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Nonequilibrium thermodynamics of glasses

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We consider the nonequilibrium thermodynamics of glasses from various perspectives. For the commonly used equilibriumlike approach based on Gibbs' fundamental form with an additional pair of conjugate variables, we discuss possible choices of the independent out-of-equilibrium variable and we illustrate some implications by concrete results for a well-known exactly solvable lattice model. The choice of variables is further illuminated from the complementary atomistic perspective offered by the inherent-structure formalism. A general formalism of nonequilibrium thermodynamics is employed (i) to derive the standard equilibriumlike approach, (ii) to formulate two self-contained levels to describe glassy dynamics and thermodynamics, and (iii) to offer guidance for future simulations of glasses. The thermodynamic approach suggests to introduce four-point correlation functions associated with structural rearrangements after imposed deformations, which might offer a possibility to detect a growing length scale at the glass transition without employing any dynamic information.

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I. INTRODUCTION AND CRITICAL REVIEW

Many systems undergo solidification into an amorphous solid state upon decreasing temperature or upon increasing density. To obtain such a *glassy state*, one needs to avoid crystallization which, in principle, can always be done by a sufficiently fast quench. In some cases, structural glasses are formed even upon slow cooling due to some kind of "frustration" in forming a crystal structure, for example, for binary mixtures of particles with appropriately different radii. For a pragmatic distinction between amorphous liquids and amorphous solids in terms of dynamic properties, one conventionally sets a viscosity level of 10^{13} P, at which typical equilibration times are of the order of minutes to hours. This viscosity value defines the *glass transition temperature*, which exhibits a slight dependence on the cooling rate or, more generally, on the details of the cooling procedure. Occasionally, a time scale of 100 s is used to define the glass transition in an alternative manner, where such general levels of viscosity or time may be inapplicable for polymeric materials.

From a statistical point of view, the hallmark of glassy systems is a breakdown of ergodicity. Within a reasonable observation time, only part of the configuration space can be sampled. Whenever ergodicity fails, one would like to identify the relevant slow observables such that accessible regions of phase space correspond to particular values of these observables. Therefore an important concept for understanding glasses are the basins of attraction associated with deep local minima of the potential energy. These basins, or groups of such basins, are sampled by the system in a short time, whereas transitions between different groups of basins separated by major energy barriers take a long time and imply a slow aging process.

During the aging process, glasses are systems under out-of-equilibrium conditions. For equilibrium systems, the pressure as a function of temperature, volume, and particle number, $p=p(V,N,T)$, is uniquely defined, whereas the pressure for a glass exhibits an additional dependence on its thermal and mechanical history. It is often assumed that a convenient out-of-equilibrium thermodynamic formalism can be employed for glasses, which is structured exactly as equilibrium thermodynamics, however, with a single additional independent variable encoding the history of the system [1,2]. To make a clear distinction from the recent systematic approach to nonequilibrium thermodynamics presented below, we refer to this kind of minimal modification of equilibrium thermodynamics as "equilibriumlike approach to nonequilibrium" (ELIANE). One of our goals is to derive ELIANE from a more general framework of nonequilibrium thermodynamics.

Whereas the so-called Kovacs effect [3] and various other experiments clearly show that, in general, a single additional variable is insufficient to characterize the state of a glass unambiguously, one should consider the final stage of an aging process, or small changes of external parameters, to stay in the potential range of validity of ELIANE (see also Ref. [4]). As it is generally the case for nonequilibrium systems, any extended set of independent variables can describe only a limited range of physical phenomena.

The focus of this work is on thermodynamic aspects of glasses. The microscopic approach is regarded only as the background to obtain unknown functions in the thermodynamic approach, either from exactly solvable models or from computer simulations. This emphasis on the thermodynamic perspective is unusual because, away from equilibrium, the microscopic description is commonly considered as the only safe ground whereas the thermodynamic approach is not considered to be well established. The ultimate goal of this work is to provide appropriate coarse grained levels of description for glasses within a consistent thermodynamic framework and thermodynamic guidance for targeted and efficient simulations.

The remainder of this Introduction (Sec. I) is dedicated to a critical review of several important approaches to the

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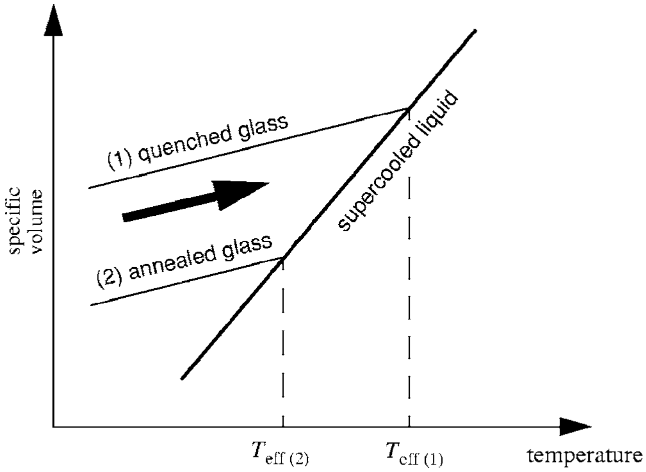

FIG. 1. Volume changes of a glass during heating at constant pressure (schematically).

theory of glasses: The equilibriumlike approach based on carefully introduced effective temperatures and inherent structure variables in addition to the usual equilibrium variables, implications for the theory of jumps in material properties at the glass transition, the inherent-structure approach based on an analysis of the potential energy landscape with explicit examples of the energy landscape (a condensed exposition of the underlying statistical mechanics is offered in Appendix A), and an exactly solvable harmonic-oscillator spherical spin model on a lattice. In Sec. II, we show how the emerging systematic theory of nonequilibrium thermodynamics can be employed to the problem of structural glasses. After summarizing the framework, we discuss possible origins of glassy behavior (including the functional form of entropy according to the classical work of Kauzmann and of Adam and Gibbs), and we employ the general framework to derive the classical equilibriumlike approach. Time evolution of structural variables in the supercooled melt is considered in Sec. III. After reviewing some phenomenological equations, we consider the formulation of evolution equations within the systematic thermodynamic approach applied to two different sets of possible structural variables. This approach suggests a natural procedure to introduce four-point correlation functions which might be useful to detect the glass transition (some details are given in Appendix B). A brief summary and outlook conclude the paper.

A. Equilibriumlike approach

More than 50 years ago, Davies and Jones [1] carefully developed and applied ELIANE in the context of glasses. The importance of an additional variable to characterize the state of glasses had been realized even earlier when, in 1931, Tool introduced the concept of a "fictive" temperature (nowadays commonly referred to as the effective temperature T_{eff}). Figure 1 illustrates schematically how effective temperatures can be associated with glasses with different thermal histories by heating them until a change of slope, that is a jump in the thermal expansivity, occurs. Loosely speaking, the effective temperature thus represents the temperature at which a liquid structure was frozen in and can hence be revived upon heating (the effective temperature may actually be lowered slowly by aging). Note that this phenomenological concept of an effective temperature differs from an alternative one based on fluctuations and responses, which may be closer to the one of statistical equilibrium thermodynamics but depends on an underlying model [5].

The main goal of the work of Davies and Jones is to relate the thermodynamic properties of glasses to those of supercooled liquids (and not to the properties of crystalline solids). It should be noted that supercooled liquids are thermodynamically unstable to crystals. However, supercooled liquids are metastable in the same way as diamond is thermodynamically unstable to graphite, but still impressively metastable. At ordinary temperatures and pressures, a transformation of diamond to graphite simply does not occur. Similarly, in the absence of freezing nuclei, a sample of supercooled liquid may often be maintained almost indefinitely [6]. Glasses are thermodynamically unstable in a more serious way than the metastable supercooled liquids. In an extremely slow continuous aging or stabilization process they develop into metastable supercooled liquids. In metastable states, a rather well-defined region of the phase space is explored during the observation time, and statistical mechanics can be employed to the restricted phase space. In particular, one can then assign an entropy to a metastable state. Davies and Jones argued carefully that, in a practical sense, an entropy can be assigned to unstable and not even metastable glassy states. Of course, the existence of entropy is a key ingredient for obtaining a "thermodynamic" description of glasses. Only after establishing the existence of an entropy function we can introduce thermodynamic material properties such as heat capacities, expansivities, or compressibilities for glasses.

In an abstract spirit, Davies and Jones introduced a more general out-of-equilibrium variable z that represents the "degree of order" or the "geometrical state of order" instead of the effective temperature. The existence of an entropy function $S(E,V,N,z)$ depending on the extensive equilibrium variables and the additional variable z implies a fundamental form,

$$dE = -pdV + \mu dN + TdS - Adz, \tag{1}$$

where the conjugate variables p, μ, T, and A are obtained as partial derivatives of $S(E,V,N,z)$ or, more directly, of the inverted function $E(V,N,S,z)$. The fundamental form (1) expresses an observation that was also stated explicitly by Davies and Jones: "A variation in z requires, in general, that energy be added to or taken from the system on account of the change in potential energy due to changing configuration." The quantity μ is the chemical potential and A is the "affinity" associated with the "degree of order,"

$$A = -\frac{\partial E(V,N,S,z)}{\partial z} = T\frac{\partial S(E,V,N,z)}{\partial z}. \tag{2}$$

For $A=0$, we recover Gibbs' fundamental form of equilibrium thermodynamics. Any dependence of S on the additional variable z implies a breakdown of ergodicity; depending on the cooling conditions, this breakdown can happen considerably above the glass transition temperature. For a magnetic system, we would have an additional work term $\boldsymbol{H}\cdot d\boldsymbol{M}$ in Eq. (1), where $\boldsymbol{H}$ is the magnetic field and $\boldsymbol{M}$ is the magnetization.

The fundamental form (1) implies that $E(V,N,S,z)$ is a thermodynamic potential containing all the information about an out-of-equilibrium system. Other thermodynamic potentials can be obtained in the usual way by Legendre transformations, for example, the Helmholtz free energy $F(V,N,T,z)=E-TS$ with

$$dF=-pdV+\mu dN-SdT-Adz, \tag{3}$$

or the Gibbs free energy $G(p,N,T,z)=E+pV-TS$ with

$$dG=Vdp+\mu dN-SdT-Adz. \tag{4}$$

These thermodynamic potentials are useful to find all the equations of state, that is, the relationships between the thermodynamic variables, and to define thermodynamic material properties in out-of-equilibrium situations. However, out-of-equilibrium states *cannot* be found by minimizing thermodynamic potentials because such states, in particular, the realized values of z, depend on the thermal and mechanical history.

If z is extensive, then we have

$$E=-pV+\mu N+TS-Az, \tag{5}$$

whereas the expression

$$E=-pV+\mu N+TS \tag{6}$$

holds for intensive z. One should, however, note that, away from equilibrium, the definition of p, μ, T (and/or further conjugate variables, such as $\boldsymbol{H}$) may depend on the choice of z, so that these variables represent different quantities in Eqs. (5) and (6). For a general transformation $z\mapsto z'=z'(V,N,S,z)$, we obtain the modified fundamental form

$$dE=\left(-p+A\frac{\partial z'/\partial V}{\partial z'/\partial z}\right)dV+\left(\mu+A\frac{\partial z'/\partial N}{\partial z'/\partial z}\right)dN+\left(T+A\frac{\partial z'/\partial S}{\partial z'/\partial z}\right)dS-\frac{A}{\partial z'/\partial z}dz', \tag{7}$$

which allows us to identify p', μ', T', and A'.

If we wish to introduce a meaningful, unambiguous thermal expansivity or heat capacity of glasses at constant pressure, then p and T should be well-defined variables even away from equilibrium (that is, even for $A\neq 0$, for example, for the glassy branches in Fig. 1). The somewhat formal discussion in the remainder of this subsection is hence crucial to understand jumps in thermodynamic properties at the glass transition and, in particular, relationships between jumps, which have caused considerable confusion in the literature. Clear concepts are also important to understand the proper thermodynamic analysis of the inherent-structure formalism.

To obtain meaningful properties, we consider equivalence classes of out-of-equilibrium variables z which are related by transformations of the type $z\mapsto z'=z'(N,z)$ and thus leave p and T invariant. If we introduce the class of (strong) *generalized effective temperatures* z of the form $z(N,T_{\mathrm{eff}})$, then the particular glassy states in Fig. 1, which have been prepared with different cooling procedures, correspond to constant values of z. The intensive and extensive generalized effective temperature variables are of the form $z=z(T_{\mathrm{eff}})$ and $z=N\hat{z}(T_{\mathrm{eff}})$, respectively.

As Fig. 1 describes experiments at constant p, we might be inclined to consider even more general effective temperatures of the form $z(p,N,T_{\mathrm{eff}})$, which we refer to as weak generalized effective temperatures. Different glassy states in Fig. 1 would still correspond to constant values of z. Note, however, that, according to Eq. (7), the out-of-equilibrium concepts of pressure and temperature associated with the effective temperature T_{eff} would differ from those associated with a weak generalized effective temperature z. It is not obvious that strong generalized effective temperatures would lead to the most meaningful definitions of pressure and temperature away from equilibrium. A particularly interesting weak effective temperature arises if we use the viscosity level rather than the temperature at which the jump in slope in Fig. 1 occurs as the out-of-equilibrium variable z_{vl}. If the viscosity level of 10^{13} P is used for defining the glass transition temperature at any pressure, then the glass transition is located at constant z_{vl}, independent of p. In the same spirit, one could introduce the weak generalized effective temperature $z=T_{\mathrm{eff}}/T_{\mathrm{g}}(p)$ as a convenient out-of-equilibrium variable, where $T_{\mathrm{g}}(p)$ is the pressure dependent glass transition temperature.

If z is a weak or strong generalized effective temperature, following the ideas developed on p. 399 of the classical paper [1], the intuitive variable T_{eff} itself can be found by solving the equation

$$A(p,N,T_{\mathrm{eff}},z)=-\frac{\partial G(p,N,T_{\mathrm{eff}},z)}{\partial z}=0. \tag{8}$$

Note that, for $A=0$, the conjugate variables in Eq. (7) are independent of the choice of z. Away from equilibrium, however, the pressure p in Eq. (8), which is kept constant in identifying T_{eff} in the spirit of Fig. 1, in general differs from the one obtained with the independent out-of-equilibrium variable $z=T_{\mathrm{eff}}$.

There exists another class of interesting out-of-equilibrium variables. As T_{eff} is the temperature at which some structural features are frozen in it must be related to a constraint in the accessible configuration space and hence to an entropy effect. Let us consider a general out-of-equilibrium variable z, which is related to T_{eff} by a known function $T_{\mathrm{eff}}(V,N,T,z)$. We then introduce the following candidate for a configurational entropy:

$$S_{\mathrm{conf}}(V,N,T,z)=\int^{z}\frac{A(V,N,T,\bar{z})d\bar{z}}{T-T_{\mathrm{eff}}(V,N,T,\bar{z})}+Ns\left(\frac{V}{N},T\right), \tag{9}$$

where the function $s(V/N,T)$ remains to be chosen properly. This definition, together with Eq. (1), implies the transformed fundamental equation

TABLE I. Generalized effective temperatures and inherent structure variables

	Strong	Weak
Effective temperatures	$z(N,T_{\mathrm{eff}})$	$z(p,N,T_{\mathrm{eff}})$
Inherent structure variables	$z(N,S_{\mathrm{conf}})$	$z(V,N,S_{\mathrm{conf}})$

$$dE = -p'dV + \mu'dN + TdS + (T_{\mathrm{eff}}-T)dS_{\mathrm{conf}} - (T_{\mathrm{eff}}-T)\frac{\partial S_{\mathrm{conf}}(V,N,T,z)}{\partial T}dT \tag{10}$$

with

$$p' = p + (T_{\mathrm{eff}}-T)\frac{\partial S_{\mathrm{conf}}(V,N,T,z)}{\partial V} \tag{11}$$

and

$$\mu' = \mu - (T_{\mathrm{eff}}-T)\frac{\partial S_{\mathrm{conf}}(V,N,T,z)}{\partial N}. \tag{12}$$

As anticipated, we find $p'=p$ and $\mu'=\mu$ only under equilibrium conditions, that is, for $T=T_{\mathrm{eff}}$. Equation (10) is an example of the general form (7) with $z'=S_{\mathrm{conf}}$ and $A'=T-T_{\mathrm{eff}}$ as out-of-equilibrium variables, provided that the frozen-in configurational entropy $S_{\mathrm{conf}}(V,N,T,z)$ is independent of the temperature T. This observation motivates us to introduce a second class of out-of-equilibrium variables z for which the function $s(V/N,T)$ in Eq. (9) can be chosen such that $S_{\mathrm{conf}}=S_{\mathrm{conf}}(V,N,z)$ becomes independent of T. Such variables are referred to as (weak) *inherent structure variables*. They describe a structure that, once frozen-in at T_{eff}, no longer depends on temperature (except through changes of V when p is kept constant). All inherent structure variables can be obtained by transformations of the type $z\mapsto z'=z'(V,N,z)$ from the unique variable $z=S_{\mathrm{conf}}$, so that we could alternatively refer to them as generalized configurational entropies corresponding to generalized effective temperatures.

