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Nonequilibrium thermodynamics: Structural relaxation, fictive temperature, and Tool-Narayanaswamy phenomenology in glasses

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Starting from the second law of thermodynamics applied to an isolated system consisting of the system surrounded by an extremely large medium, we formulate a general nonequilibrium thermodynamic description of the system when it is out of thermal and mechanical equilibrium with the medium. Our approach allows us to identify the correct form of the Gibbs free energy and enthalpy. We also obtain an extension of the classical nonequilibrium thermodynamics due to de Donder in which one normally assumes thermal and mechanical equilibrium with the medium; see text. We find that the temperature and pressure differences between the system and the medium act as thermodynamic forces, which are normally neglected in the classical nonequilibrium thermodynamics. The Prigogine-Defay ratio is found to be greater than 1 merely due to the lack of equilibrium with the medium, even though we do not consider any internal order parameters. This shows that these forces should play an important role in relaxation processes. We then apply our approach to study the general trend during structural relaxation in glasses and establish the phenomenology behind the concept of the fictive temperature and of the empirical Tool-Narayanaswamy equation on firmer theoretical foundation.

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I. INTRODUCTION

It is well known that when a liquid is disturbed suddenly from its equilibrium state by changing the temperature or pressure of the surrounding medium, or both, then the liquid undergoes a rapid, solidlike change, followed by a slower, liquidlike change toward the new equilibrium state. These changes can be seen in the variation in its thermodynamic properties such as the volume V or its enthalpy H with time. For a supercooled liquid, the above scenario plays an important role. As the temperature is lowered or the pressure is increased, the scale separation between the fast and the slow processes in supercooled liquids increases until the latter becomes too large compared to the experimental observation time τ_{obs}. In this case, the system is said to be kinetically arrested in that the liquidlike changes no longer contribute to the observed properties. The system behaves like a solid and is called a *glass* [1–8].

The glass is a system that may be far from equilibrium so one cannot apply equilibrium statistical mechanics to investigate its properties, which vary with time. One must resort to apply nonequilibrium thermodynamics [9–12] to study glasses and their relaxation in time; the latter are usually known as *structural relaxation*. It is known from the early work of Littleton [13], and Lillie [14] that the isothermal viscosity of a glass changes during relaxation, thus implying the dependence of the relaxation on changes in the state of the glass [15]. As we will see in this paper, the most vivid consequence of nonequilibrium thermodynamics is that the field variables such as temperature T, pressure P etc. of the system are usually different from those of the medium surrounding it, an aspect that is usually neglected in the formulation of nonequilibrium thermodynamics ([10], p. 221 and [11(a)], p. 111); see the *Important remark* just preceding Eq. (17) below. Thus, we need to go beyond the classical approach to incorporate the above disparity in T, P. This disparity is most certainly a property of glasses, as we will see later, because of the two widely separated time scales. The most general framework for developing nonequilibrium thermodynamics must satisfy the second law of thermodynamics or must start from it. The generality arises since the second law is independent of the processes (structural or otherwise) going inside the system. Thus, it is able to capture the possible differences of the field variables T, P etc. between the system and the medium. It is also independent of the details of the system considered and does not requires any sophisticated concepts such as ergodicity or its loss, etc. during relaxation. Our main goal in this work is to develop an appropriate nonequilibrium thermodynamics, which will then be applied to glasses with the hope to gain some new insight and to clarify at the fundamental level certain concepts extensively used in glasses.

Glassy behavior and their properties have been extensively studied and usually explained by invoking empirical rules [6,16,17] that, although they have proved invaluable and very reliable, lack theoretical justifications [3,4]. Only recently, attempts have been made [18,19] that use modern framework to investigate nonequilibrium properties of glassy relaxation at the molecular level. Our treatment here differs from these attempts in that we develop our approach using the second law that should be applicable to all systems including glasses. We do not derive the actual laws of relaxation for which one must turn to other sources such as [18,19]. Our goal is quite different. We wish to understand some of the important concepts used for glasses at a fundamental level. One of the most widely used concept in this field is that of the *fictive temperature*, first introduced by Tool [16] in an empirical fashion to describe nonlinear relaxation in glasses. The system under study slows down so much upon reducing the temperature from its initial value T', where the system was in equilibrium, to some temperature T_0 that one has to wait for a very long time before true equilibrium is reached at the final temperature. In this case, crudely speaking, the glass properties are assumed to be similar to a fictive liquid at some intermediate temperature between T' and T_0. As time goes on and as the system undergoes structural rearrangements to come to equilibrium, the fictive temperature of the system continues to change and finally becomes T_0. This already means that the fictive temperature of the system continuously changes from T' to T_0. Despite its continual usage in the field, the true meaning of the fictive temperature, though phenomenologically obvious, is not well defined in terms of fundamental quantities such as the entropy. In particular, there exists a variety of fictive temperatures, each associated with the relaxing quantity under investigation, which makes the concept not very rich. Recently, Schmelzer and Gutzow [20] have also analyzed the fictive temperature by using the de Donder approach [9–11] but under the assumption that T, P of the system are the same as those of the surrounding medium.

There is another aspect of structural relaxation. Its presence means that the glass is a nonequilibrium state. Thus, its temperature must be changing during the process of relaxation. How does one define the *instantaneous temperature* of the liquid? The instantaneous temperature itself must relax to T_0 as time goes on. Thus, there will a relaxation time describing the relaxation of the temperature of the glass. Tool [16] and Narayanaswamy [17], among others, observed that the relaxation time not only depends upon the temperature T_0, but also depends upon the fictive temperature of the system; see, for example, [2–4]. Is the instantaneous temperature of the glass the same as the fictive temperature? These are important issues as a deeper understanding of these concepts will provide a more qualitative and predictive understanding of glass transition.

The layout of the paper is as follows. We consider an isolated system consisting of the system of interest surrounded by a very large medium and follow the consequences of it in the next section. In Sec. III, we follow the consequence of partial equilibrium to develop a very general nonequilibrium thermodynamics, which is then applied to a glass in Sec. IV. The concept of the fictive temperature and the Tool-Narayanaswamy phenomenology are considered in Sec. V, and established on a firm theoretical ground. The conclusions are given in the last section.

II. CONSEQUENCES OF THE SECOND LAW

As said above, we study nonequilibrium systems by proceeding in a general manner by following the consequences of the second law, which is well established. As usual, we apply the second law to an isolated system, which we denote by Σ_0; it consists of the system Σ of interest (such as our glass) in a medium denoted by $\tilde{\Sigma}$ containing it. We will consider a single component system with no internal order parameters, which is sufficient for our purpose. An example of such a system is that of argon, where glass transition has been observed in simulations [21]. Later, we will extend the discussion to include internal order parameters. According to the second law, the entropy S_0 of an isolated system Σ_0 can never decrease in time [22],

$$\frac{dS_0(t)}{dt} \geq 0. \tag{1}$$

What happens inside the isolated system (loss of ergodicity in parts of the system, chemical reactions, phase changes, etc.) cannot affect the direction of the inequality, which makes it the most general principle of nonequilibrium thermodynamics. The law itself imposes no restriction on the actual rate of entropy change. In general, S_0 also depends on the number of particles N_0, energy E_0, and volume V_0 of Σ_0. Thus, $S_0(t)$ used above should be really written as $S_0(E_0,V_0,N_0,t)$. However, as the extensive quantities remain constant in time there is no harm in using the compact form $S_0(t)$ during approach to equilibrium. The entropy $S_0(t)$ is a *continuous* function of each of its arguments. In addition, it is at least *twice differentiable* except at isolated points with respect to its extensive variables. The energy, volume and the number of particles of Σ are denoted by E, V, and N, respectively, while that of the medium $\tilde{\Sigma}$ by $\tilde{E}$, $\tilde{V}$, and $\tilde{N}$. Obviously,

$$E_0 = E + \tilde{E}, \quad V_0 = V + \tilde{V}, \quad N_0 = N + \tilde{N}.$$

We will assume that N of the system is also fixed, which means that $\tilde{N}$ is also fixed. However, the energy and volume of the system may change with t.

When the isolated system is in equilibrium, its entropy $S_0(E_0,V_0,N_0,t)$ has reached its maximum and no longer has any *explicit* time dependence so that it can be simply written as $S_0(E_0,V_0,N_0)$ or S_0. In this case, different parts of Σ_0 have the same temperature T_0 and pressure P_0:

$$\frac{1}{T_0} = \frac{\partial S_0}{\partial E_0}, \quad \frac{P_0}{T_0} = \frac{\partial S_0}{\partial V_0}; \tag{2}$$

we have defined the temperature by setting the Boltzmann constant $k_B = 1$ in this work. Otherwise, the entropy $S_0(t)$ *continuously increases* and the isolated system is said to be not in equilibrium. The medium is considered to be very large compared to Σ, so that its temperature, pressure, etc. are not affected by the system. We assume $\tilde{\Sigma}$ to be an *internal* equilibrium (its different parts have the same temperature and pressure, but $\tilde{\Sigma}$ and Σ may not be in equilibrium with each other). Thus, its entropy $\tilde{S}$ no longer has an explicit time dependence, but has an *implicit* t dependence through the t dependence of $\tilde{E}$, and $\tilde{V}$. The time variation in $S_0(t)$ is due to the relaxation going on inside Σ as it is driven toward equilibrium with the medium.

