we consider compound transformations $(x_1,x_2,\cdots x_n)\rightarrow(u_1,u_2,\cdots u_n)\rightarrow(v_1,v_2,\cdots v_n)$, the resulting Jacobian is the product of the two Jacobians:

$$\frac{\partial(v_1,v_2,\cdots v_n)}{\partial(u_1,u_2,\cdots u_n)}\frac{\partial(u_1,u_2,\cdots u_n)}{\partial(x_1,x_2,\cdots x_n)}=\frac{\partial(v_1,v_2,\cdots v_n)}{\partial(x_1,x_2,\cdots x_n)}.$$

APPENDIX B: PERMUTATION PROPERTY OF JACOBIANS

We introduce by following examples the permutation propertyof Jacobians that would be extremely useful in the work. Consider a second-order Jacobian $\partial(u_1,u_2)/\partial(x_1,x_2)$, which can be rearranged as

$$\partial(u_1,u_2)\partial(x_1,x_2)+\partial(u_2,x_1)\partial(u_1,x_2)+\partial(x_1,u_1)\partial(u_2,x_2)=0. \tag{B1}$$

The result expresses the cyclic permutation of u_1,u_2,x_1 in the three terms with the remaining variable x_2 in the same place in all terms. As a second example, consider some quantity u as a function of three variables x,y, and z and consider the following relation between the partial derivatives:

$$(\partial u/\partial x)_y = (\partial u/\partial x)_{y,z} + (\partial u/\partial z)_{x,y}(\partial z/\partial x)_y. \tag{B2}$$

In terms of Jacobians, it can be written as

$$\begin{aligned}\partial(x,y,z)\partial(u,y) &= \partial(y,z,u)\partial(x,y) + \partial(z,u,x)\partial(y,y)\\ &\quad + \partial(u,x,y)\partial(z,y),\end{aligned} \tag{B3}$$

where we have added a vanishing second term on the right $[\partial(y,y) = 0]$ for convenience. This relation is easily constructed by considering the cyclic permutation of x,y,z,u by taking three consecutive terms at a time to form the 3-Jacobians, with the remaining variable yielding the 2-Jacobians in which the second entry is the variable y, the variable that is held fixed in all derivatives in Eq. (B2). By writing all the 3-Jacobians in the nonvanishing terms in Eq. (B3) so that y is the second entry, and then suppressing the second entry, we obtain the following relation, which is identical to Eq. (B1):

$$\partial(x,z)\partial(u,y) + \partial(z,u)\partial(x,y) + \partial(u,x)\partial(z,y) = 0.$$

APPENDIX C: RELATION BETWEEN 2- AND 3-JACOBIANS

It is very common to consider a function $F(x,y,z)$ in a subspace consisting of x,y, where x,y,z may stand for T_0,P_0,ξ, respectively. This requires manipulating a 3-Jacobians to construct a 2-Jacobians of its argument. Thus, we may consider the 2-Jacobian

$$\partial(F,y)/\partial(x,y),$$

even though F also depends on z. We can manipulate such Jacobians in the normal way. For example, we can express it as

$$\begin{aligned}\left(\frac{\partial F}{\partial x}\right)_y &= \frac{\partial(F,y)}{\partial(x,y)} = -\frac{\partial(F,y)}{\partial(K,x)}\frac{\partial(x,K)}{\partial(x,y)}\\ &= -\left(\frac{\partial K}{\partial y}\right)_x \frac{\partial(F,y)}{\partial(K,x)},\end{aligned} \tag{C1}$$

where $K(x,y,z)$ is another function. The derivation is tedious and has been given below. The situation can be generalized to many variables $z_1,z_2,\ldots$ without much complications. We will not do this here.

From

$$dF = F_{x,yz}dx + F_{y,zx}dy + F_{z,xy}dz,$$

where we have used the compact notation $F_{x,yz} \equiv (\partial F/\partial x)_{yz}$, etc.,

$$(\partial F/\partial x)_y = F_{x,yz} + F_{z,xy}(\partial z/\partial x)_y.$$

Similarly,

$$(\partial K/\partial y)_x = K_{y,zx} + K_{z,xy}(\partial z/\partial y)_x.$$

We express $F_{x,yz}$ as a 3-Jacobian and manipulate it as follows:

$$\begin{aligned}&\frac{\partial(F,y,z)}{\partial(x,y,z)}\\ &\quad = \frac{\partial(F,y,z)}{\partial(K,x,z)}\frac{\partial(K,x,z)}{\partial(x,y,z)}\\ &\quad = \frac{\partial(F,y,z)}{\partial(K,x,z)}\left[-\left(\frac{\partial K}{\partial y}\right)_x + K_{z,xy}\left(\frac{\partial z}{\partial y}\right)_x\right]\\ &\quad = -\left(\frac{\partial K}{\partial y}\right)_x\left[\frac{\partial(F,y,z)}{\partial(K,x,z)} - K_{z,xy}\left(\frac{\partial z}{\partial K}\right)_x\frac{\partial(F,y,z)}{\partial(K,x,z)}\right].\end{aligned}$$

Using this, we find that

$$\begin{aligned}\left(\frac{\partial F}{\partial x}\right)_y &= -\left(\frac{\partial K}{\partial y}\right)_x\left[\frac{\partial(F,y,z)}{\partial(K,x,z)} - K_{z,xy}\left(\frac{\partial z}{\partial K}\right)_x\frac{\partial(F,y,z)}{\partial(K,x,z)}\right.\\ &\quad \left. + F_{z,xy}\frac{\partial(z,y)}{\partial(K,x)}\right].\end{aligned}$$

The quantity in the square brackets D can be rewritten as

$$D \equiv \frac{\partial(F,y)}{\partial(K,x)}D',$$

where

$$\begin{aligned}D' &= \frac{\partial(F,y,z)}{\partial(K,x,z)}\frac{\partial(K,x)}{\partial(F,y)} - K_{z,xy}\frac{\partial(z,x)}{\partial(F,y)}\frac{\partial(F,y,z)}{\partial(K,x,z)}\\ &\quad + F_{z,xy}\frac{\partial(z,y)}{\partial(F,y)}.\end{aligned}$$

Using Eq. (B3), it can now be shown in a straightforward manner that $D' = 1$, which proves Eq. (C1), the desired result.

While we considered F and K as a function of 3 variables, we can generalize the result to any number of variables. We will not pause here to do that.

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