For all inherent structure variables, the term in the second line of Eq. (10) vanishes so that we obtain a fundamental form given by the first line of Eq. (10). Moreover, for all inherent structure variables, by construction, we have the same concept of out-of-equilibrium temperature. Note that, according to Eq. (11), an unambiguous definition of pressure associated with inherent structure variables (and hence of the heat capacity at constant pressure) is obtained only if $S_{\mathrm{conf}}=S_{\mathrm{conf}}(N,z)$ is independent of V. We hence distinguish between strong and weak inherent structure variables depending on whether or not S_{conf} has an additional dependence on V, or whether or not p is defined unambiguously. An overview of the various important classes of variables introduced in this section can be found in Table I.

For any inherent structure variable, Eq. (9) implies the following factorization of the activity:

$$A(V,N,T,z) = [T - T_{\mathrm{eff}}(V,N,T,z)]\frac{\partial S_{\mathrm{conf}}(V,N,z)}{\partial z}. \tag{13}$$

Note that our phenomenological introduction of a configurational entropy is based on the knowledge of the effective temperature.

If we write the total entropy as

$$S = S_{\mathrm{fp}} + S_{\mathrm{conf}}, \tag{14}$$

then Eq. (10) leads to the following popular form of the fundamental equation of ELIANE [2]:

$$dE = -p'dV + \mu'dN + TdS_{\mathrm{fp}} + T_{\mathrm{eff}}dS_{\mathrm{conf}}, \tag{15}$$

with two separate contributions to heat. We can now obtain a better intuitive understanding of S_{conf} and T_{eff}. The total entropy (14) consists of two distinct contributions, one of which is associated with the microstates sampled by fast processes (fp),[1] the other one with the number of long living inherent-structure configurations (conf); the corresponding temperaturelike variables are given by T, which is similar to the familiar temperature of equilibrium thermodynamics, and the effective temperature T_{eff}. A sufficiently aged glass samples microstates which are typical of a thermodynamic equilibrium state, however, with the frozen-in temperature T_{eff} different from the more intuitive one associated with fast processes [4]. From this perspective, it may be helpful to think of T as a heat bath temperature and to remember that T_{eff} is the temperature at which, in the process of cooling, ergodicity is broken. The variable T_{eff} is hence related to but does not coincide with the glass transition temperature.

In the process of aging, a glassy system slowly lowers its potential energy by moving into local energy minima, or groups of local minima, of increasing depth. Therefore the microstates explored by the system with progressing time correspond to decreasing effective temperature and we expect $T_{\mathrm{eff}}>T$. The difference $T_{\mathrm{eff}}-T$ describes the degree of completion of the aging process; small differences arise for progressed aging or small cooling rate.

In the same way as discussed after Eq. (1), the fundamental form (15) implies that the function $E(V,N,S_{\mathrm{fp}},S_{\mathrm{conf}})$ is a thermodynamic potential from which the intensive variables can be obtained by partial differentiations. Thermodynamic material properties can be obtained as suitable second-order derivatives, and we obtain generalized Maxwell relations due to the presence of an additional variable, for example, the following ones needed below to simplify various expressions for material functions:

$$\frac{\partial S_{\mathrm{conf}}(p',N,T,T_{\mathrm{eff}})}{\partial p'} = -\frac{\partial V(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}}, \tag{16}$$

$$\frac{\partial S_{\mathrm{conf}}(p',N,T,T_{\mathrm{eff}})}{\partial T} = \frac{\partial S_{\mathrm{fp}}(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}}, \tag{17}$$

and

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[1] The fast processes are sometimes referred to as equilibrium processes, but the term "equilibrium" might be confusing in describing out-of-equilibrium systems.

$$\frac{\partial V(p',N,T,S_{\text{conf}})}{\partial S_{\text{conf}}} = \frac{\partial T_{\text{eff}}(p',N,T,S_{\text{conf}})}{\partial p'}. \tag{18}$$

As emphasized before, out-of-equilibrium states cannot be found by minimizing thermodynamic potentials because such states depend on the details of the thermal and mechanical history. Actually, the Helmholtz free energy $F(V,N,T,T_{\text{eff}})$ typically increases during the aging process [7].

For a better understanding of the different temperatures, it may be useful to consider the fluctuation-dissipation theorem of the first kind, in which the relationship between equilibrium correlation functions and linear response functions involves a temperature. In the short-time regime, the relevant temperature is the quantity T associated with fast processes, whereas, in the aging regime, T_{eff} occurs in the fluctuation-dissipation theorem [2,5,8]. The role of T_{eff} in the fluctuation-dissipation theorem has been verified by simulations of a Lennard-Jones binary mixture perturbed by periodic density variations, with a careful discussion of the relevant time scales [9]. Also the response to shear flow allows a clear separation of the two temperatures T and T_{eff} [10]. The fluctuation-dissipation theorem thus offers a method for a direct calculation of T_{eff} in computer simulations without any need to analyze or parametrize the statistical distribution of energy levels. Limitations are, however, implied by the recent observation that the domain of linear response shrinks to zero as the glass transition is approached [11].

One should not take for granted or not even expect that the classes of strong generalized effective temperatures and inherent structure variables coincide, as is often done implicitly by considering S_{conf} as a function of T_{eff}. Therefore there are (at least) two possible concepts of out-of-equilibrium pressure and temperature associated with these two classes, and one needs to decide which choice is more useful or more meaningful to reflect the experimental situation. In making a choice one should keep in mind that, on the one hand, the real situation for the phenomenological introduction of the effective temperature is much less ideal than the scenario shown in Fig. 1. On the other hand, the statistical approach relies on the concept of a configurational entropy. Whereas we used the concept of T_{eff} in our phenomenological introduction of S_{conf}, the statistical approach is based directly on S_{conf} and can be used to introduce T_{eff} as a conjugate variable. Moreover, it seems preferable to have a naturally extensive variable z in the fundamental form (1). The choice of an extensive generalized temperature may remove some artificial effects from the chemical potential, but certainly not artificial pressure effects, whereas the naturally extensive configurational entropy might also lead to more natural concepts of out-of-equilibrium temperature, pressure, and chemical potential. An interesting question is whether there are situations in which a weak generalized effective temperature could be a weak inherent structure variable.

Obviously, there is a need to corroborate the use of ELIANE for the description of glasses, that is, of the existence of an out-of-equilibrium entropy function. Some confidence can be gained by comparing with exact results for a toy model [2] of glasses and with a scaling expression for the pressure for the soft-sphere potential [12].

The idea of extending equilibrium thermodynamics by introducing an additional pair of conjugated variables is not limited to the description of glasses. For example, the same idea is used in steady-state thermodynamics [13,14]; under steady-state flow conditions, deformation rates and stresses occur as particular extra variables. Although conceptual issues and operational definitions have been carefully elaborated for steady-state thermodynamics [13], in any generalization, the issue of ambiguous extensions of equilibrium quantities such as temperature and pressure arises, and natural out-of-equilibrium variables need to be revealed in order to obtain meaningful results.

B. Jumps in material properties

Just like equilibrium thermodynamics, ELIANE for glasses is extremely useful for guiding measurements, analyzing experimental results, focusing work, and revealing relationships between different experiments. The mere existence of thermodynamic potentials has important quantitative implications for the difference of thermodynamic material properties of supercooled liquids and of glasses. For example, the difference in thermal expansivity is given by

$$\Delta\alpha = \frac{1}{V}\left[\frac{\partial V(p,N,T,A)}{\partial T} - \frac{\partial V(p,N,T,z)}{\partial T}\right], \tag{19}$$

where the derivative at the constant affinity $A=0$ gives the expansivity of the metastable supercooled liquid and the derivative at a constant generalized effective temperature z corresponds to the glassy state (see Fig. 1). The temperature T is to be taken as the effective temperature corresponding to z so that one actually is at the position of the jump. With the standard rules of multivariate calculus, we obtain

$$\Delta\alpha = \frac{1}{V}\frac{\partial V(p,N,T_{\text{eff}},z)}{\partial z}\frac{\partial z(p,N,T_{\text{eff}})}{\partial T_{\text{eff}}}. \tag{20}$$

Following the classical work of Davies and Jones [1], the liquid-glass differences in the isothermal compressibility,

$$\Delta\kappa = -\frac{1}{V}\frac{\partial V(p,N,T_{\text{eff}},z)}{\partial z}\frac{\partial z(p,N,T_{\text{eff}})}{\partial p}, \tag{21}$$

and the jump in the heat capacity at constant pressure,

$$\Delta C_p = T_{\text{eff}}\frac{\partial S(p,N,T_{\text{eff}},z)}{\partial z}\frac{\partial z(p,N,T_{\text{eff}})}{\partial T_{\text{eff}}}, \tag{22}$$

are expressed in a similar manner. In view of the common factor $\partial V/\partial z$ in Eqs. (20) and (21), we obtain

$$\frac{\Delta\kappa}{\Delta\alpha} = -\frac{\partial z(p,N,T_{\text{eff}})}{\partial p}\left[\frac{\partial z(p,N,T_{\text{eff}})}{\partial T_{\text{eff}}}\right]^{-1} = \frac{\partial T_{\text{eff}}(p,N,z)}{\partial p}. \tag{23}$$

In view of the fact that Eqs. (20) and (22) also share a common factor, we write

$$\begin{aligned} T_{\mathrm{eff}} V \frac{\Delta \alpha}{\Delta C_p} &= \frac{\partial V(p,N,T_{\mathrm{eff}},z)}{\partial z}\left[\frac{\partial S(p,N,T_{\mathrm{eff}},z)}{\partial z}\right]^{-1} \\ &= -\frac{\partial A(p,N,T_{\mathrm{eff}},z)}{\partial p}\left[\frac{\partial A(p,N,T_{\mathrm{eff}},z)}{\partial T_{\mathrm{eff}}}\right]^{-1} \\ &= \frac{\partial T_{\mathrm{eff}}(p,N,z)}{\partial p}. \end{aligned} \tag{24}$$

Because the right-hand sides of Eqs. (23) and (24) are equal, we obtain

$$\frac{\Delta C_p \Delta \kappa}{T_{\mathrm{eff}} V (\Delta \alpha)^2} = 1. \tag{25}$$

The combination of jumps on the left-hand side of Eq. (25) is known as the Prigogine-Defay ratio [8,15]. Further thermodynamic relationships of a similar type can be found in Eqs. (4.4) and (4.5) of the classical paper [1]. Such general relationships are important because the jumps in thermodynamic material properties are a hallmark of glasses. According to Kauzmann (see p. 227 of Ref. [16]), "the glassy state is a form of matter which maintains the structure, energy, and volume of a liquid, but for which *changes* in energy and volume with temperature are similar in magnitude to those of a crystalline solid." General relationships between the jumps in different quantities hence underline the power of the thermodynamic approach. Experimental values between 1 and 5 have been found for the Prigogine-Defay ratio, and even values smaller than 1 have been suggested [1,8]. In view of these considerable deviations from unity, we need to reconsider the formal derivation of Eq. (25).

We first need to consider more carefully to what extent the various jumps in thermodynamic properties introduced here depend on the particular choice of the generalized effective temperature and are thus ambiguous. The expressions in Eqs. (20) and (22) actually depend on the choice of the variable $z = z(p,N,T_{\mathrm{eff}})$ only because the concepts of pressure and temperature change with the choice of z. As discussed before, for the introduction of thermodynamic properties in the glassy state, and hence for the evaluation of jumps, it is important to choose an out-of-equilibrium variable z that leads to generalizations of pressure and temperature properly reflecting the experimental situation. It is not obvious that such a choice is at all possible within the class of generalized effective temperatures.

Equation (21) depends in an even more essential way on our choice of z. The factor $\partial z(p,N,T_{\mathrm{eff}})/\partial p$ in Eq. (21) requires an assumption on how to relate generalized effective temperatures at different pressures. If z is simply taken as the effective temperature, introduced as in Fig. 1 for any pressure, then, by construction, the ratio occurring in Eqs. (23) and (24) actually turns out to be zero. This choice of z seems to be inappropriate because, if we change the pressure on a glassy sample, then the temperature at which the transition from the glass to the supercooled liquid occurs for this sample changes, too. Therefore the compressibility of the glass should not be evaluated at constant effective temperature. If we assume that effective temperatures are affected by pressure in the same way as the glass transition temperature $T_{\mathrm{g}}(p)$, then it is natural to use the generalized effective temperature

$$z_{\mathrm{g}} = T_{\mathrm{eff}} - T_{\mathrm{g}}(p), \tag{26}$$

so that

$$\frac{\partial T_{\mathrm{eff}}(p,N,z_{\mathrm{g}})}{\partial p} = \frac{dT_{\mathrm{g}}}{dp}. \tag{27}$$

From Eqs. (23) and (24) we then obtain the first and second Ehrenfest relations [8,15], respectively,

$$\frac{\Delta \kappa}{\Delta \alpha} = \frac{dT_{\mathrm{g}}}{dp}, \tag{28}$$

and

$$T_{\mathrm{g}} V \frac{\Delta \alpha}{\Delta C_p} = \frac{dT_{\mathrm{g}}}{dp}. \tag{29}$$

As an alternative, we might use the viscosity level z_{vl} as a proper out-of-equilibrium variable. This suggestion is motivated by the fact that, for many fluids, the viscosity depends only weakly on the pressure. If we consider the level of 10^{13} P, then we indeed find the Ehrenfest relations (28) and (29).

Assuming that z_{g} or z_{vl} is a proper generalized effective temperature variable in the arguments of Davies and Jones [1], then the Prigogine-Defay ratio in Eq. (25) should be unity. If this relationship is found to be violated in experiments, then this indicates that ELIANE with a single out-of-equilibrium variable z is insufficient [for several additional variables, one expects the Prigogine-Defay ratio in Eq. (25) to be larger than unity [1]], or that one has to be more careful with the out-of-equilibrium generalizations of temperature and pressure and with the introduction of thermodynamic material properties in the glassy state, properly reflecting the experimental situation. In the rest of this subsection, we suggest appropriate expressions for the jumps in thermodynamic material properties.

The atomistic approach, as described in the next subsection dealing with the inherent-structure formalism, suggests that proper out-of-equilibrium variables are based on the additional pair of variables $z' = S_{\mathrm{conf}}$ and $A' = T - T_{\mathrm{eff}}$. The jump in the thermal expansivity,

$$\begin{aligned} \Delta \alpha &= \frac{1}{V} \left. \frac{\partial V(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}} \right|_{T=T_{\mathrm{eff}}} \\ &= -\frac{1}{V} \left. \frac{\partial S_{\mathrm{conf}}(p',N,T,T_{\mathrm{eff}})}{\partial p'} \right|_{T=T_{\mathrm{eff}}}, \end{aligned} \tag{30}$$

is formally obtained by setting $z = T_{\mathrm{eff}}$ in Eq. (20), but the variables p' and T should actually be those associated with our fundamental choice $z' = S_{\mathrm{conf}}$, and the second expression follows from the Maxwell relation (16). Note that the derivative of S_{conf} with respect to p' can actually be performed in the metastable liquid state, where pressure and temperature are defined unambiguously. For practical calculations, the following expression may be more convenient:

$$\Delta\alpha = \frac{\partial S_{\mathrm{conf}}(V,N,T)}{\partial V}\kappa_{\mathrm{liquid}}, \tag{31}$$

where $S_{\mathrm{conf}}(V,N,T)$ and the isothermal compressibility are evaluated in the supercooled liquid state at $T=T_{\mathrm{eff}}$.