The entropy $S_0(t)$ of the isolated system can be written as the sum of the entropies $S(t)$ of the system and $\tilde{S}(t)$ of the medium:

$$S_0(E_0,V_0,N_0,t) = S(E,V,N,t) + \tilde{S}(\tilde{E},\tilde{V},\tilde{N}); \tag{3}$$

there is no explicit t dependence in $\tilde{S}(\tilde{E},\tilde{V},\tilde{N})$ due to internal equilibrium. The correction to this entropy due to the weak stochastic interactions between the system and the medium has been neglected, which is a common practice [22]. We expand $\tilde{S}$ in terms of the small quantities of the system [22]

$$\tilde{S}(\tilde{E},\tilde{V},\tilde{N}) \simeq \tilde{S}(E_0,V_0,\tilde{N}) - \left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)\Bigg|_{E_0} E(t) - \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)\Bigg|_{V_0} V(t).$$

It follows from the internal equilibrium of $\tilde{\Sigma}$ that

$$\left.\left(\frac{\partial \widetilde{S}}{\partial \widetilde{E}}\right)\right|_{E_0} = \frac{1}{T_0}, \quad \left.\left(\frac{\partial \widetilde{S}}{\partial \widetilde{V}}\right)\right|_{V_0} = \frac{P_0}{T_0},$$

and $\widetilde{S} \equiv \widetilde{S}(E_0, V_0, \widetilde{N})$, which is a constant, is independent of the system. Thus,

$$S_0(t) - \widetilde{S} \simeq S(E,V,N,t) - E(t)/T_0 - P_0V(t)/T_0. \tag{4}$$

Let us introduce

$$G(t) \equiv H(t) - T_0S(t), \quad H(t) \equiv E(t) + P_0V(t), \tag{5}$$

the time-dependent functions of the system Σ with the medium $\widetilde{\Sigma}$ at fixed T_0 and P_0. We thus finally have

$$S_0(t) - \widetilde{S} = S(t) - H(t)/T_0 = -G(t)/T_0, \tag{6}$$

so that the behavior noted in Eq. (1) of $S_0(t)$ of the isolated system leads to a very important conclusion about the above function $G(t)$ of the system:

$$\frac{dG(t)}{dt} \leq 0. \tag{7}$$

The function $G(t)$ decreases as the system relaxes toward equilibrium, a result quite well known in classical thermodynamics [22] provided we identify it with the Gibbs free energy of the system. From now on, we will identify $G(t)$ as the time-dependent Gibbs free energy of the system ([22], see Eq. (20.7) there), which continues to decrease and finally becomes identical to the equilibrium Gibbs free energy at the current temperature and pressure T_0, P_0. If we abruptly cool the system from some previous temperature such as T_g to a lower temperature at time $t=0$, the *initial* values of the energy, volume, and entropy at the new temperature remain equal to their respective values at the previous temperature at $t=0$. As the system relaxes, $G(t)$ continuously decreases from its initial value. It cannot increase without violating the second law. We will come back to this issue once more near the end of Sec. III.

We have given the essential steps in the derivation of Eq. (6) here not only for the sake of continuity as some of the intermediate steps will be needed later on, but also to make some important points, which we now list.

(1) In deriving the above Eq. (6), no assumption about the system Σ has been made. In particular, we have not assumed any particular aspect of its nonequilibrium nature, such as a particular form of relaxation (Arrhenius or otherwise), loss of ergodicity, etc.

(2) The identification of $S_0(t) - \widetilde{S}$ with the Gibbs free energy $G(t)$ of Σ is generally valid under the assumption of the medium being large compared to Σ, which can be satisfied as well as we wish as we wish ([22], compare in particular with Eq. (20.7) there).

(3) The Gibbs free energy $G(t)$ and the enthalpy $H(t)$ are determined by the temperature T_0 and the pressure P_0 of the large medium.

(4) The continuity and differentiability of $S_0(t)$ with respect to its arguments that was mentioned earlier also applies to the Gibbs free energy of the system.

(5) The decrease in $G(t)$ must not be violated even when there is a loss of ergodicity in the system, as is commonly believed to occur during a glass transition.

(6) For glasses, we have an additional experimental fact. The enthalpy remains continuous across the glass transition under isobaric conditions.

(7) The continuity and differentiability of $G(t)$ during relaxation implies that the entropy $S(t)$ also will remain continuous and differentiable with respect to all of its arguments, as the system relaxes. This property will be required in Sec. III.

III. NONEQUILIBRIUM THERMODYNAMICS

When the equality in Eq. (1) occurs, different parts of Σ_0 (such as Σ and $\widetilde{\Sigma}$) have the same temperature T_0 and pressure P_0. Otherwise, they have different temperatures and pressures, in which case a common assumption made by almost all workers is that of partial equilibrium (see, for example, Landau and Lifshitz ([22], see p. 13) when Σ_0 is out of equilibrium; each part is in *internal equilibrium* (local equilibrium), which then allows us to define the temperature, pressure, etc. for each part, which may all be different. In this situation, their entropies have the maximum possible values for their respective energies and volumes, and the number of particles. In other words, for fixed values of the latter quantities E, V and N, the entropy cannot change with time. As a result, there cannot be an explicit t dependence [see the equilibrium condition given in Eq. (2) above for Σ_0] in their entropies such as $S(E,V,N,t)$; their variation in time comes from the time variation in their energies, volumes, etc. The assumption of internal equilibrium allows us to write $S(E,V,N)$ for the entropy of Σ, which then determines its *instantaneous* temperature $T(t)$ and pressure $P(t)$:

$$\frac{\partial S}{\partial E} = \frac{1}{T(t)}, \quad \frac{\partial S}{\partial V} = \frac{P(t)}{T(t)}. \tag{8}$$

These are standard relations for the entropy [22], except that all quantities except S in the above equations may have an *explicit* dependence on time t that will make S depend *implicitly* on time. Accordingly:

$$\frac{\partial S}{\partial t} = 0 \tag{9}$$

under internal equilibrium. Relations such as Eq. (8) along with Eq. (9) for internal equilibrium are used commonly in nonequilibrium thermodynamics. We use them to establish that heat flows from a hot body to a cold body; see, for example, Sec. 9 in Landau and Lifshitz [22]. The glassy state, in which the fast dynamics has equilibrated and the slow dynamics is extremely slow, will thus be treated as a state in internal equilibrium, although it is not in equilibrium (with the medium). This observation will be very important when we discuss the concept of the fictive temperature in Sec. V.

Recognizing that $S(t)$ has no explicit t dependence, see Eq. (9), but is a function of $E(t)$ and $V(t)$ (N is kept a constant), we have for the differential $dS(t)$

$$dS(t) = \frac{1}{T(t)}dE(t) + \frac{P(t)}{T(t)}dV(t), \tag{10}$$

where we have used Eq. (8) and have allowed the instantaneous pressure and temperature of the system to be different from those of the medium for the sake of generality. The first law of thermodynamics follows from this equation:

$$dE(t) = T(t)dS(t) - P(t)dV(t), \tag{11}$$

which does *not* depend on the temperature and pressure of the medium. Landau and Lifshitz ([22], see just above Eq. (20.4) there) also write the first law for a system not in equilibrium with the medium in the same form [Eq. (11)]. Thus, the first law has the standard look with the first term representing the heat

$$dQ = T(t)dS(t) \tag{12}$$

added to the system and the second term without the sign denoting the work

$$dW = P(t)dV(t) \tag{13}$$

done by the system.

The form of dQ in Eq. (12) should not give the reader a wrong impression that we are considering a reversible process and that there is no irreversible entropy generation. To clear up any possible confusion, we proceed as follows. It is appropriate at this point to rewrite dQ in the standard form for the benefit of the readers more familiar with de Donder approach [9–11] by introducing the two parts of the entropy change

$$dS(t) = d_{\mathrm{e}}S(t) + d_{\mathrm{i}}S(t). \tag{14}$$

Here, $d_{\mathrm{e}}S(t)$ represents the entropy exchange with the medium and $d_{\mathrm{i}}S(t) \geq 0$ represents the irreversible entropy generation or the uncompensated transformation of Clausius [11] within the system. As Σ_0 is isolated, the heat $d\widetilde{Q}$ added to the medium $\widetilde{\Sigma}$ is the negative of the heat dQ added to the system Σ. As the heat is added to the medium isothermally at T_0, its entropy change is given by $d\widetilde{S} \equiv d\widetilde{Q}/T_0$. Thus, $d_{\mathrm{e}}S(t) \equiv -d\widetilde{S}$. Consequently,

$$dQ \equiv T_0 d_{\mathrm{e}}S(t), \tag{15}$$

and we find that irreversible entropy generation $d_{\mathrm{i}}^{(\mathrm{S})}S(t)$ due to entropy flow is given by

$$d_{\mathrm{i}}^{(\mathrm{S})}S(t) \equiv -\frac{[T(t)-T_0]}{T_0}dS(t) \equiv -\left[\frac{1}{T_0} - \frac{1}{T(t)}\right]dQ \geq 0. \tag{16}$$

We have added a superscript to express the fact that there may be other contributions such as $d_{\mathrm{i}}^{(\mathrm{V})}S(t)$ to $d_{\mathrm{i}}S(t)$; see Eq. (18) below. We find that indeed $d_{\mathrm{i}}^{(\mathrm{S})}S(t) \geq 0$ as expected; see Eq. (27) in a cooling experiment in which $dQ < 0$. In Eq. (16), $1/T_0 - 1/T(t)$ represents the thermodynamic force F_{Q} for the flow of heat dQ (or entropy) in time dt ([11(a)], p. 89). Alternatively,

$$F_{\mathrm{S}} \equiv -[T(t) - T_0]/T_0$$

represents the thermodynamic force F_{S} for the flow of entropy $dS(t)$.

Important remark. At this point, we compare our identification of $d_{\mathrm{e}}S(t)$ in Eq. (15) with the definition used in traditional nonequilibrium thermodynamics. In Eq. (4), Ch. III of the classic book by De Groot and Mazur [10], these authors identify $d_{\mathrm{e}}S(t) \equiv dQ/T$, clearly showing that their T represents the temperature of the medium and not the instantaneous temperature $T(t)$ of the system.

Using $H(t) = E(t) + P_0V(t)$ in Eq. (5), we find that

$$dH(t) = T(t)dS(t) + V(t)dP_0 + [P_0 - P(t)]dV(t), \tag{17}$$

where the last term appears due to the lack of equilibrium with the medium. Accordingly, the heat dQ, see Eq. (12), is no longer equal to $dH(t)$ at constant pressure P_0 of the medium,

$$dQ(t) = dH(t)|_{P_0} + [P(t) - P_0]dV(t).$$

The second term above represents the additional contribution $d_{\mathrm{i}}^{(\mathrm{V})}S(t) \geq 0$ to $d_{\mathrm{i}}S(t)$ due to volume change (flow)

$$d_{\mathrm{i}}^{(\mathrm{V})}S(t) \equiv \frac{[P(t) - P_0]}{T_0}dV(t) \geq 0, \tag{18}$$

with

$$F_{\mathrm{V}} \equiv [P(t) - P_0]/T_0$$

representing the thermodynamic force F_{V} for the flow of volume dV in time dt ([11(a)], p. 95).

After this brief detour, we return to the main discussion. The specific heat C_P at constant pressure is given by

$$C_P(t) \equiv \left(\frac{\partial H(t)}{\partial T_0}\right)_{P_0} + [P(t) - P_0]\left(\frac{\partial V(t)}{\partial T_0}\right)_{P_0}.$$

However, obtaining the entropy of the system from the measured values of the specific heat requires care,

$$dS(t) = \frac{C_P}{T(t)}dT_0 \leq \frac{C_P}{T_0}dT_0,$$

which follows from Eq. (27) valid after cooling, derived below.

The differential of $G(t)$, see Eq. (5), turns out to be

$$dG(t) = -S(t)dT_0 + V(t)dP_0 + [T(t) - T_0]dS(t) + [P_0 - P(t)]dV(t). \tag{19}$$

Again, the last two terms are corrections to $dG(t)$ due to the nonequilibrium nature of the system and are also obtained by Landau and Lifshitz ([22], see Eq. (20.4) there) when studying a system in a medium. We observe from Eq. (19) that

$$\left(\frac{\partial G}{\partial T_0}\right)_{P_0} = -S(t) + [T(t) - T_0]\left(\frac{\partial S(t)}{\partial T_0}\right)_{P_0} - [P(t) - P_0]\left(\frac{\partial V(t)}{\partial T_0}\right)_{P_0},$$

$$\left(\frac{\partial G}{\partial P_0}\right)_{T_0} = V(t) + [T(t) - T_0]\left(\frac{\partial S(t)}{\partial P_0}\right)_{T_0} - [P(t) - P_0]\left(\frac{\partial V(t)}{\partial P_0}\right)_{T_0}.$$

Again, the last two terms in each equation are the corrections due to nonequilibrium nature of the process, and would be absent in an equilibrium process.

One can compare the Gibbs free energy differential in Eq. (19) with the approach developed by de Donder [9–11]. The last two terms in Eq. (19) look identical in form to the contributions from two different "structural order parameters" or "degree of advancement" terms. In the present context, the two "parameters" are determined by the instantaneous entropy and volume

$$\xi_{\mathrm{S}} \equiv \frac{S(t) - S(\infty)}{S(0) - S(\infty)}, \quad \xi_{\mathrm{V}} \equiv \frac{V(t) - V(\infty)}{V(0) - V(\infty)},$$

and the corresponding affinities are given by

$$A_{\mathrm{S}} \equiv -[T(t) - T_0][S(0) - S(\infty)],$$

$$A_{\mathrm{V}} \equiv [P(t) - P_0][V(0) - V(\infty)].$$

Thus, we have

$$[T(t) - T_0]dS(t) - [P(t) - P_0]dV(t) \equiv -A_{\mathrm{S}}d\xi_{\mathrm{S}} - A_{\mathrm{V}}d\xi_{\mathrm{V}},$$

so that each of the two contributions $-A_\alpha d\xi_\alpha \leq 0$, $\alpha = \mathrm{S}, \mathrm{V}$, as expected from the variation in $G(t)$ during relaxation at constant T_0, P_0. We also note that we can write the first law as

$$dE(t) = T_0 dS(t) - P_0 dV(t) - A_{\mathrm{S}}d\xi_{\mathrm{S}} - A_{\mathrm{V}}d\xi_{\mathrm{V}}, \qquad (20)$$

as expected from the standard formulation by de Donder [9–11]. It should be noted that dQ is not given by $T_0 dS(t)$ in the above equation, but by Eq. (12) or by $T_0 dS(t) - A_{\mathrm{S}}d\xi_{\mathrm{S}}$. Similarly, dW is given by Eq. (13) or by $P_0 dV(t) - A_{\mathrm{V}}d\xi_{\mathrm{V}}$, and not by $P_0 dV(t)$.

It is a good place to include any internal order parameters ξ_i that may be present in the system. These internal order parameters may arise due to orientation of a molecule, deformation due to flow, elastic deformation, etc. ([11(a)], Sec. 10.2 and [11(b)], Sec. 11, Chap. III); see also de Groot and Mazur ([10], Sec. 6, Chap. 10). The idea is by now well established and can be found in many books dealing with nonequilibrium thermodynamics [9–11]. Associated with an internal order parameter is a chemical potential or affinity. We follow the standard practice and express the differential $dS(t)$ in Eq. (10) by treating $S(t)$ as a function of these additional internal order parameters also. The additional contribution will also modify Eq. (11) to

$$dE(t) = T_0 dS(t) - P_0 dV(t) - A_{\mathrm{S}}d\xi_{\mathrm{S}} - A_{\mathrm{V}}d\xi_{\mathrm{V}} - \sum_i A_i d\xi_i, \qquad (21)$$

where A_i are the affinities associated with the internal order parameter ξ_i; see ([10], Eq. (142), p. 221). In this form, it is evident that ξ_{S} and ξ_{V} are formally two additional "order parameters" due to the absence of equilibrium, when temperature and pressure deviations between the system and the medium are taken into account. These deviations are normally not considered in the classical nonequilibrium thermodynamics [9–11] in which it is implicitly assumed that the system and the medium have a common temperature and pressure. Thus, the forces F_{S} and F_{V} are taken to be zero. While one does not need to be convinced of the correctness of the classical formalism by de Donder [9–11], which has been widely tested, it is nice to know that our general derivation provides an independent and direct demonstration of its validity. It should also be noted that even in the absence of the conventional order parameters ξ_i, there are two formal "order parameters" ξ_{S} and ξ_{V}. Hence, according to the well-known result [23], the Prigogine-Defay ratio Π should be larger than unity; see Eq. (31) later.