The expression for the heat capacity at constant pressure is similar to Eq. (30),

$$\begin{aligned}\Delta C_p &= T_{\mathrm{eff}} \left.\frac{\partial S(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}}\right|_{T=T_{\mathrm{eff}}} \\ &= T_{\mathrm{eff}}\left[\frac{\partial S_{\mathrm{conf}}(p',N,T,T_{\mathrm{eff}})}{\partial T} \right.\\ &\quad \left. + \frac{\partial S_{\mathrm{conf}}(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}}\right]_{T=T_{\mathrm{eff}}},\end{aligned} \tag{32}$$

where the decomposition in Eq. (14) and the Maxwell relation (17) have been used. In terms of the configurational entropy $S_{\mathrm{conf}}(p',N,T)$ of the metastable liquid, we thus have

$$\Delta C_p = T \left.\frac{\partial S_{\mathrm{conf}}(p',N,T)}{\partial T}\right|_{T=T_{\mathrm{eff}}}, \tag{33}$$

which reflects the freezing of the configurational entropy contribution in the glassy state as the origin of the jump. Together with Eq. (31), we can rewrite this equation as

$$\Delta C_p = TV\frac{\alpha_{\mathrm{liquid}}}{\kappa_{\mathrm{liquid}}}\Delta\alpha + T\frac{\partial S_{\mathrm{conf}}(V,N,T)}{\partial T}, \tag{34}$$

where the configurational entropy, the thermal expansivity, and the isothermal compressibility are evaluated in the supercooled liquid at $T=T_{\mathrm{eff}}$. Equations (31) and (34) characterize the configurational entropy $S_{\mathrm{conf}}(V,N,T)$ in the metastable liquid in terms of experimentally accessible quantities.

From Eqs. (30) and (33), we obtain the following generalization of the second Ehrenfest relation (29):

$$T_{\mathrm{eff}}V\frac{\Delta\alpha}{\Delta C_p} = \frac{\partial T(p',N,S_{\mathrm{conf}})}{\partial p'}. \tag{35}$$

The right-hand side of this relationship involves only the relationship between T and S_{conf} for fixed p' and N in the metastable liquid state. This generalized Ehrenfest relation holds for any jump of slope in Fig. 1 at a temperature $T=T_{\mathrm{eff}}$, not only at the glass transition, that is, for jumps caused by different cooling rates. Our discussion of the jumps is thus more general than in the work [8], which uses the same nonequilibrium definitions of p' and T in the glassy state by assuming the fundamental form (15) but considers only jumps at the glass transition. Actually, the more general discussion is more transparent because, in Eq. (2.23) and the following equations of Ref. [8], both the glass transition temperature and an effective temperature appear in a confusing way.

Equation (29) would be recovered at the glass transition if the configurational entropy at $T_g(p')$ was independent of p'. If we rather assume that $T_g(p')S_{\mathrm{conf}}(p',N,T_g(p'))$ is independent of p', which would imply a constant characteristic equilibration time according to the arguments of Adam and Gibbs [see Eq. (93) below], then we arrive at

$$\begin{aligned}T_g V\frac{\Delta\alpha}{\Delta C_p} &= \frac{dT_g}{dp'}\left\{1 + \left[\frac{T}{S_{\mathrm{conf}}(p',N,T)}\frac{\partial S_{\mathrm{conf}}(p',N,T)}{\partial T}\right]^{-1}_{T=T_g}\right\} \\ &= \frac{dT_g}{dp'}\left(1 + \frac{S_{\mathrm{conf}}}{\Delta C_p}\right).\end{aligned} \tag{36}$$

Note that Eq. (36) is based on a particular assumption for the behavior of the configurational entropy along the glass transition line and hence is less general than Eq. (35).

In order to evaluate the jump in the isothermal compressibility we need to characterize the cooling conditions at different pressures through a curve $T_{\mathrm{eff}}(p')$. We do not need to restrict ourselves to the glass transition with $T_{\mathrm{eff}}(p')=T_g(p')$. The further discussion can be based on the following expressions for the volume in the liquid and glassy situations obtained by suitable choices of the effective temperature in the general formula for $V(p',N,T,T_{\mathrm{eff}})$,

$$V_{\mathrm{liquid}}(p',N,T) = V(p',N,T,T), \tag{37}$$

and

$$V_{\mathrm{glass}}(p',N,T) = V(p',N,T,T_{\mathrm{eff}}(p')), \tag{38}$$

where the transition at $T=T_{\mathrm{eff}}(p')$ is clearly continuous. The resulting jump in the thermal expansivity is given by Eq. (30), and the jump in isothermal compressibility is obtained as

$$\Delta\kappa = \frac{1}{V}\left.\frac{\partial V(p',N,T,T_{\mathrm{eff}})}{\partial T_{\mathrm{eff}}}\right|_{T=T_{\mathrm{eff}}=T_{\mathrm{eff}}(p')}\frac{dT_{\mathrm{eff}}(p')}{dp'}. \tag{39}$$

We thus obtain the generalized first Ehrenfest relation,

$$\frac{\Delta\kappa}{\Delta\alpha} = \frac{dT_{\mathrm{eff}}(p')}{dp'}, \tag{40}$$

which, as emphasized in Ref. [8] for the special case $T_{\mathrm{eff}}(p')=T_g(p')$, is simply a geometric relationship for the continuous transition between Eqs. (37) and (38) along a given line.

C. Inherent-structure formalism

In the general context of ELIANE, it is natural to split the entropy in the form (14). As a next step, we split also the energy by identifying a contribution associated with "inherent structures." Whereas the entropy split is based entirely on thermodynamic arguments, we need to understand atomistic configurations to obtain a split of energy by statistical mechanics. In addition, we get an atomistic interpretation of S_{conf} instead of an indirect approach based on the somewhat vague phenomenological concept of effective temperature. This direct statistical interpretation makes the inherent-structure approach particular attractive, but it is only one of several possibilities to implement the consequences of geometric "frustration," that is, the incompatibility between spatial extension of the locally preferred order and tiling of the whole space [17].

In the inherent-structure formalism [18], the configuration space is divided into basins. A basin consists of all the configurations moving to the same local minimum of the potential energy when evolved according to the artificial steepest-descent dynamics,

$$\frac{d\boldsymbol{r}_j}{dt} = -\tilde{\mu}\frac{\partial\Phi}{\partial\boldsymbol{r}_j}, \tag{41}$$

where $\tilde{\mu}$ is a constant parameter, Φ is the total potential energy, and $\boldsymbol{r}_j$ gives the configurational coordinates of particle j. The local minimum of Φ defines the inherent structure for its basin, in particular, an energy level E_{is}. Moreover, one usually determines also the eigenvalues of the quadratic form describing the energy near the local minimum, which lead to the harmonic approximation for the entropy associated with fast processes deep in the basin.

The inherent-structure formalism provides a statistical background for ELIANE. Noting that transitions from one deep basin to another deep basin, known as α processes [19], are very slow, the entropy S_{fp} and the corresponding temperature T can be obtained by standard statistical mechanics for the system constrained to a deep basin (see Appendix A). More conveniently, from the canonical statistical mechanics of our system constrained to a particular basin, we obtain the Helmholtz free energy $F_{\text{fp}}(V,N,T,E_{\text{is}})$ where we assume that this free energy does not depend on the particular basin but only on the energy of the inherent structure (otherwise, F_{fp} needs to be introduced through an average partition function for given E_{is}; see Appendix A). Fast processes in a deep basin are known as β processes. A clear distinction between α and β processes requires a two-scale potential-energy landscape with deep large-scale "craters" or "megabasins" (see Fig. 7 of Ref. [20] or Fig. 4 of Ref. [21]). The entropy $S_{\text{conf}}=S_{\text{conf}}(V,N,E_{\text{is}})$ is associated with the number of basins for a given value of the energy of the inherent structure. The implicit assumption that all basins are equally important in calculating thermodynamic properties is convenient but not obvious; it has, for example, been carefully analyzed in Ref. [22]. Because $S_{\text{conf}}(V,N,E_{\text{is}})$ is by construction independent of T, E_{is} is an example of a inherent structure variable (in general, a weak one). We next consider the auxiliary function [12],

$$\tilde{F}(V,N,T,T_{\text{eff}},E_{\text{is}}) = E_{\text{is}} - T_{\text{eff}}S_{\text{conf}}(V,N,E_{\text{is}}) + F_{\text{fp}}(V,N,T,E_{\text{is}}). \tag{42}$$

In order to obtain ELIANE, we need to establish a relationship between the two additional variables T_{eff} and E_{is} such that

$$F(V,N,T,T_{\text{eff}}) = \tilde{F}(V,N,T,T_{\text{eff}},E_{\text{is}}(V,N,T,T_{\text{eff}})) \tag{43}$$

becomes the total Helmholtz free energy of the equilibrium-like approach with the additional variable T_{eff} and separate Legendre transforms for S_{fp} and S_{conf} in Eq. (15). This explicit relationship $E_{\text{is}}(V,N,T,T_{\text{eff}})$ between a weak inherent structure variable and the effective temperature is given by the requirement

$$\frac{\partial F(V,N,T,T_{\text{eff}})}{\partial T_{\text{eff}}} = -S_{\text{conf}}, \tag{44}$$

which can be rewritten in the mathematically convenient form

$$\frac{\partial \tilde{F}(V,N,T,T_{\text{eff}},E_{\text{is}})}{\partial E_{\text{is}}} = 0 \tag{45}$$

or as a physically illuminating expression for the effective temperature [(see Eq. (4) of Ref. [9]],

$$\frac{1}{T_{\text{eff}}(V,N,T,E_{\text{is}})} = \frac{\partial S_{\text{conf}}(V,N,E_{\text{is}})}{\partial E_{\text{is}}}\left[1+\frac{\partial F_{\text{fp}}(V,N,T,E_{\text{is}})}{\partial E_{\text{is}}}\right]^{-1}. \tag{46}$$

Equation (45) is the nonequilibrium generalization of the saddle-point approximation used in Appendix A, and Eq. (46) is the generalization of Eq. (A8) when T and E_{is} are used as independent variables in ELIANE.

When the statistical mechanics of a basin is independent of its depth, we have $\partial F_{\text{fp}}/\partial E_{\text{is}}=0$ and the correction factor in Eq. (46) is absent [12]. Only then, $T_{\text{eff}}(V,N,E_{\text{is}})$ would be an inherent structure variable. This assumption is questioned in Fig. 2 of Ref. [9] where the relationship between T_{eff} and E_{is} is studied explicitly for the aging of a Lennard-Jones binary mixture after a temperature jump from above to below the glass transition temperature. Note the further relationship

$$\frac{\partial F(V,N,T,T_{\text{eff}})}{\partial T} = \frac{\partial F_{\text{fp}}(V,N,T,E_{\text{is}})}{\partial T} = -S_{\text{fp}}, \tag{47}$$

reflecting conventional statistical mechanics in a given basin. Because $F(V,N,T,T_{\text{eff}})$ is the Helmholtz free energy obtained as the double Legendre transform of the energy with the fundamental form Eq. (15), the concepts of temperature and pressure occurring in the inherent-structure formalism are those associated with any strong inherent structure variable z.

Equation (45) is useful for evaluating partial derivatives of the Helmholtz free energy (43) because any dependence via E_{is} can be neglected. For example, one obtains the pressure

$$\begin{aligned} p' &= -\frac{\partial F(V,N,T,T_{\text{eff}})}{\partial V} = -\frac{\partial \tilde{F}(V,N,T,T_{\text{eff}},E_{\text{is}})}{\partial V} \\ &= T_{\text{eff}}\frac{\partial S_{\text{conf}}(V,N,E_{\text{is}})}{\partial V} - \frac{\partial F_{\text{fp}}(V,N,T,E_{\text{is}})}{\partial V}, \end{aligned} \tag{48}$$

suggesting a clear distinction of inherent-structure and fast-process contributions to the pressure [12]. By means of Eq. (46) and standard rules of multivariate calculus, the inherent-structure contribution to the pressure can be rewritten as

$$p_{\text{is}} = -\frac{\partial E_{\text{is}}(V,N,S_{\text{conf}})}{\partial V}\left[1+\frac{\partial F_{\text{fp}}(V,N,T,E_{\text{is}})}{\partial E_{\text{is}}}\right], \tag{49}$$

which shows that, in general, the correction factor leads to a T dependence in addition to the expected dependence of the inherent-structure contribution p_{is} on V, N, and E_{is}. This T dependence has been neglected in Eq. (9) of Ref. [12]. If we choose E_{is} as the out-of-equilibrium variable z in the fundamental form (1), then the corresponding affinity is given by the dimensionless quantity

$$A = (T - T_{\text{eff}})\frac{\partial S_{\text{conf}}(V,N,E_{\text{is}})}{\partial E_{\text{is}}} = \left(\frac{T}{T_{\text{eff}}} - 1\right) \times\left[1 + \frac{\partial F_{\text{fp}}(V,N,T,E_{\text{is}})}{\partial E_{\text{is}}}\right] = \left(1 - \frac{T}{T_{\text{eff}}}\right)p_{\text{is}}\left[\frac{\partial E_{\text{is}}(V,N,S_{\text{conf}})}{\partial V}\right]^{-1}. \qquad (50)$$

In a large number of publications, the inherent-structure formalism has been used to analyze the results of molecular-dynamics simulations. The intrinsic problem of such simulations is the limited simulation time (typically, of the order of a few microseconds). Therefore cooling rates need to be extremely large; even cooling rates larger than 10^{10} K/s have been considered "slow." Upper and lower limits on cooling rates have been discussed by Jäckle [15]. Cooling must be sufficiently fast to avoid crystallization, and it should be sufficiently slow so that at least the vibrational degrees of freedom remain at equilibrium at any time.

The above discussion of inherent structures is based on the energy landscape. However, inherent structures have also been identified for hard-sphere glasses, where stable packings require percolating frameworks of rigidly jammed spheres and the effects of density are most relevant. Speedy [23] performed simulations to study the equation of state and the entropy of the hard-sphere glass. He concluded that the glass transition in hard spheres is a consequence of the geometry of the configuration space with a narrow distribution of the densities of inherent structures, and not simply a kinetic phenomenon. However, this conclusion cannot easily be generalized to other systems.

D. Models of energy landscape

Models of the functional forms of $S_{\text{conf}}(V,N,E_{\text{is}})$ and $F_{\text{fp}}(V,N,T,E_{\text{is}})$ have been obtained both from theoretical considerations [24,25] and from simulation results [26] (see also Ref. [27] and references therein). Successful fits of simulation data are given by

$$S_{\text{conf}}(V,N,E_{\text{is}}) = Nk_B\left[\alpha_0 - \frac{1}{2}\alpha_1\left(\frac{E_{\text{is}}}{N} - \alpha_2\right)^2\right] \qquad (51)$$

and

$$F_{\text{fp}}(V,N,T,E_{\text{is}}) = F_0(V,N,T) + \alpha_3 T(E_{\text{is}} - \alpha_2 N), \qquad (52)$$

where α_0, α_1, α_2, and α_3 are functions of the single variable V/N. In view of the extensivity of S_{conf} and F_{fp}, the key findings are the quadratic dependence and the linear dependence on E_{is}, respectively. In Ref. [26], the functional forms (51) and (52) have been verified and three combinations of the four functions α_j of V/N have been determined explicitly for the Lewis-Wahnström potential [28] providing a model of the fragile glass former ortho-terphenyl, which is one of the most studied glass forming liquids. Because of the quadratic dependence of S_{conf} on E_{is}, Eq. (51) is known as the Gaussian model of the configurational entropy. From Eq. (46), we obtain for the Gaussian model with the help of Eq. (52)

$$E_{\text{is}}(V,N,T,T_{\text{eff}}) = N\left(\alpha_2 - \frac{1 + \alpha_3 T}{\alpha_1 k_B T_{\text{eff}}}\right). \qquad (53)$$

By inserting $E_{\text{is}}(V,N,T,T)$ into expression (51), we obtain the configurational entropy of the supercooled liquid ($T = T_{\text{eff}}$) for the Gaussian model,

$$S_{\text{conf}}(V,N,T) = Nk_B\left[\alpha_0 - \frac{1}{2\alpha_1}\left(\frac{1 + \alpha_3 T}{k_B T}\right)^2\right]. \qquad (54)$$

Note that this expression for $S_{\text{conf}}(V,N,T)$ determines the model predictions for the jumps in the thermal expansivity and heat capacity according to Eqs. (31) and (34). The configurational entropy vanishes at the temperature

$$T_{\text{K}} = (k_B\sqrt{2\alpha_0\alpha_1} - \alpha_3)^{-1}, \qquad (55)$$

below which the metastable supercooled liquid cannot exist. The Gaussian model has been carefully discussed and compared to so-called hyperbolic and logarithmic models in Ref. [29].