We once more look at the definition of the Gibbs free energy and enthalpy $G(t)$ and $H(t)$ in Eq. (5). Let us consider an instantaneous isobaric cooling (at a fixed pressure P_0) from a temperature T' above the glass transition temperature T_{g} to a lower temperature T_0 below T_{g}. At T', the system is in equilibrium and has its equilibrium Gibbs free energy $G' = E' - T'S' + P_0 V'$, where all the quantities with a prime refer to the equilibrium values at T'. We first consider the Gibs free energy definition. If we (incorrectly) identify the Gibbs free energy with

$$\hat{G}(t) \equiv E(t) - T(t)S(t) + P(t)V(t) \quad \text{at} \quad T_0, \qquad (22)$$

then at $t=0$, it has the value $\hat{G}(0) \equiv E' - T'S' + P_0 V' = G'$. Now, the equilibrium Gibbs free energy $G_0 = E_0 - T_0 S_0 + P_0 V_0$ at T_0 must be higher than the equilibrium Gibbs free energy G' at T'. Thus, $\hat{G}(t)$ will have to increase in time from G' to G_0

$$\frac{d\hat{G}(t)}{dt} > 0,$$

which contradicts the conventional wisdom expressed in Eq. (7). Our choice $G(t)$, and consequently, $H(t)$ in Eq. (5) resulting directly from the general second law is the correct choice.

IV. RELAXATION

A. General behavior

Again, for simplicity, we consider our simple system with no internal order parameters and apply the above formalism in the glassy state; however, the formalism is applicable to other nonequilibrium states also as noted below. Above the glass transition temperature T_{g} but below the melting temperature, the system is a supercooled liquid (SCL) as the relaxation time τ of Σ remains less than the observation time τ_{obs}. At any temperature T_0 below T_{g}, τ becomes larger than τ_{obs}, and the system turns into a glass. Let us consider the system in the glassy state. With time, the glass (Σ) will relax so as to come to equilibrium (the corresponding SCL state obtained by increasing τ_{obs} to the relaxation time at that temperature) with the medium if we wait longer than τ_{obs}. It should be noted again that, due to the internal equilibrium of the system, there is no explicit t dependence in S on the right side of Eq. (3) or (4). Accordingly, the t dependence in S, H, and G is implicit through $E(t)$, and $V(t)$. In the following, the glass is considered to be formed under *isobaric* conditions so the pressure of the medium is kept fixed at P_0 as its temperature is stepwise varied. Accordingly, we will assume that its instantaneous pressure $P(t)$ is always equal to P_0 of the medium

$$P(t) = P_0, \tag{23}$$

but its temperature will in general be different than T_0 and vary in time, as we will show below. This is equivalent to setting the force $F_{\mathrm{V}}=0$, and $d_{\mathrm{i}}^{(\mathrm{V})}S(t)/dt=0$. The initial enthalpy $H(0)$ at T_0 is the enthalpy H' of the glass at temperature T', and $H(\infty)=H_0$ after complete relaxation at temperature T_0; here, H_0 is the value of the SCL enthalpy. It is experimentally found that the enthalpy decreases with time during an isothermal relaxation so that

$$H(t=0) > H(t \to \infty). \tag{24}$$

This decrease is a general property of thermodynamics which follows from the specific heat being non-negative. Since T' is above the glass transition temperature, the system is in the SCL state at T'. As $T' > T_0$, the enthalpy $H'=H(0)$ of SCL at T' must be higher than the enthalpy $H_0=H(t\to\infty)$ of SCL at T_0. The same is also true of the volume in many cases, which relaxes to a smaller value in an isothermal relaxation. However, this property of the volume is not a thermodynamic requirement. Accordingly, as a general rule

$$\frac{dH(t)}{dt} < 0, \tag{25}$$

during isothermal structural relaxation in glasses. In the following, we will only use the above general property of the enthalpy, and not of the volume. Now, if T' is below the glass transition, then from the result just derived, we conclude that $H(0)$ is even larger than the SCL enthalpy at T'. This even strengthens the above inequality (24).

Let us now turn to the time derivative of the entropy S_0, which is changing because the energy and volume of Σ are changing with time [22]. Thus,

$$\begin{aligned}\frac{dS_0(t)}{dt} &= \frac{dS}{dt} - \frac{1}{T_0}\frac{dE(t)}{dt} - \frac{P_0}{T_0}\frac{dV(t)}{dt}\\ &= \left(\frac{\partial S}{\partial E} - \frac{1}{T_0}\right)\frac{dE(t)}{dt} + \left(\frac{\partial S}{\partial V} - \frac{P_0}{T_0}\right)\frac{dV(t)}{dt} \geq 0,\end{aligned}$$

as the relaxation goes on in the system Σ. It is clear that

$$\frac{\partial S}{\partial E} \neq \frac{1}{T_0}, \quad \frac{\partial S}{\partial V} \neq \frac{P_0}{T_0},$$

if $dS_0/dt > 0$. Thus, as long as the relaxation is going on due to the absence of equilibrium, the two inequalities must hold true. Accordingly, the derivative $\partial S/\partial E$, which by definition represents the inverse temperature $1/T(t)$ of the system, see Eq. (8), must be *different* from $1/T_0$ of the medium,

$$T(t) \neq T_0.$$

As $\partial S/\partial V = P_0/T(t)$, we see immediately that

$$\frac{dS_0(t)}{dt} = \left(\frac{1}{T(t)} - \frac{1}{T_0}\right)\frac{dH(t)}{dt} \geq 0. \tag{26}$$

From Eq. (25), we observe $dH(t)/dt < 0$ during relaxation in glasses. Thus, we are forced to conclude that

$$T(t) \geq T_0, \tag{27}$$

the equality occurring only when equilibrium has been achieved. The instantaneous temperature can be presumably measured by using a small "thermometer" so as not to disturb the internal equilibrium of the glass. Such a measurement will allow us to explore its variation in time.

Let us pause here for a moment and ask: can we measure the temperature of a glass? We cannot just immerse a thermometer inside and take a reading. We can only measure it indirectly, if at all; see [24] for a discussion of this possibility. There are several possible ways. One possible method is to use the violation of the fluctuation-dissipation theorem, as was done by Grigera and Israerloff [25], and the other method is to implant a thermometer inside the sample before the glass is formed, as was done by, for example, Montanini and D'Acquisto [26]. Both methods clearly show that the temperature of the glass is different from that of the medium, as we have concluded above. However, it should be mentioned that the idea of a thermometer requires establishing its equilibrium with the system. As the instantaneous temperature $T(t)$ continues to vary in time, there is no way to ensure that the equilibrium has established. Therefore, it does not seem possible to measure it directly. Despite this, $T(t)$ has the property that it decreases with the enthalpy of the system, as is easily seen from Eq. (26). Both factors on the right side must have the same sign. In addition, it appears in the first law in Eq. (11) and also relates the amount of heat and the entropy change in Eq. (12). When $T(t)=T_0$, equilibrium must have occurred as $dS_0(t)/dt=0$, the condition for equilibrium. Thus, $T(t)$ has the required properties of a temperature.

The above calculation also shows that

$$\frac{dS(t)}{dt} = \frac{1}{T(t)}\frac{dH(t)}{dt}, \tag{28}$$

which is the first term in Eq. (26). The equation above can also be obtained from Eq. (17). Using $P(t)=P_0$ for an isobaric process, which is the normal situation in most experiments, we see that the last term in Eq. (17) vanishes. Hence,

$$dQ = dH(t) = T(t)dS(t)$$

is valid in all isobaric processes, from which Eq. (28) follows immediately.

The relaxation that occurs in the glass originates from its tendency to come to thermal equilibrium during which its temperature $T(t)$ varies with time; recall that we are considering a cooling experiment. The relaxation process results in the lowering of the corresponding Gibbs free energy, as is seen from Eq. (7), which is a consequence of the second law in Eq. (1). Accordingly, there are changes in its enthalpy and entropy, which are in the same direction; see Eq. (28). The

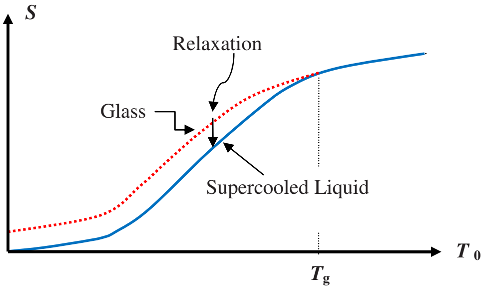

FIG. 1. (Color online) Schematic behavior of the entropy for SCL (solid curve) and GL (dotted curve). The GL entropy decreases, shown by the downward arrow, as it isothermally (constant temperature T_0 of the medium) relaxes toward SCL, during which its temperature $T(t)$ also decreases toward T_0.

lowering of $G(t)$ with time results in not only lowering the enthalpy in a cooling experiment, as observed experimentally, but also the entropy $S(t)$ during relaxation,

$$(dS(t)/dt) \leq 0,$$

as shown in Fig. 1. At constant P_0 and T_0, we see from Eq. (19) that

$$dG(t) = [T(t) - T_0]dS(t), \tag{29}$$

from which it follows that

$$\frac{dG(t)}{dS(t)} = T(t) - T_0,$$

showing that $G(t)$ converges to its equilibrium value more slowly compared to the convergence of $S(t)$ as $T(t) \to T_0$, i.e., as $t \to \infty$ as the above derivative vanishes in this limit.

We have assumed above that we are below the glass transition only because we were not interested in the relaxation during the observation time. The above formalism is also applicable during the observation time τ_{obs}. Thus, the analysis above is applicable at all times for any nonequilibrium state, not necessarily a glassy state.

B. Simple model of a nonequilibrium temperature

The possibility of a temperature disparity can be heuristically demonstrated by considering a simple nonequilibrium laboratory problem. Consider a system as a "black box" consisting of two parts at different temperatures T_1 and $T_2 > T_1$, but insulated from each other so that they cannot come to equilibrium. The two parts are like slow and fast motions in a glass, and the insulation allows us to treat them as independent, having different temperatures. We wish to identify the effective temperature of the system. To do so, we imagine that each part is added a certain *infinitesimal* amount of heat, which we denote by dQ_1 and dQ_2. The amount of heat dQ added to the system is their sum. We assume the entropy changes to be dS_1 and dS_2. Then, we have

$$dQ = dQ_1 + dQ_2,$$

$$dS = dS_1 + dS_2.$$

Let us introduce a temperature T by

$$dQ = TdS,$$

which from Eq. (12) can be identified as the effective temperature of the system. It immediately follows after applying Eq. (12) to each of the parts that

$$dQ(1/T - 1/T_2) = dQ_1(1/T_1 - 1/T_2).$$

By introducing

$$x = dQ_1/dQ,$$

which is determined by the setup, we find that T is given by

$$\frac{1}{T} = \frac{x}{T_1} + \frac{1-x}{T_2}. \tag{30}$$

As x is between 0 and 1, it is clear that T lies between T_1 and T_2 depending on the value of x. Thus, we see from this heuristic model calculation that the effective temperature of the system is not the same as the temperature of either parts, a common property of a system not in equilibrium (see [24,27,28], and references cited therein).

If a "thermometer" is coupled to part 1, its reading will be T_1; if it couples to the other part, its reading will be T_2. Also, the parameter x depends on the physical properties of both parts. As these properties will usually change with their temperatures, x will in general also depend on these temperatures.

The above calculation is for fixed T_1 and T_2 since the infinitesimal heats do not change the temperatures. It is the value of x that uniquely determines the temperature T of the system, which is different from the temperatures of the two parts. The entropy change dS is also fixed at dQ/T. If the insulation between the parts is not perfect, there is going to be some energy transfer between the two parts, which would result in maximizing the entropy of the system. As a consequence, their temperatures will eventually become the same. During this time, the temperature T of the system will lie between the changing temperatures of the two parts, and will itself be changing.

The behavior of the system in phase space, which will be useful later in the next section, can be characterized as follows. The phase space Γ of the system is a product space $\Gamma_1 \otimes \Gamma_2$ formed by the phase spaces Γ_1, Γ_2 of the two parts. The representative point of the system consists of two points, each belonging to Γ_1, Γ_2, respectively, and represent the states of the two parts. These representative states of the two parts move independently in *slices* of their respective phase spaces. The average energies E_1 and E_2 in these slices correspond to the temperatures T_1 and T_2, respectively. The corresponding independent slices in the two phase spaces represent the states of the system. If the insulation is not perfect, the two slices will move around their respective phase spaces and will eventually have a common temperature when the equilibration between the two parts has occurred.

C. Specific heats and Prigogine-Defay ratio

It is instructive to compare the specific heat of the glass with the specific heat of the corresponding fully relaxed state obtained as $t \to \infty$. Let us assume that at time $t=0$, we change the temperature of Σ form some initial temperature T' to T_0 instantaneously. We consider the system at $t=t_{\mathrm{obs}}$ and determine its enthalpy. The specific heat of the glassy sample at this instant is given by

$$C_{P,\mathrm{g}} = \lim_{\Delta T \to 0} \frac{H(0) - H(t_{\mathrm{obs}})}{\Delta T}.$$

The corresponding specific heat after complete relaxation is given by

$$C_{P,\mathrm{relax}} = \lim_{\Delta T \to 0} \frac{H(0) - H(\infty)}{\Delta T} \geq C_{P,\mathrm{g}}.$$

Let us now compute the Prigogine-Defay ratio Π when we allow only ξ_{S} (*we set* $F_{\mathrm{V}}=0$). The situation is similar to the case of a single order parameter for which Schmelzer and Gutzow [20] have already expressed Π in a simplified form; see their Eq. (28),

$$\Pi = \frac{(\partial H/\partial \xi_{\mathrm{S}})_{P_0,T_0}}{T_0(\partial S/\partial \xi_{\mathrm{S}})_{P_0,T_0}} = \frac{T(t)}{T_0} > 1, \tag{31}$$

which clearly shows the nonequilibrium effect usually neglected in the conventional nonequilibrium thermodynamics [9–11]. This ratio is equal to 1 in the conventional nonequilibrium thermodynamics [23] because of the assumption $T(t)=T_0$ at all times. It should be pointed out that Schmelzer and Gutzow [20] also find $\Pi>1$ for a single order parameter case ξ. This again reinforces our conclusion that ξ_{S} formally acts like an internal order parameter, even though one usually does not consider S and V as internal order parameters.

V. FICTIVE TEMPERATURE AND THE TOOL-NARAYANASWAMY EQUATION

A. Partitioning the degrees of freedom

So far, we have mostly considered a very general situation of relaxation in a nonequilibrium state. This relaxation is reflected in the temporal variation in all thermodynamic properties of the system. For example, the instantaneous temperature $T(t)$ of the system will continuously vary and approach the temperature of the medium. At high enough temperatures, this time variation can be described as a single simple exponential with a characteristic time scale τ, the relaxation time. In this situation, the slice containing the states of the system, see Sec. IV B, corresponds to an average energy $E(t)$ This happens when all the degrees of freedom (dof) come to equilibrium simultaneously with the same relaxation time. At any time t before equilibrium is reached, the system has a temperature $T(t)$; it also has energy $E(t)$, $V(t)$, etc. The slice in its phase space defined over an average volume $V(t)$ contains the states of the system, see Sec. IV B, such that the average energy is $E(t)$.

At low temperatures, this is not true for many systems. In such systems, there are slow and fast modes noted in Sec. I. It is this situation that is similar to the simple model considered in Sec. IV B, which we now imagine to be in a medium at temperature T_0. Both parts will strive to come to equilibrium with the medium but they may have widely separated relaxation times describing the fast and slow modes in the system.

We now need to turn our attention to the distinction between the fast and slow degrees of freedom, a characteristic of any glass. Situation similar to this also occurs in the attainment of thermal equilibrium between the nuclear spins and their environment during nuclear relaxation [29], where the spin-lattice relaxation is extremely slow. The explanation of this kind of behavior (slow and fast dof) in a wide class of substances lies in internal molecular motions other than simple vibrations. The fast dof cool down and equilibrate very fast, while the slow dof take much longer to transfer their energy and equilibrate because of very weak coupling with the surrounding medium. Here, we are talking about equilibration with the medium. We will denote those dof that have equilibrated with the medium at time t by a subscript "e," and the remaining that are not equilibrated by "n."

A similar situation also occurs in glasses to which we now turn. Assume that at $t=0$ the system is cooled instantaneously from an equilibrated supercooled liquid at T' to a glass state at T_0. Immediately prior to cooling at $t=0$, all dof are in equilibrium at T'. At $t=0$, all dof are out of equilibrium with the medium at T_0. The fast dof equilibrate within the observation time t_{obs}, with the slow dof remaining out of equilibrium [30]. Eventually, as $t\to\infty$, all dof come to equilibrium with the medium. The above discussion suggests that the number of dof that are in equilibrium with the medium at T_0 does not remain constant. They increase from zero to the the entire dof in time. Let D denote the total number of the dof in the system, which is determined by the number of particles N in it; hence, it remains constant. Let $D_{\mathrm{e}}(t)$ and $D_{\mathrm{n}}(t)$ denote its partition in equilibrated and nonequilibrated dof, respectively:

$$D = D_{\mathrm{e}}(t) + D_{\mathrm{n}}(t);$$

evidently, they are functions of time. As said above, the clear distinction between the two kinds of dof arises because of a *very weak coupling* between them and of the slow dof with the medium. The weak coupling allows us to treat them as almost uncorrelated and *quasi-independent*, which then immediately leads to the following partition of the entropy, the energy and the volume into two contributions, one from each kind because of their quasi-independence mentioned above,

$$S(t) = S_{\mathrm{e}}(t) + S_{\mathrm{n}}(t), \tag{32a}$$

$$E(t) = E_{\mathrm{e}}(t) + E_{\mathrm{n}}(t), \tag{32b}$$

$$V(t) = V_{\mathrm{e}}(t) + V_{\mathrm{n}}(t), \tag{32c}$$

where the notation is self-evident. It should be noted that $S_{\mathrm{e}}(t)$ and $S_{\mathrm{n}}(t)$ stand for $S_{\mathrm{e}}[E_{\mathrm{e}}(t), V_{\mathrm{e}}(t)]$ and $S_{\mathrm{n}}[E_{\mathrm{n}}(t), V_{\mathrm{n}}(t)]$. The corrections to each of the partitions due to the very weak coupling are small enough to be neglected.