A logarithmic energy landscape was formulated by Debenedetti *et al.* [24] by theoretical considerations based on a two-state model. A more sophisticated two-state model with Gaussian widths for the site energies of both ground and excited states has recently been developed [25] (this work, moreover, contains an up-to-date review of models of the energy landscape).

E. Exactly solvable lattice model

For the purpose of illustrating various concepts of ELIANE by specific results, in particular in the light of the inherent-structure formalism, we summarize the basic features of an exactly solvable model proposed and studied by Leuzzi and Nieuwenhuizen [19,30]. They formulated a microscopic lattice model for a set of N noninteracting harmonic oscillators X_i (slow variables) coupled to a set of N spherical spins S_i with $\Sigma_i S_i^2 = N$ (fast variables). The Hamiltonian,

$$\mathcal{H}(X_i,S_i) = \frac{1}{2}K\sum_{i=1}^{N} X_i^2 - H\sum_{i=1}^{N} X_i - J\sum_{i=1}^{N} X_i S_i - L\sum_{i=1}^{N} S_i, \qquad (56)$$

contains the parameters K, J, and L, which we assume to have given values representing a particular situation or chemical system, and the external field H. We here ignore dynamic aspects and focus entirely on the thermodynamic aspects of equilibrium and of ELIANE. As thermodynamic variables, we use the temperature T and the external field H acting on the harmonic oscillators. In a given thermodynamic equilibrium state (N,T,H), the average first and second moments of the slow harmonic oscillators can be expressed as

$$m_1 = m_1^{\text{eq}}(T,H), \quad m_2 = m_2^{\text{eq}}(T,H), \qquad (57)$$

where the functions $m_1^{\text{eq}}(T,H)$ and $m_2^{\text{eq}}(T,H)$ have been evaluated by Leuzzi and Nieuwenhuizen in the saddle-point approximation [see Eqs. (2.15) and (2.16) of Ref. [19]; see also Eq. (70) below]. We here prefer to work with the variance μ_2 instead of the second moment m_2,

$$\mu_2 = m_2 - m_1^2. \tag{58}$$

The saddle-point approximation suggests the following form of the thermodynamic potential per oscillator, where we suppress the trivial dependence on the number of particles N because we focus on the intensive quantity $\bar{F}/N$ [see Eq. (2.17) of Ref. [19]]:[2]

$$\frac{\bar{F}(T,H)}{N} = \frac{1}{2}K\mu_2 + \frac{1}{2}Km_1^2 - Hm_1 - w + \frac{k_BT}{2}\left[\ln\frac{(k_BT/2)+w}{k_BT} - (1+\ln\mu_2)\right]. \tag{59}$$

To identify the functional dependence of m_1, μ_2, and w on T and H, we consider the differential of the thermodynamic potential $\bar{F}$:

$$d\left(\frac{\bar{F}}{N}\right) = -m_1dH - \frac{1}{2}k_B\left[1 - \ln\frac{(k_BT/2)+w}{k_BT} + 1 + \ln\mu_2\right]dT + \frac{1}{2}Kd\mu_2 + (Km_1 - H)dm_1 - \frac{1}{2}\frac{d[w^2 - (k_BT)^2/4]}{(k_BT/2)+w} - \frac{k_BT}{2\mu_2}d\mu_2. \tag{60}$$

The proper thermodynamic relationship for the free energy $\bar{F}(T,H)$ with the average first moment m_1 and the total equilibrium entropy

$$S = \frac{1}{2}Nk_B\left[1 - \ln\frac{(k_BT/2)+w}{k_BT} + 1 + \ln\mu_2\right] \tag{61}$$

is obtained by requiring that the contributions in the last two lines of Eq. (60) add up to zero. We hence assume

$$w^2 = \frac{(k_BT)^2}{4} + g(m_1,\mu_2), \tag{62}$$

and we then obtain the conditions

$$H + \frac{1}{2}\frac{1}{(k_BT/2)+w}\frac{\partial g}{\partial m_1} = Km_1, \tag{63}$$

and

$$K - \frac{1}{(k_BT/2)+w}\frac{\partial g}{\partial \mu_2} = \frac{k_BT}{\mu_2}. \tag{64}$$

The explicit functional form of $g(m_1,\mu_2)$ in Eq. (62), as obtained by the saddle-point approximation, is given by [see Eq. (2.4) of Ref. [19]]

$$w^2 = \frac{(k_BT)^2}{4} + J^2\mu_2 + (Jm_1 + L)^2, \tag{65}$$

and we hence obtain

$$H + \frac{JL}{(k_BT/2)+w} = \left(K - \frac{J^2}{(k_BT/2)+w}\right)m_1, \tag{66}$$

and

$$K - \frac{J^2}{(k_BT/2)+w} = \frac{k_BT}{\mu_2}. \tag{67}$$

If we introduce the auxiliary variables

$$\tilde{H} = H + \frac{JL}{(k_BT/2)+w} \tag{68}$$

and

$$\tilde{K} = K - \frac{J^2}{(k_BT/2)+w}, \tag{69}$$

then we obtain the relationships

$$m_1^{\mathrm{eq}} = \frac{\tilde{H}}{\tilde{K}}, \quad \mu_2^{\mathrm{eq}} = \frac{k_BT}{\tilde{K}}, \tag{70}$$

where $\tilde{H}$ and $\tilde{K}$ depend on the equilibrium values of m_1 and μ_2 through w. The explicit functional dependence of m_1^{eq} and μ_2^{eq} on T and H is hence more complicated. It can be obtained in closed form by solving fourth-order equations.

The dynamics of the microscopic harmonic-oscillator spherical spin model is defined by a Monte Carlo procedure, where the jump probabilities depend on T and H. By averaging, this dynamics can be used to derive time-evolution equations for the moments m_1 and m_2, or for m_1 and μ_2 [19,30]. We here do not go into the details of the slow dynamics of the exactly solvable model.

A typical situation to be analyzed is as follows. The system is equilibrated at a high temperature T_0 and an external field H_0 in the liquid state. Equations (70) are used to calculate the equivalent equilibrium values m_1 and μ_2. One then quenches the system to T and H in the neighborhood of the glass transition temperature and one calculates the slow evolution of $m_1(t)$ and $\mu_2(t)$ from the time-evolution equations. This aging process after a quench can be expressed equivalently in terms of the effective thermodynamic variables $T_{\mathrm{eff}}(t)$ and $H(t)$ characterizing the out-of-equilibrium state, which are to be derived in terms of $m_1(t)$ and $\mu_2(t)$ my means of the inherent-structure approach.

Although there exists no complex potential-energy landscape in the model of Leuzzi and Nieuwenhuizen, and certainly not a two-scale landscape with deep craters, we wish to illustrate some basic features of the inherent-structure ap-

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[2] The thermodynamic potential $\bar{F}(T,H)$ is usually referred to as the Helmholtz free energy; note, however, that *two* Legendre transformations of the energy need to be performed to pass from the entropy to the temperature and from the average moment to the external field as intensive independent variables, $\bar{F}=E-TS-NHm_1$. We therefore use an overbar to distinguish $\bar{F}(T,H)$ from $F(T,m_1)$, which requires only *one* Legendre transformation and which can be obtained as $F=E-TS=\bar{F}+NHm_1$.

proach for the harmonic-oscillator spherical spin model. The most natural out-of-equilibrium Helmholtz free energy is obtained by generalizing Eq. (59):

$$\frac{F}{N}=\frac{F(m_1,N,T,\mu_2)}{N}=\frac{1}{2}K\mu_2+\frac{1}{2}Km_1^2-w+\frac{k_BT}{2}\left[\ln\frac{(k_BT/2)+w}{k_BT}-(1+\ln\mu_2)\right], \tag{71}$$

where, compared to the free energy in Eq. (3), the first moment m_1 plays the role of V/N, μ_2 is taken as the out-of-equilibrium variable z, and $w=w(T,m_1,\mu_2)$ is given in Eq. (65). The term $-Hm_1$ has been dropped because we here do not perform a Legendre transformation from the moment to the external field.[3] The identification of the expression (71), in which m_1, T, and μ_2 are independent variables, from the equilibrium result with redundant variables according to Eq. (70) is not unique. Although the occurrence of the different variables in Eq. (71) looks natural, the crucial check is whether the resulting ELIANE reproduces the results for the exactly solvable model of strong glasses in the aging regime near $T=0$.

By differentiating Eq. (71) with respect to μ_2, we obtain the corresponding activity variable

$$A(m_1,N,T,\mu_2)=\frac{1}{2}N\left[\frac{k_BT}{\mu_2}-K+\frac{J^2}{(k_BT/2)+w}\right], \tag{72}$$

and by differentiating F/N with respect to T, we obtain the entropy (61). There is a natural entropy contribution in Eq. (61) that is independent of temperature and suggests that μ_2 is an inherent structure variable [see Eq. (2.14) of Ref. [19]]:

$$S_{\text{conf}}=S_{\text{conf}}(N,\mu_2)=\frac{1}{2}Nk_B(1+\ln\mu_2). \tag{73}$$

Because S_{conf} is independent of m_1, the inherent structure variable μ_2 is of the strong type that allows an unambiguous evaluation of the external field H in out-of-equilibrium situations. Instead of a quadratic energy dependence of the configurational entropy in Eq. (51), we here find a nonalgebraic functional form involving a logarithm. With the derivative of the configurational entropy,

$$\frac{\partial S_{\text{conf}}(N,\mu_2)}{\partial\mu_2}=\frac{1}{2}N\frac{k_B}{\mu_2}, \tag{74}$$

the expression (72) for the activity indeed is of the general form (13), and we obtain

$$T_{\text{eff}}(m_1,T,\mu_2)=\frac{\mu_2}{k_B}\left[K-\frac{J^2}{(k_BT/2)+w}\right]. \tag{75}$$

To introduce the unambiguous external field H in out-of-equilibrium situations, we finally differentiate Eq. (71) with respect to m_1 to find

$$H=\tilde{K}m_1-\frac{JL}{(k_BT/2)+w}. \tag{76}$$

The results (75) and (76) coincide with the exact formulas given by Leuzzi and Nieuwenhuizen for strong glasses [see Eq. (2.44) of Ref. [19]]. For the harmonic-oscillator spherical spin model, we thus have achieved full consistency between the exact solution of the model and ELIANE. We have seen how the strong inherent structure variable $z=\mu_2$ can be used to describe out-of-equilibrium states, and we have encountered explicit examples of functional forms for the Helmholtz free energy and the entropy contributions of ELIANE. Less suitable definitions of the effective temperature in the inherent-structure approach have been compared in Figs. 3 and 4 of Ref. [19].

So far, we have not identified an inherent-structure contribution E_{is} to the total energy E which follows from Eqs. (71) and (61),

$$\frac{E}{N}=\frac{1}{2}K\mu_2+\frac{1}{2}Km_1^2+\frac{1}{2}k_BT-w, \tag{77}$$

where $w=w(T,m_1,\mu_2)$ is given in Eq. (65). For completeness, we also specify the function $E_{\text{is}}(m_1,N,\mu_2)$. According to Leuzzi and Nieuwenhuizen [see Eq. (3.16) of Ref. [19]], this function can be obtained by setting $T=0$ in Eq. (77). We thus obtain

$$\frac{E_{\text{is}}}{N}=\frac{1}{2}K\mu_2+\frac{1}{2}Km_1^2-\sqrt{J^2\mu_2+(Jm_1+L)^2}. \tag{78}$$

Note that, like μ_2, E_{is} is an inherent structure variable but, unlike μ_2, it leads to a modified external field H' because it is of the weak type. We can use the expression for E_{is} to evaluate the main contribution to the effective temperature in Eq. (46),

$$\begin{aligned}T_{\text{eff,app}}&=\left(\frac{\partial S_{\text{conf}}(m_1,N,E_{\text{is}})}{\partial E_{\text{is}}}\right)^{-1}\\&=\left(\frac{\partial S_{\text{conf}}(N,\mu_2)}{\partial\mu_2}\right)^{-1}\frac{\partial E_{\text{is}}(m_1,N,\mu_2)}{\partial\mu_2}\\&=\frac{\mu_2}{k_B}\left[K-\frac{J^2}{\sqrt{J^2\mu_2+(Jm_1+L)^2}}\right].\end{aligned} \tag{79}$$

This approximate expression, which coincides with Eq. (75) only for $T=0$, has been introduced as the "conceptually more properly chosen" definition of the effective temperature in Eq. (3.27) of Ref. [19], where it was compared to a less reliable energy-matching procedure for defining T_{eff}. Whereas this approximation gives "a good approximation but is nevertheless never analytically correct in the description of the real temperature dynamics" [19], by reproducing the exact result, we have shown that this discrepancy is not an intrinsic problem of the inherent-structure approach. While $T_{\text{eff,app}}$ is an inherent structure variable, T_{eff} is not because of the T dependence in Eq. (75). In particular, $S_{\text{conf}}(m_1,N,T,T_{\text{eff}})$ hence depends explicitly on T in addition to T_{eff}.

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[3] This omission corresponds to the previously mentioned relationship $F=\bar{F}+NHm_1$.

II. GENERIC PERSPECTIVE

Time-evolution equations for nonequilibrium systems have a well-defined structure in which reversible and irreversible contributions are identified separately. In particular, the reversible contribution is generally assumed to be of the Hamiltonian form and hence requires an underlying geometric structure which reflects the idea that the reversible time evolution should be "under mechanistic control." The remaining irreversible contribution is driven by the gradient of a nonequilibrium entropy.

A. Abstract framework

Our discussion is based on the GENERIC ("general equation for the nonequilibrium reversible-irreversible coupling") formulation of time-evolution for nonequilibrium systems [31–33],

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}, \tag{80}$$

where x represents the set of independent variables required for a complete description of a given nonequilibrium system, E and S are the total energy and entropy expressed in terms of the variables x, and L and M are certain linear operators, or matrices, which can also depend on x. The two contributions to the time evolution of x generated by the total energy E and the entropy S in Eq. (80) are the reversible and irreversible contributions, respectively. Because x typically contains position-dependent fields, such as the local mass, momentum, and energy densities of hydrodynamics, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication, which can alternatively be considered as the application of a linear operator, hence implies not only summations over discrete indices but also integrations over continuous labels, and $\delta/\delta x$ typically implies functional rather than partial derivatives. Equation (80) is supplemented by the complementary degeneracy requirements

$$L\frac{\delta S}{\delta x} = 0 \tag{81}$$

and

$$M\frac{\delta E}{\delta x} = 0. \tag{82}$$

The requirement that the entropy gradient $\delta S/\delta x$ is in the null space of L in Eq. (81) expresses the reversible nature of the L contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the operator generating the reversible dynamics. The requirement that the energy gradient $\delta E/\delta x$ is in the null space of M in Eq. (82) expresses the conservation of the total energy in a closed system by the M contribution to the dynamics.

Further general properties of L and M are discussed most conveniently in terms of the Poisson and dissipative brackets,

$$\{A,B\} = \frac{\delta A}{\delta x}L\frac{\delta B}{\delta x}, \tag{83}$$

$$[A,B] = \frac{\delta A}{\delta x}M\frac{\delta B}{\delta x}, \tag{84}$$

where A, B are sufficiently regular real-valued functions on the space of independent variables. In terms of these brackets, Eq. (80) and the chain rule lead to the following time-evolution equation of an arbitrary function A in terms of the two separate generators E and S,

$$\frac{dA}{dt} = \{A,E\} + [A,S]. \tag{85}$$

The further conditions for L can now be stated as the antisymmetry property

$$\{A,B\} = -\{B,A\}, \tag{86}$$

the product or Leibniz rule

$$\{AB,C\} = A\{B,C\} + B\{A,C\}, \tag{87}$$

and the Jacobi identity

$$\{A,\{B,C\}\} + \{B,\{C,A\}\} + \{C,\{A,B\}\} = 0, \tag{88}$$

where C is another arbitrary sufficiently regular real-valued function on the state space. These properties are well-known from the Poisson brackets of classical mechanics, and they capture the essence of reversible dynamics.