One should not confuse dof$_{\mathrm{e}}$ with only fast dof. To see this most clearly, we recall that at $t=0$, none of the dof have equilibrated at the new temperature T_0, so that $D_{\mathrm{e}}(t=0)=0$. But all of the same dof were equilibrated at T', implying that dof$_{\mathrm{e}}$ at T' contains fast and slow dof. The same happens as $t\to\infty$, in which case $D_{\mathrm{e}}(t)\to D$ at T_0 implying that all dof, fast and slow, have equilibrated. Thus, in general, $D_{\mathrm{e}}(t)$ contains both fast and slow dof. Let us now consider $\mathrm{dof}_{\mathrm{n}}$. At $t=0$, none of the dof have equilibrated at the new temperature T_0. Accordingly, $D_{\mathrm{n}}(t=0)=D$, so that $\mathrm{dof}_{\mathrm{n}}$ contains both fast and slow dof. However, for $t>t_{\mathrm{obs}}$, only (or mostly) the slow dof remain in $D_{\mathrm{n}}(t)$.

What we discuss below does not really depend on the actual t dependence of $D_{\mathrm{e}}(t)$ and $D_{\mathrm{n}}(t)$. Despite this, it is natural to understand this dependence. To make any clear statement about the behavior of the two dof in time requires some additional knowledge. What we currently know about the dynamics in glass formers is based on simulations and provides the following picture. We follow the potential energy landscape picture of Goldstein [30], in which the fast dof are identified with the vibrational modes within a basin and the slow dof are identified with configurational modes associated with probing various basins. We assume the glass to be confined in a certain basin at $t=0$. The fast dof equilibrate to T_0 within the observation time t_{obs}, with the slow dof remaining out of equilibrium [30]. The slow dof related to various possible basins are too slow to equilibtate at the new temperature. On the other hand, both were at equilibrium (at T') at $t=0$. Further equilibration at $t>0$ occurs as the glass begins to probe other basins by leaving the current basin. A large body of simulations [31–35] have established a very clear pattern for the mean square displacement of a particle as a function of time t, starting from a ballistic regime to a plateau to a final diffusive regime. Indeed, the system first probes nearby (in the landscape) basins belonging to what is known as a *metabasin*, sometimes gets trapped in the metabasin for a long time and then jumps out of this metabasin to be trapped in another nearby metabasin for a long time, finally escapes this metabasin to be trapped in another metabasin, and so on; see Fig. 2 in Weeks *et al.* [32] for a very clear demonstration of this trapping in megabasins. As time increases, there will also be back tracking among previously visited megabasins [35]. It is found that the system can either graze a metabasin or spend a long period inside it [33]. In the latter scenario, we can safely assume that the relevant configurational dof associated with this metabasin have come to equilibration, while the others configurational dof that are unvisited so far are still out of equilibrium. There does not seem to be a way for *all* basins to come to the same temperature as there is no way for the system to probe *all* basins as soon as $t>0$. We expect the system to visit all the basins in the diffusive regime. Thus, we will assume that $D_{\mathrm{e}}(t)$ and $D_{\mathrm{n}}(t)$ change continuously, even though this assumption is not crucial for the discussion below.

B. Fictive temperature

Let us now introduce the following derivatives of the energy partitions

$$x(t) \equiv \frac{dE_{\mathrm{e}}(t)}{dE(t)}, \quad 1-x(t) \equiv \frac{dE_{\mathrm{n}}(t)}{dE(t)}, \tag{33}$$

at a given t, so that

$$\frac{\partial S_{\mathrm{e}}(t)}{\partial E(t)} = x(t)\frac{\partial S_{\mathrm{e}}(t)}{\partial E_{\mathrm{e}}(t)}, \quad \frac{\partial S_{\mathrm{n}}(t)}{\partial E(t)} = [1-x(t)]\frac{\partial S_{\mathrm{n}}(t)}{\partial E_{\mathrm{n}}(t)}. \tag{34}$$

The derivatives in the two equations above are at fixed $V_{\mathrm{e}}(t)$ and $V_{\mathrm{n}}(t)$, respectively. At $t=0$, $D_{\mathrm{e}}(t=0)=0$, $E_{\mathrm{e}}(t=0)=0$ and $x(t=0)=0$. At $t\to\infty$, $D_{\mathrm{e}}(t)\to D$, $E_{\mathrm{n}}(t)=0$ so that $x(t)=1$. As time goes on, more and more of the "n" dof equilibrate, thus increasing $D_{\mathrm{e}}(t)$ and $x(t)$.

By definition, we have

$$\frac{\partial S_{\mathrm{e}}(t)}{\partial E_{\mathrm{e}}(t)} = \frac{1}{T_0},$$

which follows from the equilibrium of the $\mathrm{dof}_{\mathrm{e}}$ with the medium, while the $\mathrm{dof}_{\mathrm{n}}$ will have a temperature different from this. Accordingly, we introduce a new temperature $T_{\mathrm{n}}(t)$, defined by the derivative

$$\frac{\partial S_{\mathrm{n}}(t)}{\partial E_{\mathrm{n}}(t)} = \frac{1}{T_{\mathrm{n}}(t)}. \tag{35}$$

The following identity

$$\frac{1}{T(t)} = \frac{x(t)}{T_0} + \frac{1-x(t)}{T_{\mathrm{n}}(t)} \tag{36}$$

easily follows from considering $\partial S(t)/\partial E(t)$ and using Eqs. (32a) and (34). This equation should be compared with Eq. (30) obtained earlier using a heuristic model. Initially, $x(0)=0$ so that $T(0)=T_{\mathrm{n}}(0)=T'$, while $T(t)\to T_0$ as $t\to\infty$, as expected. This division of the instantaneous temperature $T(t)$ into T_0 and $T_{\mathrm{n}}(t)$ is identical in form to that suggested by Narayanaswamy [17], except that we have given thermodynamic definitions of the nonlinearity parameter $x(t)$ in Eq. (33) and of the new temperature $T_{\mathrm{n}}(t)$ in Eq. (35) in our approach. Both these quantities, being intensive, can only depend on energy and volume per particle, through which these quantities gain their implicit t dependence.

Let us now understand the significance of the above analysis. The partition of the thermodynamic quantities in Eq. (32) along with the definition of the fraction $x(t)$ shows that the partition satisfies a lever rule: the relaxing glass can be *conceptually* (but not physically) thought of as a "mixture" consisting of two different "components" corresponding to $\mathrm{dof}_{\mathrm{e}}$ and $\mathrm{dof}_{\mathrm{n}}$: the former is at temperature T_0 and has a weight $x(t)$; the latter with a complementary weight $1-x(t)$ is at a temperature $T_{\mathrm{n}}(t)$. Thinking of a system conceptually as a mixture of two components is quite common in theoretical physics. One common example is that of a superfluid, which can be thought of as a mixture of a normal viscous component and a superfluid component ([36], Sec. 23). In reality, there exist two simultaneous motions [36], one of which is "normal" and the other one is "superfluid." A similar division can also be carried out in a superconductor: the total current is a sum of a "normal current" and a "superconducting current" ([36], Sec. 44).

The division of the dof envisioned above is no different from similar divisions in a superfluid or a superconductor. However, because of the nonequilibrium nature of the system, there is an important difference here compared to a superfluid or a superconductor. The e component is in equilibrium (with the medium), but the n component is only in internal equilibrium. While the significance of the former as a SCL component at T_0, P_0 (dof=D_e) is obvious, the significance of the latter requires clarification. At $t=0$, $T_n(t)$ represents the temperature T' of the equilibrated SCL (dof $=D$) from which the current glass is obtained by cooling. At this time, the entropy $S_n(t=0)$ of initial state of the glass at T_0 is equal to the entropy $S_{SCL}(T')$ of the equilibrated SCL (dof=D) at the previous temperature T'. The latter has the energy and volume $E_{SCL}(T')=E_n(t=0)$ and volume $V_{SCL}(T')=V_n(t=0)$. At any later time $t>0$, $T_n(t)$ represents the temperature associated with the energy $E_n(t)$ and volume $V_n(t)$ of the nonequilibrated component of the glass and has a weight $1-x(t)$. This component, being in internal equilibrium, can be identified as a *fictive* SCL [dof=$D_n(t)$] at temperature $T_n<T'$ of energy $E_{SCL}=E_n(t)$ and volume $V_{SCL}=V_n(t)$. In other words, the relaxing glass at any time t can be considered as consisting of two SCL components, one at temperature T_0 [dof=$D_e(t)$] and the other one [dof=$D_n(t)$] at temperature $T_n(t)$. The temperature $T\equiv T_n(t)$ *uniquely* determines the energy $E_{SCL}(T)\equiv E_n(t)$ and volume $V_{SCL}(T)\equiv V_n(t)$ of the corresponding *fictive* SCL [dof=$D_n(t)$].