Further properties of M can be formulated in terms of the symmetry condition

$$[A,B] = [B,A], \tag{89}$$

and the non-negativeness condition

$$[A,A] \geq 0. \tag{90}$$

This non-negativeness condition, together with the degeneracy requirement (81), guarantees that the entropy is a nondecreasing function of time,

$$\frac{dS}{dt} = \frac{\delta S}{\delta x}M\frac{\delta S}{\delta x} = [S,S] \geq 0. \tag{91}$$

The properties (89) and (90) imply the symmetry and the positive-semidefiniteness of M (for a more sophisticated discussion of the Onsager-Casimir symmetry properties of M, see Secs. 3.2.1 and 7.2.4 of Ref. [33]). From a physical point of view, M may be regarded as a friction matrix. The Jacobi identity (88), which is a highly restrictive condition for formulating proper reversible dynamics, expresses the invariance of Poisson brackets in the course of time (time-structure invariance).

B. Entropy or friction?

From the GENERIC perspective, the origin of glassy behavior can lie in a singularity of the entropy S or the friction matrix M (or both). Singular S corresponds to the idea of a thermodynamic origin of glassy behavior, whereas singular behavior of M without any peculiarities in S indicates a purely kinematic phenomenon.[4] Kauzmann [16] distinguished between a thermodynamic mechanism and a relaxation mechanism for the freezing-in of degrees of freedom. Both possibilities have been considered in the literature.

As early as 1948, Kauzmann [16] noticed that the difference between the supercooled liquid entropy and the crystal entropy would become negative if extrapolated to zero temperature. He proposed the existence of a "lower metastable limit" at the temperature where the entropy difference vanishes, which is nowadays referred to as the Kauzmann temperature T_{K}. He argued that, below the "pseudocritical point" at T_{K}, the metastable supercooled liquid ceases to exist. The aging of an amorphous state to the metastable liquid would take even longer than the crystallization process. Therefore if an amorphous state is observed below T_{K}, it must be of the glassy type [16].

It is generally assumed that Kauzmann's pseudocritical point would be accompanied by the experimentally observed exponential divergence of the characteristic time scale τ for structural relaxation (and hence also of the viscosity) with temperature T according to the Vogel-Fulcher-Tammann-Hesse law,

$$\tau \propto \exp\left\{\left(\frac{T_{\mathrm{A}}}{T-T_{\mathrm{K}}}\right)^{\gamma}\right\}, \tag{92}$$

with parameters T_{A} and γ for fragile glasses, where $\gamma=1$ is often suggested in the literature (for strong glasses, one observes Arrhenius behavior corresponding to $T_{\mathrm{K}}=0$ and $\gamma=1$; for a recent discussion of kinetic and thermodynamic concepts of fragility, that is, sensitivity to temperature variations, see Ref. [29], where the relation between these two different concepts is given by the Adam-Gibbs relation (93) derived below; a residual contribution to the excess entropy resulting from sub-T_{g} relaxations unrelated to transitions between deep basins might lead to a diverging time scale at temperatures above T_{K} [34]). Note that the functional form in Eq. (92) should not be considered as an accurate physical description of the relaxation process but as a candidate for a good fitting function over a considerable range of temperatures [20]. Fragile glass behavior results for a two-scale potential-energy landscape with deep "craters" [21] (strong glasses, on the other hand, correspond to a uniformly rough landscape with a single energy scale). Contrary to ordinary continuous phase transitions, the divergence of the relaxation time is nonalgebraic, and no susceptibility diverges at the singular point. The Adam-Gibbs relation

$$\tau \propto \exp\left\{\frac{cN}{TS_{\mathrm{conf}}}\right\}, \tag{93}$$

where c is a constant of the order of a molecular interaction energy, suggests that the exponential divergence of the relaxation time and hence of the viscosity has its origin in the small configurational entropy available at the Kauzmann temperature. Equation (93) is meant to describe the increase of the relaxation time in approaching the glass transition temperature T_{g} from above. Therefore the configurational entropy is considered as a function $S_{\mathrm{conf}}(V,N,T)$. Equation (93) for the characteristic relaxation time has successfully been extended through the glass transition temperature by considering the configurational entropy for out-of-equilibrium states (see remarks on p. 231 of Ref. [35]).

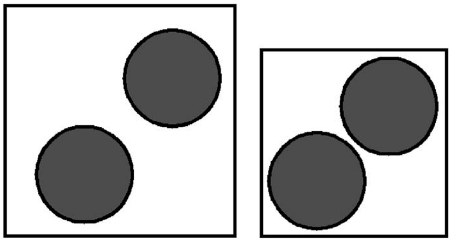

FIG. 2. Loss of ergodicity for two disks in a square box with increasing density.

The original derivation of Eq. (93) [36] is based on the observation that, with decaying configurational entropy, the following situation may arise:

$$\frac{S_{\mathrm{conf}}}{N} < k_B \ln 2 = z^* \frac{S_{\mathrm{conf}}}{N}, \tag{94}$$

where the equation part defines z^*. The quantity z^* can be interpreted as the minimum number of molecules in a cooperative region in which relaxation can take place because at least two different states (that is, the entropy $k_B \ln 2$) are required for the occurrence of a collective rearrangement. By assuming that τ is inversely proportional to the fraction of states permitting cooperative rearrangements, one expects $\tau \propto \exp\{z^* \Delta\mu / k_B T\}$, where the difference in chemical potential $\Delta\mu$ is largely the potential energy hindering the cooperative rearrangement per molecule and should hence be in the range of typical molecular interaction energies. By inserting the estimate for z^* obtained from Eq. (94), we thus arrive at Eq. (93) with $c=\Delta\mu \ln 2$. The argument of Adam and Gibbs explains the divergence of τ at the Kauzmann temperature. However, it suggests that z^* becomes very large whereas, in reality, the cooperative regions seem to contain only a few molecules. While this thermodynamic picture of fragile glasses is widely accepted, some doubts about the existence of the Kauzmann temperature arose in Monte Carlo simulations of the bond-fluctuation model for a polymer melt [37] and of a binary Lennard-Jones glass former [38].

A more general scaling approach to the time scale for structural relaxation can be found in Eqs. (34) and (35) of Ref. [17]. This approach is based on the idea of geometric "frustration" which leads to a mosaic of domains with a distribution of sizes (avoiding criticality by finite domain sizes, typically of the order of 5–10 molecular diameters at T_{g}).

A simple example for the origin of a singularity in the entropy is illustrated in Fig. 2. For two disks in a square box, only part of the configuration space is accessible when the density becomes so large that the diameter of the disks is larger than half of the box size. If one is willing to treat this

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[4] Assuming that the regression of fluctuations is governed by the same laws as macroscopic relaxation, a singularity in S is expected to lead also to a singular behavior of M.

small two-disk system by standard statistical mechanics, one finds a singularity of the entropy at the corresponding critical density. It has been conjectured that similar geometric reasons are the origin of the glass transition of hard-sphere systems upon increasing density [23].

In the exactly solvable model of Leuzzi and Nieuwenhuizen [19,30], both thermodynamic and kinematic effects are built in. A singularity of the entropy occurs only at $T=0$, so that merely strong glasses are modeled in a purely thermodynamic manner. To model fragile glasses, Leuzzi and Nieuwenhuizen design a Monte Carlo dynamics using random displacements with a configuration dependent variance. Only through this configuration dependent variance governing the dynamic behavior, which, in the spirit of GENERIC, corresponds to a singularity in the friction matrix M, the nonzero Kauzmann temperature is introduced. As a matter of fact, the variance is tuned carefully to cancel the Arrhenius behavior and to replace it by the Vogel-Fulcher-Tammann-Hesse law [see Eq. (2.24) of Ref. [19]].

C. Different regimes for glass formers

Because the relaxation time becomes infinite at the Kauzmann temperature T_{K} whereas relaxation is merely slow (typically of the order of minutes) at the glass-transition temperature T_{g}, we have $T_{\mathrm{K}}<T_{\mathrm{g}}$. Even above the glass transition, there generally exists a dynamic critical temperature where a rapid separation of slow and fast processes sets in. This temperature T_{da} at which a dynamic anomaly occurs is associated with a transition in the simple mode-coupling theory [39–41]. The characteristic temperatures

$$T_{\mathrm{K}} < T_{\mathrm{g}} < T_{\mathrm{da}} \tag{95}$$

define four different temperature regimes for glass formers. Because all these temperatures are below the melting point, the amorphous liquid phase is only metastable. We describe these regimes in the order of decreasing temperature [30].

(i) Above T_{da}, the system is in a metastable disordered liquid phase and the part of the configuration space associated with a deep minimum of the free energy is appropriately sampled on the typical time scale of an experiment.

(ii) Between T_{g} and T_{da}, the system is still in a disordered supercooled liquid phase, but the viscosity becomes large and relaxation times reach the limit of experimental possibilities.

(iii) Between T_{K} and T_{g}, we observe a slow aging process of our system, which is amorphous but, from a practical point of view, basically solid (the viscosity is larger than 10^{13} P). Asymptotically, the system would be ergodic and reach a metastable liquid state. However, in practice, it slowly explores basins of decreasing potential energy.

(iv) Below T_{K}, the system gets stuck in a single basin forever and ergodicity is broken for any time scale. The system would rather crystallize than reach a static amorphous limit in an aging process.

D. Relationship to ELIANE

To construct ELIANE from GENERIC, we follow the ideas used in the derivation of equilibrium thermodynamics from GENERIC (see Sec. 1.2.3 of Ref. [33]). To analyze the equilibrium solutions of GENERIC, both reversible and irreversible dynamics are generated by the function

$$\Omega(x;\lambda_E,\lambda_N) = S(x) - \lambda_E E(x) - \lambda_N N(x), \tag{96}$$

where the constant parameters λ_E and λ_N, which play the role of Lagrange multipliers, are related to the temperature and chemical potential at the equilibrium state reached in the course of time. The particle number $N(x)$ is degenerate for both the reversible and irreversible dynamics and hence does not contribute to the time evolution. The generalization to ELIANE is obtained by assuming that there is a further slow variable $z(x)$ for which we have the approximate degeneracy properties

$$L\frac{\delta z}{\delta x} = M\frac{\delta z}{\delta x} = 0. \tag{97}$$

In the spirit of the previous discussion, the approximately degenerate variable z could be the configurational entropy or the inherent-structure contribution to the energy. We here only assume that z is an extensive variable. The slower the aging process is, the better is the approximation (97). Because we now have a further constraint for the time evolution, we introduce an additional Lagrange multiplier into Eq. (96):

$$\Omega(x;\lambda_E,\lambda_N,\lambda_z) = S(x) - \lambda_E E(x) - \lambda_N N(x) - \lambda_z z(x). \tag{98}$$

According to the fundamental evolution equation (80), the entropy S increases until a steady state is reached for given values of E, N, and z. In constraining z, we have assumed that the steady state is reached on a time scale compared to which the aging process can be considered as infinitely slow.

The frozen state $x_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z)$ with a constant z is characterized by

$$\left.\frac{\delta\Omega(x;\lambda_E,\lambda_N,\lambda_z)}{\delta x}\right|_{x=x_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z)} = 0. \tag{99}$$

We next define the function

$$\Omega_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z,V) = \Omega(x_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z);\lambda_E,\lambda_N,\lambda_z), \tag{100}$$

where, like at equilibrium, a dependence on the volume of the isolated system has been indicated explicitly. Because λ_E, λ_N, and λ_z are intensive, the extensive quantity Ω_{f} must actually be proportional to V,

$$\frac{\partial\Omega_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z,V)}{\partial V} = \frac{\Omega_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z,V)}{V}. \tag{101}$$

From the definition (100) and Eqs. (98) and (99), we obtain

$$\frac{\partial\Omega_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z,V)}{\partial\lambda_E} = -E(x_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z)), \tag{102}$$

$$\frac{\partial\Omega_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z,V)}{\partial\lambda_N} = -N(x_{\mathrm{f}}(\lambda_E,\lambda_N,\lambda_z)), \tag{103}$$

and

$$\frac{\partial\Omega_{\rm f}(\lambda_E,\lambda_N,\lambda_z,V)}{\partial\lambda_z} = -z(x_{\rm f}(\lambda_E,\lambda_N,\lambda_z)). \qquad (104)$$

Equations (101)–(104) imply that $\Omega_{\rm f}$ is the Massieu function belonging to V and the conjugates of E, N, and z as independent variables, we conclude that

$$\Omega_{\rm f} = \frac{pV}{T}, \qquad (105)$$

and we recognize the Lagrange multipliers as

$$\lambda_E = \frac{1}{T}, \quad \lambda_N = -\frac{\mu}{T}, \quad \lambda_z = \frac{A}{T}. \qquad (106)$$

The resulting chain rule

$$d\Omega_{\rm f} = -E d\frac{1}{T} + N d\frac{\mu}{T} - z d\frac{A}{T} + \frac{p}{T}dV \qquad (107)$$

implies the fundamental form (1) of ELIANE with the entropy expression

$$S = S(x_{\rm f}) = \Omega_{\rm f} + \frac{1}{T}E - \frac{\mu}{T}N + \frac{A}{T}z. \qquad (108)$$

We have thus completed our construction of ELIANE from GENERIC by assuming the existence of an almost degenerate or almost infinitely slow variable $z(x)$. Note that a minimization of Ω is used to find the value of x in a frozen state for given Lagrange multiplier λ_z. However, there is no minimization procedure to find λ_z from the functional form of the Massieu function $\Omega_{\rm f}$. An out-of-equilibrium state is rather determined by the history of the system. As mentioned before, the significance of $\Omega_{\rm f}$ is that it determines the form of all equations of state and the thermodynamic material functions.

In the special case of a slow variable $z(x)=\xi$ included into the list of variables x and just one further variable y in x (in addition to the equilibrium variables and ξ), a similar derivation of ELIANE has been given by Grmela and Cournoyer [42]. Equation (15) of that paper may be considered as the full time-evolution equation comprising fast and slow processes, and their Eq. (25) as an approximate time evolution fulfilling the degeneracy requirements (97). The kinetics of the aging process is described by Eq. (8) of Ref. [42]. The difference between our generators (96) and (98) corresponds to the difference between $\varphi^{(1)}$ and $\varphi_1^{(1)}$ in Ref. [42]. By assuming that the fast variable y represents the rate of change of the slow variable ξ, by considering a quadratic dependence of $\varphi^{(1)}$ on the variable y, and by matching the aging processes with and without explicit consideration of y, Grmela and Cournoyer obtained the functional form of $\varphi_1^{(1)}$ and the corresponding thermodynamic potential for this particular situation.

III. TIME EVOLUTION

From the GENERIC perspective, it is most natural to formulate time-evolution equations. These equations should characterize the flow behavior of the supercooled melt when approaching the glass transition temperature, and even the viscoelastic behavior of the glass in the range between the glass transition temperature and the Kauzmann temperature as well as the slow aging dynamics below the glass transition temperature. The faster processes at an arrested effective temperature are related to the relaxation behavior of a glass, for example, as determined by rheometry on experimentally accessible time scales. Moreover, such time-evolution equations imply a more detailed version of the diagram in Fig. 1, with properties depending on the rate of temperature change and a hysteresis effect between cooling and heating (see p. 184 of Ref. [15]).

In addition to the hydrodynamic variables $x_{\rm hyd} = (\rho, \boldsymbol{M}, \epsilon_{\rm fp})$, where ρ is the mass density, $\boldsymbol{M}$ is the momentum density, and $\epsilon_{\rm fp}$ is the internal energy density associated with fast processes, we need slow structural variables. In order to get a rich rheological behavior, we cannot simply use a scalar effective temperature or inherent structure variable as introduced in the absence of flow. We need to introduce variables which allow us to characterize the anisotropic structures arising in flow. In the following, we consider two types of structural variables: the pair correlation for inherent structures and the combination of a related tensor and a scalar. Once a set of structural variables is specified, we need to determine the GENERIC building blocks. For polymer glasses, it may be necessary to introduce further variables describing the entangled polymer network in order to incorporate the proper strain hardening behavior observed for large deformations (see, for example, Ref. [43]).

Monte Carlo and molecular dynamics simulations are the key tools to determine GENERIC building blocks from first principles (see Chap. 8 of Ref. [33]). Once the coarse grained variables are specified, the statistical background of GENERIC provides straightforward recipes for the introduction of nonequilibrium ensembles and the quantities to be evaluated. The experience with thermodynamically guided simulations shows that they can be successful even at low flow rates thus probing the relaxation behavior on long time scales [44]. At the lowest rates, one can introduce Lagrange multipliers affecting only the slowest variables.

The simplest phenomenological equation describing the relaxation of the effective temperature reads

$$\frac{dT_{\rm eff}}{dt} = -\frac{1}{\tau(T,T_{\rm eff})}(T_{\rm eff}-T), \qquad (109)$$

where both $T_{\rm eff}$ and T depend on time. For the functional form of $\tau(T,T_{\rm eff})$, simple Arrhenius-type factors are often assumed for the dependence on both T and $T_{\rm eff}$ (for a detailed discussion of this and alternative forms of $\tau(T,T_{\rm eff})$, see Sec. 3.2 of Ref. [35]). From the Adam-Gibbs relation (93) with a hyperbolic model for the dependence of the configurational entropy on the effective temperature, as another example, one obtains

$$\tau(T,T_{\rm eff}) \propto \exp\left\{\frac{T_{\rm A}T_{\rm eff}}{T(T_{\rm eff}-T_{\rm K})}\right\} \qquad (110)$$

with parameter $T_{\rm A}$, which is known as the Adam-Gibbs-Fulcher form.

The nonlinear differential equation (109) can be rewritten as an integral equation,

$$T_{\rm eff}(t) = T(t) - \int_{-\infty}^{t} \exp\left\{ - \int_{t'}^{t} \frac{dt''}{\tau(t'')} \right\} \frac{dT(t')}{dt'} dt', \quad (111)$$

with $\tau(t'') = \tau(T(t''), T_{\rm eff}(t''))$. This formula gives the deviation of $T_{\rm eff}(t)$ from $T(t)$ as a superposition of contributions resulting from all previous temperature decreases, weighted with an exponential decreasing as a function of the time difference. For a small decrease of the temperature of a supercooled melt at T_0, Eq. (111) implies a linear response of the effective temperature with a single exponential $\exp\{-t/\tau(T_0,T_0)\}$. In reality, one rather observes a stretched exponential, also known as Kohlrausch-Williams-Watts formula. Therefore Eq. (111) is changed into (see Sec. 6.2 of Ref. [15])

$$T_{\rm eff}(t) = T(t) - \int_{-\infty}^{t} \exp\left\{ - \left(\int_{t'}^{t} \frac{dt''}{\tau(t'')} \right)^{\beta} \right\} \frac{dT(t')}{dt'} dt' \quad (112)$$

with a fractional exponent β $(0 < \beta < 1)$. However, rather than describing glassy behavior by such an *ad hoc* modification of a relaxation equation for a single scalar out-of-equilibrium variable, the full complexity of glasses should be understood from more detailed structural variables, where possible choices are proposed and discussed in this section. Attempts in this direction have been made by Diezemann, who formulates a master equation for the probability density of free energy values in a free energy landscape model, coupled to position and orientation jumps of a particle (see Ref. [45] and references therein). An additional variable to account for aging and rejuvenation effects has also been introduced into a purely phenomenological model for glassy polymers [46], which then describes the large deformation (postyield) response, aging and mechanical rejuvenation effects on the yield stress and long-time failure of polycarbonate quantitatively. In the following, the choice of a additional structural variables is based on the inherent-structure formalism because it offers a direct atomistic interpretation of the variables. At least for a phenomenological theory, alternative formulations of the consequences of geometric "frustration" could lead to alternative variables, such as local order parameters in a geometric approach or topological defect densities in a dual approach [17].

A. Structural variable: Pair correlation

Motivated by the inherent-structure formalism, we introduce the pair correlation function for inherent structures as an additional variable. Starting from the positions $\boldsymbol{r}_j$ of N particles, we find the positions $\boldsymbol{r}_j^{\rm is}$ for the corresponding inherent structure by means of the steepest-descent dynamics (41). We then define the atomistic inherent structure pair correlation function by

$$\hat{g}_{\rm is}(\boldsymbol{r},\boldsymbol{R};\{\boldsymbol{r}_j\}) = \frac{m}{\rho(\boldsymbol{r})} \frac{V}{N} \sum_{j,k=1}^{N} \delta(\boldsymbol{r}_j^{\rm is} - \boldsymbol{r})\, \delta(\boldsymbol{r}_k^{\rm is} - \boldsymbol{r}_j^{\rm is} - \boldsymbol{R}), \quad (113)$$

and the corresponding coarse grained variable $g_{\rm is}(\boldsymbol{r},\boldsymbol{R})$ is obtained as an ensemble average of $\hat{g}_{\rm is}(\boldsymbol{r},\boldsymbol{R};\{\boldsymbol{r}_j\})$. Note that we consider $\hat{g}_{\rm is}$ as a function of the particle positions $\boldsymbol{r}_j$, so that the position vectors $\boldsymbol{r}_j^{\rm is}$ of the inherent structure need to be found in terms of the positions $\boldsymbol{r}_j$, and $\hat{g}_{\rm is}$ becomes a really interesting variable deeply related to the energy landscape of glasses.

By integrating Eq. (113) over $\boldsymbol{R}$, we obtain

$$\int_V \hat{g}_{\rm is}(\boldsymbol{r},\boldsymbol{R};\{\boldsymbol{r}_j\}) d^3R = \frac{mV}{\rho(\boldsymbol{r})} \sum_{j=1}^{N} \delta(\boldsymbol{r}_j^{\rm is} - \boldsymbol{r}), \quad (114)$$

and, if the ensemble average of the mass density of the inherent structure can be taken to be equal to the mass density of the actual physical configuration, we have

$$\int_V g_{\rm is}(\boldsymbol{r},\boldsymbol{R}) d^3R = V. \quad (115)$$

For large homogeneous isotropic systems, this standard normalization of the pair correlation functions implies

$$g_{\rm is}(\boldsymbol{r},\boldsymbol{R}) \to 1 \quad \text{for} \quad |\boldsymbol{R}| \to \infty. \quad (116)$$

For our construction of a thermodynamic description of glasses, $g_{\rm is}(\boldsymbol{r},\boldsymbol{R})$ needs to be a smooth function of $\boldsymbol{r}$ and $\boldsymbol{R}$. To obtain a smooth dependence on $\boldsymbol{R}$, we need to assume amorphous structures and to exclude crystalline structures. Even for amorphous structures one needs to be careful because the passage from the original to the inherent structure produces a sharpening of the pair correlation function (see, for example, Fig. 9 of Ref. [18]).

A complete set of variables for the coarse grained description of a glass is now assumed to be given by $x = (\rho, \boldsymbol{M}, \epsilon_{\rm fp}, g_{\rm is})$. The internal energy density $\epsilon_{\rm fp}$ associated with fast processes is obtained by subtracting the inherent-structure contribution $\epsilon_{\rm is}$ from the total internal energy density. In mixtures, such as the frequently studied binary Lennard-Jones glasses [38,41], several inherent-structure pair correlation functions need to be introduced. By formulating the GENERIC building blocks E, S, L, and M, we obtain the flow and aging behavior of our glassy system. We next discuss which of the building blocks can be constructed naturally and which ones require simulations, preferably under the thermodynamic guidance available after choosing a coarse grained level of description. We then obtain some important insights into the general features of the time-evolution equations on the chosen level of description, in particular, about the existence and significance of a characteristic static length scale.

In the spirit of the inherent-structure formalism, we obtain the total energy as

$$E(x) = \int \left[\frac{1}{2} \frac{\boldsymbol{M}(\boldsymbol{r})^2}{\rho(\boldsymbol{r})} + \epsilon_{\mathrm{fp}}(\boldsymbol{r}) + \epsilon_{\mathrm{is}}(\boldsymbol{r}) \right] d^3 r \tag{117}$$

with

$$\epsilon_{\mathrm{is}}(\boldsymbol{r}) = \frac{1}{2} \frac{N}{V} \frac{\rho(\boldsymbol{r})}{m} \int d^3 R \, \phi(\boldsymbol{R}) g_{\mathrm{is}}(\boldsymbol{r}, \boldsymbol{R}), \tag{118}$$

where $\phi(\boldsymbol{R})$ is the interaction potential between particles. Equations (117) and (118) provide the explicit functional form of $E(x)$. In particular, its gradient is given by

$$\frac{\delta E}{\delta x} = \begin{pmatrix} -\frac{1}{2}\boldsymbol{v}^2 + \frac{\epsilon_{\mathrm{is}}}{\rho} \\ \boldsymbol{v} \\ 1 \\ \frac{1}{2}\frac{N}{V}\frac{\rho}{m}\phi \end{pmatrix} \tag{119}$$

with $\boldsymbol{v} = \boldsymbol{M}/\rho$.

The formulation of an entropy functional is much less straightforward. For example, we can attempt to write the total entropy as

$$S(x) = S_{\mathrm{fp}}(\rho, \epsilon_{\mathrm{fp}}, \epsilon_{\mathrm{is}}[g_{\mathrm{is}}]) + S_{\mathrm{conf}}(\rho, g_{\mathrm{is}}), \tag{120}$$

where S_{fp} describes the entropy of the system constrained to a basin with an inherent structure described by g_{is} and S_{conf} is given by the number of inherent structures consistent with the pair correlation function g_{is}. We have made the assumption that, if S_{fp} depends on the inherent structure at all, then only through the energy density of the inherent structure. Whereas an expression of the famous type $-\int f \ln f$ describes the configurational entropy for the extreme cases of f being the distribution function in the full phase space or the single-particle distribution function, such a form is inappropriate for the pair correlation function [47]. Accordingly, the potential ϕ is changed into a nontrivial effective potential ϕ_{eff} to account for entropy effects. For the further steps, however, we do not need the explicit form of the entropy $S(x)$.

The natural choice of a Poisson operator in the presence of a structural variable depending on an additional vector $\boldsymbol{R}$ has been discussed on p. 445 of Ref. [33]. In view of Eq. (4.121) of Ref. [33], we only need to give the element $-L_{24}$ associated with the components $\boldsymbol{M}$ and g_{is} of x [see Eq. (4.146) of Ref. [33] for a similar situation]:

$$-L_{24} = \frac{\partial g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})}{\partial \boldsymbol{r}} + \frac{\partial}{\partial \boldsymbol{r}}(1+3c) g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R}) + \frac{\partial}{\partial \boldsymbol{r}} \cdot g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R}) \times \left\{ \boldsymbol{R}\left[\boldsymbol{1} - h(R)\frac{\boldsymbol{R}\boldsymbol{R}}{R^2}\right] + c\boldsymbol{1}[1-h(R)]\boldsymbol{R} \right\} \cdot \frac{\partial}{\partial \boldsymbol{R}}. \tag{121}$$

The function $h(R)$ expressing a hindrance of affine deformations and the constant c describing compressibility effects in the convective behavior of the pair correlation function g_{is} in Eq. (121) remain to be determined. The first two contributions on the right-hand side of Eq. (121) reflect the normalization (116) of g_{is}. According to the GENERIC structure, the total pressure tensor occurring in the momentum balance equation is obtained as

$$\boldsymbol{\Pi} = \left(sT - \rho T \frac{\delta S}{\delta \rho} - \epsilon_{\mathrm{fp}} - \epsilon_{\mathrm{is}} \right) \boldsymbol{1} - \int g_{\mathrm{is}} \left[\boldsymbol{R}\left(\boldsymbol{1} - h \frac{\boldsymbol{R}\boldsymbol{R}}{R^2} \right) + c\boldsymbol{1}(1-h)\boldsymbol{R} \right] \cdot \frac{\partial}{\partial \boldsymbol{R}} \left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} \right) d^3 R - 3c \times \int g_{\mathrm{is}} \left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} \right) d^3 R \boldsymbol{1}, \tag{122}$$

where we have assumed that the total entropy possesses a density $s(\rho, \epsilon_{\mathrm{fp}}, g_{\mathrm{is}})$ independent of momentum density and we have introduced the temperature T by

$$\frac{1}{T} = \frac{\partial s(\rho, \epsilon_{\mathrm{fp}}, g_{\mathrm{is}})}{\partial \epsilon_{\mathrm{fp}}}. \tag{123}$$

In isotropic states, the first integral in Eq. (122) represents a pressure contribution of the form

$$\hat{p}_{\mathrm{is}} = -\left(\frac{1}{3} + c \right) \int g_{\mathrm{is}} (1-h) R \frac{\partial}{\partial R} \left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} \right) d^3 R. \tag{124}$$

Compared to a naive expression for the pressure tensor contribution associated with an inherent structure,

$$-\int g_{\mathrm{is}} \boldsymbol{R} \frac{\partial}{\partial \boldsymbol{R}} \frac{\delta E}{\delta g_{\mathrm{is}}} d^3 R, \tag{125}$$

Eq. (122) includes entropic and nontrivial convection effects.

A nonzero dimensionless function $h(R)$ implies the existence of a characteristic length scale R_{c} associated with convection. A particularly appealing choice of the convection mechanism is given by

$$h(R) = \left(\frac{R_{\mathrm{c}}}{R} \right)^3, \tag{126}$$

for which a uniform pair correlation function, $g_{\mathrm{is}} \equiv 1$, is fully consistent with the convection mechanism. At least, the asymptotic behavior for large R should be governed by Eq. (126) and can hence be used to introduce the scale R_{c} unambiguously. The natural occurrence of the length scale R_{c} is the first important consequence of the GENERIC approach. This characteristic length scale is associated with the collective rearrangements required to find new local minima of the potential energy after deformation. Such rearrangements have nothing to do with the physical time evolution of the system. For an affine convection mechanism, we find $R_{\mathrm{c}} = 0$.