Let us try to understand how the system can be viewed from the point of view of its phase space. In analogy with the phase space description given in Sec. IV B, we can state the following. The phase space Γ of the system is a product space of two phase spaces $\Gamma_e(t)$ and $\Gamma_n(t)$ associated with $D_e(t)$ and $D_n(t)$, respectively. There is internal equilibrium in each of the two phase spaces. At any time before equilibrium with the medium is reached, the phase space slice of the system consists of two disjoint slices in the two phase spaces; these slices correspond to the temperatures T_0 and $T_n(t)$, respectively. At equilibrium, the two slices have a common temperature.

As the above fictive liquid at $T\equiv T_n(t)$ contains only (or mostly) the slow dof, it does not yet really represent a SCL associated with the system at $T\equiv T_n(t)$, as the former lacks dof$_e$, while the latter contains all dof. This does not pose any problem as the missing dof$_e$ at $T\equiv T_n(t)$ are in equilibrium not only with the dof$_n$ at $T\equiv T_n(t)$, the fictive SCL mentioned above, but also with the medium at $T\equiv T_n(t)$. Thus, one can consider "adding" these missing dof$_e$ (dof=D_e) to the fictive liquid, which now represents the equilibrated SCL (dof=D) at $T\equiv T_n(t)$. This SCL is not the same as the glass with its fictive $T_n(t)$, as the latter has its dof$_e$ at T_0 while the SCL has all of its dof at $T_n(t)$. However, all of their thermodynamic properties associated with dof$_n$ must be the same, as their entropy functions are the same for both liquids. Similarly, the SCL component at T_0, P_0 (dof=D_e) should also be "supplemented" by the missing dof$_n$ to give rise to the equilibrated SCL at T_0, P_0 (dof=D).

We are now in a position to decide which of the temperatures $T(t)$ and $T_n(t)$ qualifies as the *fictive temperature*. We will identify this temperature to characterize only the nonequilibrated dof (with respect to the medium, but having internal equilibrium among themselves) in the system, though other definitions are also possible. As $T(t)$ contains information about both kinds of dof, it is not the appropriate temperature to be identified as the fictive temperature. The temperature $T_n(t)$, on the other hand, depends only on nonequilibrated dof$_n$, and should be identified as the fictive temperature of the relaxing glass at time t. This temperature is not the instantaneous temperature of the glass at this time, but represents the equilibrium temperature of the corresponding SCL at $T\equiv T_n(t)$ as noted above.

C. Tool-Narayanaswamy phenomenology: single slow relaxation

As first pointed out by Littleton [13] and Lillie [14], and discussed by several authors, see, for example, [4,6,15], the viscosity keeps changing with time during relaxation. Thus, if one uses an Arrhenius form for the viscosity, it must depend not on T_0, but on $T(t)$; it is the instantaneous temperature that characterizes the instantaneous state of the glass. Thus, if we assume that the viscosity, which is usually taken to be proportional to the relaxation time, is Arrhenius in form then it must be expressed as

$$\eta(t)=\eta_0\exp\left[\frac{B}{T(t)}\right]=\eta_0\exp\left[B\left(\frac{x(t)}{T_0}+\frac{1-x(t)}{T_n(t)}\right)\right], \tag{37}$$

the form conventionally identified as the phenomenological Tool-Narayanaswamy form [16,17]. Here, η_0 and B are some parameters of the system and may depend on T_0, P_0 and also on time t. Our derivation above justifies this form on a solid theoretical ground and provides another independent justification for identifying $T_n(t)$ as the fictive temperature.

One can carry out a similar analysis with decomposing the volume; see Eq. (32c). However, we do not obtain any new result as $P(t)=P_0$. To see this, we proceed exactly as above but use the volumes instead of the energies. Introducing the parameter $x_v(t)$ defined by

$$x_v(t)\equiv\frac{\partial V_e(t)}{\partial V(t)}$$

at fixed $E_e(t)$, which may be different from $x(t)$, and using

$$\frac{\partial S_e(t)}{\partial V_e(t)}=\frac{P_0}{T_0},\qquad\frac{\partial S_n(t)}{\partial V_n(t)}=\frac{P_0}{T_{n,v}(t)},$$

at fixed $E_e(t)$ and $E_n(t)$, respectively, along with $\partial S(t)/\partial V(t)=P_0/T(t)$, see Eqs. (8) and (23), we find the following decomposition of the inverse instantaneous temperature:

$$\frac{1}{T(t)}=\frac{x_v(t)}{T_0}+\frac{1-x_v(t)}{T_{n,v}(t)}.$$

Now, the new fictive temperature $T_{n,v}(t)$ represents the temperature $T=T_{n,v}(t)$ of corresponding fictive SCL [dof $=D_n(t)$] with energy and volume $E_{SCL}(T)=E_n(t)$ and volume $V_{SCL}(T)=V_n(t)$. This fictive liquid is the same as noted above as far as the energy and volume are concerned. However, as SCL is an equilibrated state, the specification of energy and volume *uniquely* determines the temperature, which from the earlier analysis was seen to be exactly $T_n(t)$. Thus, we conclude

$$T_{n,v}(t) \equiv T_n(t).$$

In order for the above decomposition to be consistent with Eq. (36) at all times, we must ensure that

$$x_v(t) = x(t).$$

In other words, our definition of the fictive temperature gives the same value whether we consider the energy relaxation or the volume relaxation.

D. Experimental fit

It should be noted that our definition of the fictive temperature $T_n(t)$ makes it somewhat different from the conventional definition used in the literature [1–6,8], which takes different values for different quantities such as the enthalpy and the volume. Therefore, we need to follow the consequences of this difference in their definition. This will require a particular model of the dynamics in the system. Usually, these dynamics in glass forming liquids do not follow simple exponentials. A common acceptable form is the Kohlrausch form, which includes a stretching exponent β. The exponential itself may be taken to be a function of time and temperature to account for deviations seen at short times $[x(t) \simeq 0]$ and long times $[x(t) \simeq 1]$ [8]. Usually, β increases monotonically with the temperature. Thus, it will also change during relaxation as $T(t)$ changes. Let us assume for the moment that our $T_n(t)$ is not very different from the customary fictive temperature. Conventionally, the viscosity is fitted by taking x as a constant close to 0.5, but allowing three other adjustable parameters (η_0, B, and β) to obtain the best fit ([1], see the contribution by Moynihan *et al.*, p. 15); all four parameters will generally have some time dependence, but their time dependence is neglected in finding the best fit. Indeed, even the values of the fictive temperature have appreciable uncertainties depending on the procedure to find it. Therefore, such fits do not rule out a slowly varying $x(t)$. Time dependence of $x(t)$ has been recognized for quite some time in the literature; see Wunderlich ([37], p. 683).

Let us now turn to the experimental determination of the various parameters in the Tool-Narayanaswamy Eq. (37) [38,39]. Han *et al.* [38] have carried out an experimental investigation of the structural relaxation of the enthalpy in an inorganic glass (Li_2O2SiO_2), and report the variation in B, x, and β with aging time t. Over a period of 930 min from $t=30$ min to $t=960$ min, they observe that $x(t)$ has grown from 0.21 to 0.35, and that the stretching exponent β decreases from 0.50 to 0.46 at a temperature 30 °C below the glass transition temperature. They also find $x(t)$ and β to depend on the aging temperature. The variation in β with time and temperature is also reported by Černošek *et al.* [39]. We refer the reader to the original work [38,39]. The variation in $x(t)$ is consistent with our general prediction above.

There cannot be any doubt that a constant x in Eq. (37) is an approximation when used to describe experiments. This should be contrasted with the original picture of Tool [16,17], in which x is not considered to depend explicitly on aging conditions. But this will not be true in any experimental situation. Even Tool [16] had doubts about x being independent of aging conditions. According to Tool's original idea, the state of an aging glass moves through all the microstates in the slice of an equilibrium liquid of the right average energy $E(t)$ at the fictive temperature. This is then used to argue that x should be independent of the aging conditions [16]. But this idea most certainly cannot be correct as no nonequilibrium state, in which $D_e(t)$ have a different temperature T_0 than $D_n(t)$, that have the temperature $T_n(t)$, can be identified with an equilibrium state with all dof D at temperature $T_n(t)$. Recall that there is a unique relationship between $E_{SCL}[T_f] = E(t)$ and the temperature T_f. However, there can be a variety of glasses with different energies but all having the same fictive temperature T_f. Thus, the original picture cannot relate all these glasses to the same fictive liquid and cannot be correct. What our calculation shows is that aging glass has two disjoint slices associated with T_0 and $T_n(t)$, respectively, as noted above. The equilibrated SCL has the entire slice at the same temperature $T_n(t)$. Only the nonequilibrated dof of the glass should be identified with the equilibrated liquid at $T_n(t)$. This picture now no longer supports aging-independent $x(t)$. This is where our new understanding differs from the original idea of Tool. This also makes data fitting a challenge. This is the price to be paid for changing x from an empirical parameter to a thermodynamic quantity. However, the benefit of our approach is that the fictive temperature is the same whether we consider the energy or the volume. It would be interesting to see what kind of time and temperature dependence $x(t)$ will exhibit with our definition $T_n(t)$ of the fictive temperature. This will require introducing a particular dynamics, which is not our aim in this work. We hope to return to it at some later time.