The most natural formulation of the damping or relaxation term for pair correlation functions is based on diffusion (see p. 94 of Ref. [48]). Guided by Eq. (59) of Ref. [32], we hence write for the friction matrix

$$M = M(x) = 2\frac{V}{N}\frac{m}{\rho}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \displaystyle\int \frac{2Tg_{\mathrm{is}}(\boldsymbol{R})\boldsymbol{f}(\boldsymbol{R})^2}{\zeta} d^3R & \displaystyle\frac{2Tg_{\mathrm{is}}(\boldsymbol{R}')\boldsymbol{f}(\boldsymbol{R}')}{\zeta}\cdot\frac{\partial}{\partial \boldsymbol{R}'} \\ 0 & 0 & \displaystyle -\frac{\partial}{\partial \boldsymbol{R}}\frac{2Tg_{\mathrm{is}}(\boldsymbol{R})\boldsymbol{f}(\boldsymbol{R})}{\zeta} & \displaystyle -\frac{\partial}{\partial \boldsymbol{R}}\frac{2Tg_{\mathrm{is}}(\boldsymbol{R})}{\zeta}\cdot\frac{\partial}{\partial \boldsymbol{R}} \end{pmatrix}, \tag{127}$$

where

$$\boldsymbol{f}(\boldsymbol{R}) = -\frac{\partial}{\partial \boldsymbol{R}}\frac{\delta E}{\delta g_{\mathrm{is}}(\boldsymbol{R})} \tag{128}$$

is a force density, ζ is a friction coefficient, and the degeneracy condition (82) is taken into account. The prefactor in Eq. (127) is chosen such that ζ coincides with the friction coefficient in Ref. [48]. Whereas a further contribution to the friction matrix accounting for heat conduction should be added, an explicit viscous contribution should be negligible because the dominant influence on the viscosity arises from the inherent structures. Moreover, the effect of diffusion on the $\boldsymbol{r}$ dependence of $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$ has been neglected. This effect could be introduced by replacing half of the friction matrix (127) by

$$\begin{pmatrix} 0 \\ 0 \\ \boldsymbol{f} + \dfrac{1}{2}\dfrac{N}{V}\dfrac{\phi}{m}\dfrac{\partial\rho}{\partial \boldsymbol{r}} \\ -\dfrac{\partial}{\partial \boldsymbol{R}} + \dfrac{\partial}{\partial \boldsymbol{r}} \end{pmatrix} \cdot 2\frac{V}{N}\frac{m}{\rho}\frac{Tg_{\mathrm{is}}}{\zeta}\begin{pmatrix} 0 \\ 0 \\ \boldsymbol{f} + \dfrac{1}{2}\dfrac{N}{V}\dfrac{\phi}{m}\dfrac{\partial\rho}{\partial \boldsymbol{r}} \\ \dfrac{\partial}{\partial \boldsymbol{R}} - \dfrac{\partial}{\partial \boldsymbol{r}} \end{pmatrix}^T . \tag{129}$$

The time-evolution equation for the pair correlation function $g_{\mathrm{is}}=g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$ obtained from Eq. (80) by combining the GENERIC building blocks is of the form

$$\begin{aligned} \frac{\partial g_{\mathrm{is}}}{\partial t} = {} & -\boldsymbol{v}\cdot\frac{\partial g_{\mathrm{is}}}{\partial \boldsymbol{r}} + (1+3c)g_{\mathrm{is}}\mathrm{tr}\boldsymbol{\kappa} - \frac{\partial}{\partial \boldsymbol{R}}\cdot\Bigg\{\bigg[\boldsymbol{1} \\ & - h(R)\frac{\boldsymbol{RR}}{R^2}\bigg]\cdot\boldsymbol{\kappa}\cdot\boldsymbol{R} + c[1-h(R)](\mathrm{tr}\boldsymbol{\kappa})\boldsymbol{R}\Bigg\}g_{\mathrm{is}} \\ & + \frac{\partial}{\partial \boldsymbol{R}}\cdot\frac{4Vm}{\zeta N\rho}g_{\mathrm{is}}\frac{\partial}{\partial \boldsymbol{R}} \\ & \times\left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}}\right), \end{aligned} \tag{130}$$

where $\boldsymbol{\kappa}$ is the transposed velocity gradient tensor. The occurrence of the Helmholtz free energy in Eqs. (122) and (130) is natural because the equilibrium $g_{\mathrm{is}}^{\mathrm{eq}}$ of the inherent structure pair correlation function is determined by minimization of the free energy,

$$\left.\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}}\right|_{g_{\mathrm{is}}=g_{\mathrm{is}}^{\mathrm{eq}}} = 0. \tag{131}$$

An effective pair interaction potential can then be introduced by the definition

$$g_{\mathrm{is}}^{\mathrm{eq}} = \exp\left\{-\frac{\phi_{\mathrm{eff}}}{k_B T}\right\}. \tag{132}$$

As an alternative to the diffusive friction matrix in Eq. (127), we can assume a relaxation mechanism by replacing the diffusion operator by

$$M_{44} = 2\frac{V}{N}\frac{m}{\rho}\frac{g_{\mathrm{is}}(\boldsymbol{R})}{\tau k_B}, \tag{133}$$

where τ is a characteristic relaxation time. Actually, Hess and Hanley suggested to introduce different relaxation times for scalar and tensorial parts of the pair correlation [49]. After fixing the other components of the friction matrix by degeneracy and symmetry, we find the following alternative time-evolution equation for the pair correlation function:

$$\begin{aligned} \frac{\partial g_{\mathrm{is}}}{\partial t} = {} & -\boldsymbol{v}\cdot\frac{\partial g_{\mathrm{is}}}{\partial \boldsymbol{r}} + (1+3c)g_{\mathrm{is}}\mathrm{tr}\boldsymbol{\kappa} - \frac{\partial}{\partial \boldsymbol{R}}\cdot\Bigg\{\bigg[\boldsymbol{1} \\ & - h(R)\frac{\boldsymbol{RR}}{R^2}\bigg]\cdot\boldsymbol{\kappa}\cdot\boldsymbol{R} + c[1-h(R)](\mathrm{tr}\boldsymbol{\kappa})\boldsymbol{R}\Bigg\}g_{\mathrm{is}} \\ & - \frac{M_{44}}{T}\left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}}\right). \end{aligned} \tag{134}$$

This formula actually includes Eq. (130) by choosing M_{44} according to Eq. (127). The time evolution described by this equation is the slow relaxation towards the supercooled liquid around the glass-transition temperature.

In order to obtain the zero-shear-rate viscosity of the supercooled liquid near the glass-transition temperature, we consider homogeneous steady flows with $\mathrm{tr}\boldsymbol{\kappa}=0$. The deformation rate must be so small that even the slowest relaxation process can take place. For larger deformation rates, one would reach a steady state for which only part of the relaxation processes can be active so that shear tinning would be observed [10]. The viscosity can be obtained from Eqs. (122) and (134), or from an energy dissipation argument,

$$\eta = \frac{T[S,S]}{\boldsymbol{\kappa}:(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)} = \frac{1}{T\boldsymbol{\kappa}:(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)} \int \left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} \right) M_{44} \left(\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} \right) d^3R. \tag{135}$$

In view of Eq. (131), we need to find the linear dependence of the gradient of free energy on the velocity gradient to obtain the manifestly nonnegative zero-shear-rate viscosity. This can be done by inverting M_{44} in Eq. (134) for homogeneous steady flows. For the relaxation process described by Eq. (133) the inversion is trivial and, after exploiting the spherical symmetry, we obtain

$$\eta = \frac{2\pi k_B T \tau N \rho}{15 V m} \int_0^\infty \left[(1-h)\frac{d \ln g_{\mathrm{is}}^{\mathrm{eq}}}{dR} - \frac{dh}{dR} - 3\frac{h}{R} \right]^2 g_{\mathrm{is}}^{\mathrm{eq}} R^4 dR. \tag{136}$$

This expression for the viscosity in the case of relaxation as the dissipative mechanism can be rewritten as

$$\eta = \frac{2\pi k_B T \tau N \rho}{15 V m} \int_0^\infty \left[(1-h)\frac{d}{dR} \ln \frac{g_{\mathrm{is}}^h}{g_{\mathrm{is}}^{\mathrm{eq}}} \right]^2 g_{\mathrm{is}}^{\mathrm{eq}} R^4 dR, \tag{137}$$

where we have introduced a formal pair correlation function g_{is}^h associated the physical hindrance h,

$$g_{\mathrm{is}}^h(R) = \exp\left\{ -\int_R^\infty \frac{1}{[1-h(R')]R'^3} \frac{d[h(R')R'^3]}{dR'} dR' \right\}. \tag{138}$$

For $g_{\mathrm{is}}^{\mathrm{eq}} = g_{\mathrm{is}}^h$, the viscosity would vanish.

The inversion of M_{44} is more difficult for the diffusion operator than for relaxation. If we are interested only in the corrections to equilibrium that are linear in the velocity gradient tensor, then the driving force must be of the form

$$\frac{\delta E}{\delta g_{\mathrm{is}}} - T\frac{\delta S}{\delta g_{\mathrm{is}}} = \frac{\zeta N \rho}{8 V m} f(R) \boldsymbol{R}\cdot\boldsymbol{\kappa}\cdot\boldsymbol{R} + \text{const.} \tag{139}$$

The dimensionless scalar function $f = f(R)$ needs to be obtained from the diffusion equation (130) which leads to the following second-order ordinary differential equation:

$$\left(1 - h - f - \frac{R}{2}\frac{df}{dR} \right) \frac{d \ln g_{\mathrm{is}}^{\mathrm{eq}}}{dR} = 3\frac{df}{dR} + \frac{R}{2}\frac{d^2 f}{dR^2} + 3\frac{h}{R} + \frac{dh}{dR}. \tag{140}$$

The integration constants should be fixed by requiring that f decays sufficiently rapidly for large R. By closer inspection of Eq. (140), we expect f to decay with the same power-law behavior as h, that is, according to Eq. (126), as R^{-3}.

With Eq. (139), we can now evaluate the viscosity expression in Eq. (135). After exploiting the spherical symmetry at equilibrium, we obtain the following manifestly positive expression for the viscosity in the case of diffusion as the dissipative mechanism,

$$\eta = \frac{\pi \zeta N \rho}{10 V m} \int_0^\infty \left[f^2 + \frac{2}{3}\left(f + \frac{R}{2}\frac{df}{dR} \right)^2 \right] g_{\mathrm{is}}^{\mathrm{eq}} R^4 dR. \tag{141}$$

This expression can be further simplified by means of an integration by parts and the differential equation (140),

$$\eta = \frac{\pi \zeta N \rho}{30 V m} \int_0^\infty \left[(1-h)\frac{d}{dR} \ln \frac{g_{\mathrm{is}}^h}{g_{\mathrm{is}}^{\mathrm{eq}}} \right] f g_{\mathrm{is}}^{\mathrm{eq}} R^5 dR, \tag{142}$$

where we have assumed that

$$g_{\mathrm{is}}^{\mathrm{eq}} R^2 \frac{d}{dR}(f^2 R^4) \tag{143}$$

vanishes at zero and infinity. The viscosity formula in Eq. (141) or in Eq. (142) is a second important result of the GENERIC framework. Note that an analogous result can be obtained for the usual pair correlation function (rather than that of inherent structures), presumably with $h=0$ and $g_{\mathrm{is}}^h = 1$. A comparison of the viscosity formulas in Eqs. (137) and (141) with an atomistic expression for the viscosity would allow us to decide whether relaxation or diffusion is the more appropriate dissipative mechanism.

Because the function $h(R)$, which we introduced by purely thermodynamic arguments, plays a central role in identifying a characteristic length scale R_{c} and in evaluating the viscosity, we discuss how this function can be determined by statistical mechanics. We consider the effect of a homogeneous space transformation characterized by a deformation tensor $\tilde{\boldsymbol{\kappa}}$,

$$\boldsymbol{r} \mapsto \bar{\boldsymbol{r}} = \boldsymbol{r} + \tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{r}, \tag{144}$$

which needs to be elevated to the coarse grained level, in particular, to obtain the transformation behavior of $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$ (see Sec. 6.1.6 and Appendix B.4 of Ref. [33]). According to the general theory, the function $h(R)$ is obtained in the limit of small deformations.

An important subtlety arises from the fact that we need the transformation behavior of the inherent structure positions $\boldsymbol{r}_j^{\mathrm{is}}$ resulting from the overall deformation Eq. (144). We look for a regime of deformations that are sufficiently large to explore the full structure of the potential energy landscape, including megabasins consisting of many local minima, and sufficiently small to construct an infinitesimal action of the group of deformations on the approximately continuous thermodynamic variable $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$. The occurrence of a two-scale potential-energy landscape with deep large-scale "craters" or megabasins separated by major energy barriers as sketched in Fig. 7 of Ref. [20] and in Fig. 4 of Ref. [21] requires a minimum magnitude of the deformations (see also Fig. 2(a) of Ref. [50] for a distinction of deep traps and shallow megabasins). The megabasins have been identified in an elegant dynamical manner because they, in contrast to the basins, allow the description of diffusion as a random walk between megabasins [50,51]. According to previous work on the shear deformation of Lennard-Jones binary mixtures [52,53], we expect to stay in a single metabasin for deformations up to the order of 1%, so that the inherent structure energy is almost constant, and large jumps between megabasins start to happen only for somewhat larger deformations.

The 1% level is confirmed in an early atomistic simulation of rejuvenation by planar elongation of a Lennard-Jones binary mixture [54]. To explore the full structure of the potential energy landscape one should hence consider deformations of the order of 10%.

While, from a macroscopic perspective, the difference between $\boldsymbol{r}_j$ and $\boldsymbol{r}_j^{\mathrm{is}}$ is expected to be small and does not cause noticeable deviations from affine behavior in the first argument of $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$, one can have important hindrance effects on $\boldsymbol{R}$. The rearrangement of particles after deformation in a new megabasin causes a nontrivial transformation behavior of $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$. In Appendix B, we discuss how the calculation of the transformation behavior of $g_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R})$ naturally leads to four-point correlation functions involving deformed and undeformed configurations, how these are related to the four-point correlation functions employed in the theory of dynamic correlations, and how the hindrance function $h(R)$ can be determined. The important message at this point is that four-point correlation functions associated with the transformation behavior might be sufficient to characterize a growing length scale [55–57] without using any dynamic information.

In conclusion, beyond-equilibrium thermodynamics for a description of glasses based on the inherent-structure pair correlation function suggests a possibility to identify a characteristic length scale. This length scale is associated with collective rearrangements to obtain local minima of potential energy after deformations. It is important to realize that these rearrangements after deformation are not directly related to dynamic processes. Beyond-equilibrium thermodynamics moreover provides a formula for the viscosity in terms of the convection mechanism. The underlying statistical mechanics elucidates that the characteristic length scale is a static quantity and offers a recipe to obtain the relevant information from computer simulations. Once the convection mechanism $h(R)$, the entropy $S(x)$ and the friction coefficient ζ, or the relaxation time τ, are determined, all aspects of the viscoelastic and aging behavior of a glass can be studied in detail.

B. Structural variables: Tensor and scalar

A pair correlation function depending on a continuous variable $\boldsymbol{R}$ represents rather detailed information and might pose serious challenges for thermodynamically guided simulations. For example, in flow, the pair correlation function needs to be controlled by a Lagrange multiplier that depends on the three-dimensional label $\boldsymbol{R}$. One possibility would be to expand the angular dependence of the pair correlation function in spherical harmonics and to consider the lowest-order expansion coefficients as functions of the length of $\boldsymbol{R}$ only [58,59]. We here consider the even coarser possibility to use a certain moment tensor $\boldsymbol{c}$, together with ϵ_{is}, as structural variables, so that $x=(\rho,\boldsymbol{M},\epsilon_{\mathrm{fp}},\boldsymbol{c},\epsilon_{\mathrm{is}})$ is proposed as a possible level of description for glasses. The simplest choice of a tensor would be

$$\boldsymbol{c} \propto \int \boldsymbol{R}\boldsymbol{R}(g_{\mathrm{is}}-1)d^3R. \tag{145}$$

From the more detailed level considered in the preceding section we anticipate that interesting features of glasses are contained in a nontrivial convection mechanism. For a proper convective coupling of ϵ_{is} and $\boldsymbol{c}$ it might hence be more appropriate to define

$$\boldsymbol{c} \propto \int \boldsymbol{R}\left(\boldsymbol{1} - h\frac{\boldsymbol{R}\boldsymbol{R}}{R^2}\right)\cdot\frac{\partial\phi}{\partial\boldsymbol{R}} g_{\mathrm{is}} d^3R. \tag{146}$$

Such a definition would, however, require *a priori* assumptions about the form of h. We will hence neglect h in this definition of $\boldsymbol{c}$.

The coarse grained level implied by a tensor and a scalar as structural variables in addition to the hydrodynamic fields has been explored in great detail in Sec. 4.2 of Ref. [33]. In particular, the general rules for formulating a coupled convection mechanism have been established. If we could choose the proper function h in the definition (146), then the coupling tensor $\boldsymbol{g}$ in the convection mechanism [see Eq. (4.37) of Ref. [33]] would be given by a constant tensor. However, because h is unknown, we here choose the following atomistic expression for the tensor variable:

$$\begin{aligned}\hat{\boldsymbol{c}}(\boldsymbol{r};\{\boldsymbol{r}_j\}) &= \frac{m}{\rho(\boldsymbol{r})}\sum_{j,k=1}^{N}(\boldsymbol{r}_k^{\mathrm{is}}-\boldsymbol{r}_j^{\mathrm{is}})\frac{\partial\phi(\boldsymbol{r}_k^{\mathrm{is}}-\boldsymbol{r}_j^{\mathrm{is}})}{\partial\boldsymbol{r}_k^{\mathrm{is}}}\delta(\boldsymbol{r}_j^{\mathrm{is}}-\boldsymbol{r})\\ &= \frac{N}{V}\int \boldsymbol{R}\frac{\partial\phi}{\partial\boldsymbol{R}}\hat{g}_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R};\{\boldsymbol{r}_j\})d^3R.\end{aligned} \tag{147}$$

We then expect a more complicated coupling tensor $\boldsymbol{g}$ and a slip contribution to the friction matrix with a slip coefficient ξ expressing the lack of codeformational behavior of inherent structures [see Eq. (4.68) of Ref. [33]]. In accordance with Eq. (118), we use the atomistic definition

$$\hat{\epsilon}_{\mathrm{is}}(\boldsymbol{r};\{\boldsymbol{r}_j\}) = \frac{1}{2}\frac{N}{V}\frac{\rho(\boldsymbol{r})}{m}\int\phi(\boldsymbol{R})\hat{g}_{\mathrm{is}}(\boldsymbol{r},\boldsymbol{R};\{\boldsymbol{r}_j\})d^3R. \tag{148}$$

Because the variable Λ used in Ref. [33] is a scalar rather than a scalar density, it actually corresponds to $\epsilon_{\mathrm{is}}/\rho$ of this paper. Note that the total energy (117) does not depend on $\boldsymbol{c}$.