E. Several slow relaxations

It is highly likely that the slow relaxation consists of many different relaxation modes, which we index by $j = 1, 2, \ldots$. However, there does not seem to be any strong argument to suggest that all these different relaxation modes are almost decoupled as was the case for the fast and slow relaxations [30] studied above. In that case, it is not possible to partition the thermodynamic quantities such as the entropy, etc. associated with dof_n as a sum over these different modes. Despite this, let us follow the consequences of such an assumption. We express $D_n(t)$ as a sum over j

$$D_n(t) \equiv \sum_j D_n^{(j)}(t),$$

where the notation is quite transparent. We similarly express all of the n quantities in Eq. (32) as a sum over j. We can similarly express

$$1 - x(t) \equiv \sum_j y_j,$$

where

$$y_j \equiv \frac{dE_n^{(j)}(t)}{dE(t)}.$$

We can now introduce a fictive temperature for each jth n-dof

$$\frac{\partial S_n^{(j)}(t)}{\partial E_n^{(j)}(t)} = \frac{1}{T_n^{(j)}(t)},$$

such that

$$\frac{1-x(t)}{T_n(t)} \equiv \sum_j \frac{y_j}{T_n^{(j)}(t)},$$

a decomposition also described by Narayanaswamy [17]. However, because of the above equality, the presence of more than one kind of relaxation modes does not change the earlier decomposition [Eq. (36)]. In other words, no new insight is gained by such an assumption. One can introduce an equilibrated fictive SCL at each of the fictive temperatures as above. We will not stop here to do so as it is straightforward.

VI. CONCLUSIONS

We have developed a nonequilibrium thermodynamics to study systems away from equilibrium by starting with the second law applied to an isolated system. This particular approach does not seem to have been followed in the literature to the best of our knowledge. It is quite general and is not limited to systems close to equilibrium. Even though we have considered a simple one-component system with no internal order parameters, the approach is easily extended to include internal order parameters. The second law allows us to identify the correct form of the Gibbs free energy and enthalpy for a system not in equilibrium with the medium; see Eq. (5) and the discussion near Eq. (22). The classical approach by de Donder [9–11] invariably assumes that the system is in thermal and mechanical equilibrium with the medium so that the thermodynamic forces F_S and F_V are absent, which is usually not the case in most nonequilibrium systems. In particular, by considering a simple toy model, we show that the instantaneous temperature of the system is not always that of the medium as it relaxes; see Eq. (30). Thus, we need to extend this approach where we exploit the generality of the second law. To make progress in this direction, we assume internal equilibrium in the system, a common practice in the field, and which also forms the corner stone of the classical nonequilibrium thermodynamics [9–11]. Our extension allows us to find the corrections to the differential free energies in terms of the thermodynamic forces F_S and F_V that are consistent with de Donder-Prigogine approach to nonequilibrium thermodynamics, but which are neglected because of the assumption of thermal and mechanical equilibrium; see, for example, Eq. (20). The corrections show that the entropy and volume also can be formally treated as "order parameters" in the de Donder approach. We have mainly considered a simple monatomic system with no internal order parameters such as argon that can undergo a glass transition. This has simplified our presentation by not allowing internal order parameters ξ_i. But the latter can be easily included by adding differentials $A_i d\xi_i$ to dG, as shown in Eq. (21).

Even though we have mainly discussed supercooled liquids, the approach does not require the presence of a melting transition and an equilibrium crystal for its application. Thus, it should also be applicable to other glassy systems such as spin glasses, where there is no equilibrium crystal as the true equilibrium state. The only requirement is that enough time has passed after the system has been disturbed so that the instantaneous temperature, pressure, etc. can be defined via Eq. (8) for the system even if they are changing with time. In other words, there is partial equilibrium in the isolated system. We then apply this thermodynamics to study glasses and calculate the Prigogine-Defay ratio Π in the simple case when we assume that the thermodynamic force F_V is absent. Surprisingly, we find that $\Pi > 1$ even though we do not have any internal order parameter in the system. The deviation of this ratio from 1 is due to a lack of thermal equilibrium with the medium. This shows that one should not neglect the absence of the thermal equilibrium in glasses. We have not considered the absence of the mechanical equilibrium in this work for the sake of simplicity. We hope to return to this issue in a later publication. We also clarify the concept of the fictive temperature $T_n(t)$ widely used in the study of glasses by identifying it as a thermodynamic quantity; see Eq. (35). Our analysis shows that the fictive temperature has the same value even if we change the relaxing quantity from the energy to the volume. This temperature is not identical to but is related to the instantaneous temperature $T(t)$ in a glass; see Eq. (36). We use this relationship to establish the Tool-Narayanaswamy Eq. (37) for the relaxation time on a solid theoretical ground. This form does not change even if we have more than one kind of slow relaxation; the latter results in many different fictive temperatures, one for each kind of slow relaxation. However, as we have been able to offer a thermodynamic interpretation of $x(t)$, it no longer is merely a parameter following the original idea of Tool. Application of Eq. (37) to experimental situation invariably gives rise to aging dependent $x(t)$ and β [38,39]. Therefore, it is not surprising that the time dependence of $x(t)$ requires reinterpreting Tool's original idea of the fictive temperature. It should not be interpreted as the fictive temperature at which the glass is in equilibrium; rather, it is only the nonequilibrated dof of the glass that is compared with the equilibrium liquid at the fictive temperature $T_n(t)$, as we have discussed above.

We should finally contrast our approach with other approaches available in the literature that use some concept of an effective temperature. A very readable discussion of several such attempts is given in Sec. VI of the paper by Cugliandolo, *et al.* [24]. We can use Eq. (32a) to express $dS(t) = dS_e(t) + dS_n(t)$. However, each term is still multiplied by $T(t)$, implying that $dS_e(t)$ or $dS_n(t)$ are not multiplied by their respective temperatures T_0 or $T_n(t)$. Thus, one cannot consider $S_e(t)$ and $S_n(t)$ as separate in the first law [Eq. (11)] or in Eq. (29). This should be contrasted with the approach developed by Nieuwenhuizen [40], where the entropy is divided into fast and slow dof; see also [41]. More recently, Schmelzer *et al.* [20,42] have studied glasses and the fictive temperature by using the approach of de Donder [9–11]; consequently, they assume that T, P of the system are the same as those of the surrounding medium. There fictive temperature is given by

$$T_{\text{fic}}^{(\text{S-G})} \equiv T_0 - A\left(\frac{\partial \xi}{\partial S}\right)_V$$

for the single internal order parameter ξ ([20], Eq. (48)). Using ξ_S in place of ξ above, we find that

$$T_{\text{fic}}^{(\text{S-G})} \equiv T(t),$$

the instantaneous temperature of the system. This makes their definition of the fictive temperature different from ours. Indeed, these authors identify their fictive temperature and pressure ([20], see Eq. (61)) with the instantaneous temperature and pressure in our first law of thermodynamics [Eq. (11)]. A recent approach by Wolynes [18(b)] provides a local description of the relaxation in an inhomogeneous mosaic form, but the interest is in the dynamics, whereas our focus is not on any particular dynamics.

After this work was completed, we became aware of the work by Bouchbinder and Langer [27] who have considered a driven glassy system in which they also assume that a glass has a different temperature than the medium. It is nice to recognize that there appear to be remarkable similarities in some of our results on glassy systems even though our approaches and the starting points are somewhat different, and so are our aims.

An anonymous referee has suggested that $D_{\text{n}}(t)$ actually remains unchanged, but the temperature $T_{\text{n}}(t)$ of the nonequilibrated dof continuously changes during relaxation, until finally as $t \to \infty$, they also equilibrate with the medium. While it is hard for us to understand it in view of the simulations [31–35] discussed above, it will only be fair to accept the possibility that this scenario is right. This does not affect out final conclusions about the partition [Eq. (36)], about $T_{\text{n}}(t)$ playing the role of the fictive temperature, and that this temperature is the same whether we consider the entropy (or energy) relaxation or the volume relaxation, as we have note earlier.

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