For the friction matrix on the level of a tensor and a scalar, we expect a coupled relaxation according to Eq. (4.55) of Ref. [33] with a fourth-rank tensor of the form

$$(\boldsymbol{R}_3)_{ijkl} = \delta_{ik}\tilde{R}_{jl} + \tilde{R}_{ik}\delta_{jl} + \delta_{il}\tilde{R}_{jk} + \tilde{R}_{il}\delta_{jk} \tag{149}$$

and a coupling tensor

$$\boldsymbol{\Phi} = \frac{1}{4}\frac{\rho}{m}\boldsymbol{1}. \tag{150}$$

An additional mode of purely tensorial relaxation of $\boldsymbol{c}$, independent of the scalar variable, according to Eq. (4.54) of Ref. [33] would be possible, where $\boldsymbol{R}_2$ should be of the same order of magnitude as $\boldsymbol{R}_3$, but symmetric under permutations of all indices.

For the zero-shear-rate viscosity of an isotropic system we find

$$\eta = \frac{c_0^2(1-\xi)^2 T}{\bar{R}_0 + 2\tilde{R}_0}, \tag{151}$$

where the quantities c_0, $\bar{R}_0$, and $\tilde{R}_0$ are given by the isotropic properties

$$\boldsymbol{c} = c_0 \mathbf{1}, \tag{152}$$

$$(\boldsymbol{R}_2)_{ijkl} = \bar{R}_0(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{153}$$

and

$$\tilde{R}_{jk} = \tilde{R}_0 \delta_{jk}. \tag{154}$$

On this level of description, any significant increase of the viscosity must result from decreasing relaxation rates $\bar{R}_0$ and $\tilde{R}_0$.

IV. SUMMARY AND OUTLOOK

For the equilibriumlike approach to nonequilibrium (ELIANE), we have discussed the possible choice of the additional independent out-of-equilibrium variable. Generalized effective temperatures and inherent structure variables have first been introduced phenomenologically and then via the inherent-structure formalism based on the properties of potential energy landscapes. The key ideas have been illustrated by means of well-known exact results for a harmonic-oscillator spherical spin model.

ELIANE has been derived from GENERIC, a systematic framework of nonequilibrium thermodynamics. Two different levels for a self-contained description of glassy dynamics and thermodynamics have been introduced and elaborated within GENERIC, one based on the inherent structure pair correlation function, the other one based on a moment tensor and the inherent structure energy density.

To me, as a beginner in the field of glasses, the following results and insights seem to be new or, at least, not generally recognized in the literature:

(i) The elucidation of the subtle role of out-of-equilibrium variables by introducing the relevant classes of generalized effective temperatures and inherent structure variables of the strong and weak type by purely thermodynamic considerations.

(ii) The importance of the proper choice of an out-of-equilibrium variable for obtaining physically meaningful definitions of the temperature T, the pressure p, and the chemical potential μ away from equilibrium.

(iii) The importance of meaningful out-of-equilibrium concepts of temperature and pressure for obtaining the Ehrenfest relations; natural generalizations for jumps in thermodynamic material properties occurring after different cooling procedures are formulated, and a Prigogine-Defay ratio different from unity arises.

(iv) The consistent definition of the effective temperature in the inherent-structure approach such that the exact results are reproduced for the solvable model of Leuzzi and Nieuwenhuizen. In contrast to an approximate version, the exact effective temperature is not an inherent structure variable.

(v) The observation that, in general, it is inappropriate to express the configurational entropy in terms of the effective temperature because there is an additional temperature dependence.

(vi) The general derivation of the equilibriumlike approach to nonequilibrium systems from the GENERIC framework of nonequilibrium thermodynamics.

(vii) The formulation of two levels of description for the dynamics of glassy systems, including the explicit form of the convection behavior of the structural variables and formulas for the zero-shear-rate viscosity.

(viii) The definition of four-point correlation functions associated with collective particle rearrangements after a given deformation; these correlation functions might be used to identify a length scale that is a purely static quantity characterizing the potential energy landscape.

This paper moreover offers a work program for future simulations of glasses, how they shall be performed in suitable nonequilibrium ensembles and how they should be analyzed by facing simulations with coarse grained levels of description. A consistent perspective of various frameworks (GENERIC, ELIANE, inherent-structure formalism) provides a safe background for optimized simulations. The enormous potential of thermodynamically guided simulations, which has been established for various systems (see Chap. 8 of the recent textbook [33]) will be explored for glasses in future publications.

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APPENDIX A: SPLITTING OF PARTITION FUNCTIONS

Let us assume that we wish to evaluate a partition function

$$Z(T) = \int_{\mathcal{P}} e^{-\beta E(z)} dz, \tag{A1}$$

where $\mathcal{P}$ is the phase space for N particles in a volume V, $\beta = 1/(k_B T)$ is the inverse temperature, and $E(z)$ is the energy of the microstate $z \in \mathcal{P}$. The implicit dependence of various quantities on N and V through $\mathcal{P}$ is suppressed in the notation of this Appendix. We further assume that the following classification of microstates is given:

(i) There exists a partition of the phase space $\mathcal{P}$ into mutually disjoint classes $\mathcal{C}_j$ of microstates, that is,

$$\mathcal{P} = \bigcup_j \mathcal{C}_j, \quad \mathcal{C}_j \cap \mathcal{C}_k = \emptyset \quad \text{for } j \neq k. \tag{A2}$$

(ii) The classes $\mathcal{C}_j$ themselves are further classified according to a discrete set of characteristic energies E_n; J_n is the set of labels j for which the classes $\mathcal{C}_j$ have a characteristic energy E_n. We denote the number of labels in J_n, that is, the number of classes with characteristic energy E_n, by $\mathcal{N}(E_n)$.

For example, the classes $\mathcal{C}_j$ could be inherent structures, and they are further classified according to their inherent-structure energies. Another attractive option is the classification according to the values of a suitable nonequilibrium variable, which would immediately allow us to proceed to nonequilibrium statistical mechanics.

In the described situation, the partition function can be evaluated by partial summation,

$$Z(T) = \sum_n e^{-\beta E_n} \sum_{j \in J_n} \int_{\mathcal{C}_j} e^{-\beta[E(z)-E_n]} dz. \tag{A3}$$

If we introduce the quantities $S_{\rm conf}$ and $F_{\rm fp}$ by

$$S_{\rm conf}(E_n) = k_B \ln \mathcal{N}(E_n) \tag{A4}$$

and

$$F_{\rm fp}(T,E_n) = -k_B T \ln\left\{ \frac{1}{\mathcal{N}(E_n)} \sum_{j \in J_n} \int_{\mathcal{C}_j} e^{-\beta[E(z)-E_n]} dz \right\}, \tag{A5}$$

then Eq. (A3) can be rewritten as

$$Z(T) = \sum_n \exp\{-\beta[E_n - TS_{\rm conf}(E_n) + F_{\rm fp}(T,E_n)]\}. \tag{A6}$$

The quantity $S_{\rm conf}(E_n)$ is the configurational entropy associated with the number of classes for a given characteristic energy, and $F_{\rm fp}(T,E_n)$ is the Helmholtz free energy associated with the average partition function for classes with a given characteristic energy. The subscript "fp" indicates the underlying idea that the classes $\mathcal{C}_j$ are sampled efficiently by fast processes, whereas transitions between different classes are slow.

To simplify Eq. (A6), we make a saddle-point approximation and assume that the sum is dominated by its maximum term. We then obtain the final result

$$F(T) = -k_B T \ln Z(T) = E - TS_{\rm conf}(E) + F_{\rm fp}(T,E), \tag{A7}$$

where the temperature T and the characteristic energy E are related by the maximum condition for the exponential in Eq. (A6),

$$1 - T\frac{\partial S_{\rm conf}(E)}{\partial E} + \frac{\partial F_{\rm fp}(T,E)}{\partial E} = 0. \tag{A8}$$

This relationship implies, in particular, that the total entropy can be obtained as

$$S(T) = -\frac{\partial F(T)}{\partial T} = S_{\rm conf}(E) - \frac{\partial F_{\rm fp}(T,E)}{\partial T}. \tag{A9}$$

The saddle-point approximation should not be perceived as a severe assumption. It merely reflects the usual idea of the equivalence of microcanonical and canonical ensembles for large systems. Accepting the equivalence of ensembles, or assuming reliable statistics for the characteristic energies, the equilibrium free energy and entropy expressions in Eqs. (A7)–(A9) are exact for any classification scheme. These are the main results of this Appendix. For practical reasons, we consider a less rigorous further step.

As a more serious but often useful approximation, we consider the harmonic approximation, in which $E(z)-E_n$ in Eq. (A5) is assumed to be a quadratic function of positions and momenta. Then, the integrations of a Gaussian can be performed. The assumed quadratic behavior of the potential energy function within a class is determined by spring constants H_i or frequencies ω_i of vibrational normal modes, where $\omega_i^2 = H_i/m$ for particles of mass m. In the classical limit, the contribution of $N_{\rm vib}$ vibrational modes to the Helmholtz free energy is of the form

$$F_{\rm fp}^{\rm vib}(T,E) = -k_B T \ln\left\langle \prod_{i=1}^{N_{\rm vib}} \frac{k_B T}{\hbar \omega_i} \right\rangle_E, \tag{A10}$$

where $\hbar$ is Planck's constant and the average is over all classes with a characteristic energy E. For the unbound degrees of freedom one expects a free energy contribution of the ideal gas type,

$$F_{\rm fp}^{\rm free}(T,E) = -k_B T N_{\rm free} \ln\left(c \frac{V}{N_{\rm free}} T^{3/2} \right), \tag{A11}$$

for $N_{\rm free} = N - (N_{\rm vib}/3)$ free particles, where indistinguishability between these particles is assumed. The constant c, which makes the argument of the logarithm dimensionless, involves Planck's constant and particle masses. A more detailed discussion of the types of contributions should be based on the atomic structure of all the molecules in the system and on quantum mechanical considerations (in the classical limit). To compose the total free energy it is helpful to note that the difference between the free energies $F_{\rm fp}^{\rm vib}$ and $F_{\rm fp}^{\rm free}$ per particle is fully determined by the ratio of two length scales, namely the distance between free particles, $(V/N_{\rm free})^{1/3}$, and the spatial extension of a vibrational mode, $(k_B T/H_i)^{1/2}$. For distinguishable particles, the system size would appear instead of the distance between particles, so that the importance of quantum effects and the reason for the occurrence of Planck's constant are obvious.

APPENDIX B: FOUR-POINT CORRELATIONS

While the distinction of a glass from a melt from static information is a major challenge, the transition from a melt to a glass can easily be recognized in dynamic measurements. Careful investigations reveal extreme heterogeneity in dynamics, where one region of a supercooled liquid near the glass transition can be orders of magnitude faster than dynamics in another region only a few nanometers away [6]. Most particles are trapped in cages for long times before they reach a diffusive regime by jumping from cage to cage. It has been argued [56] that not only the characteristic time scale diverges in approaching the glass transition but also a dynamic length scale, although with a much smaller exponent (a diverging length scale is predicted also by the "excitation-chain theory," which assumes that structural relaxation takes place by thermally excited chains of small molecular displacements [60]).

The characteristic dynamic features in approaching the glass transition can be observed in several different ways.

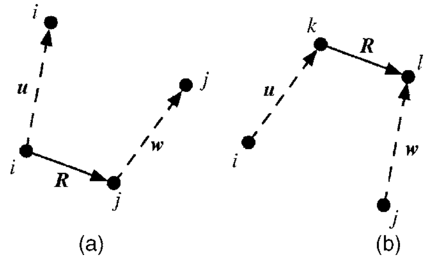

FIG. 3. Symbolic representation of different four-point correlation functions.

One possibility is to consider the probability distribution of single particle displacements within a certain time and to analyze the deviations from a Gaussian distribution. This approach has been applied successfully both in simulations of supercooled binary Lennard-Jones liquids [61,62] and in experiments on colloidal glasses [63]. From the results, one can readily identify a characteristic time scale associated with maximum non-Gaussian behavior and one can try to reveal a dynamic correlation length by comparing the pair correlation functions for mobile and immobile particles.

An alternative procedure to detect the characteristics of glassy dynamics is based on four-point correlation functions employed to recognize correlated particle displacements. Also this approach has been applied successfully both in simulations [55] and in experiments [57]. A characteristic time scale can be associated with maximum correlations, and the peak height can be used to estimate a dynamic correlation length. Experiments for glycerol with $T_g \approx 185$ K show a mild increase of the correlation length from 0.9 nm at 232 K to 1.5 nm at 192 K [57] (note that also the domain sizes found in a scaling approach to geometric "frustration" are only of a few molecular diameters [17]; on the other hand, the "excitation-chain theory" [60] predicts a correlation length scale of about 30 molecular diameters at the glass transition).

Different types of four-point correlations have been studied in the literature. In Ref. [55], the correlation of the displacements of two particles i and j have been studied. This situation corresponds to Fig. 3(a), where $\boldsymbol{u}$ and $\boldsymbol{w}$ are the displacements of the particles i and j initially separated by $\boldsymbol{R}$ during a time interval Δt as obtained by solving the equations of motion. Both the normalized covariance of $|\boldsymbol{u}|$ and $|\boldsymbol{w}|$ for given $\boldsymbol{R}$ and suitable integrals over $\boldsymbol{R}$ have been studied in Ref. [55].

In many experiments, one is unable to track given particles so that the four-point correlation involving four different particles as shown in Fig. 3(b) is more appropriate. This diagram symbolizes the probability for finding two particles k and l of the time-evolved system at positions $\boldsymbol{u}$ and $\boldsymbol{w}$ relative to the particles i and j of the original system, given a fixed relative position $(\boldsymbol{R}+\boldsymbol{u}-\boldsymbol{w})$ of j with respect to i. Similar four-point correlations have been discussed in detail in Ref. [64], where they are related to an experimentally accessible nonlinear susceptibility. This type of correlation is also the basis for the discussion in Ref. [57].

In the remainder of this Appendix we show that the information contained in the hindrance function $h(R)$ introduced to describe nonaffine convection can be expressed in terms of similar four-point correlation functions. However, the displacements $\boldsymbol{u}$ and $\boldsymbol{w}$ in Fig. 3 no longer correspond to the real time evolution of the system but to the changes of inherent structure positions caused by prescribed deformations of a highly supercooled liquid. To see this, we represent the inherent structure pair correlation function after deformation in terms of conditional probability densities,

$$\bar{\rho}_{\rm is}(\boldsymbol{r})\bar{g}_{\rm is}(\boldsymbol{r},\boldsymbol{R}) = \int d^3u\, d^3w\, \rho_{\rm is}(\boldsymbol{r}-\boldsymbol{u})\, g_{\rm is}(\boldsymbol{r}-\boldsymbol{u},\boldsymbol{R}+\boldsymbol{u}-\boldsymbol{w}) \times \frac{1}{N^2}\sum_{i,j,k,l=1}^{N} p(\bar{\boldsymbol{r}}_k^{\rm is}=\boldsymbol{r},\bar{\boldsymbol{r}}_l^{\rm is}=\boldsymbol{r}+\boldsymbol{R}|\boldsymbol{r}_i^{\rm is}=\boldsymbol{r}-\boldsymbol{u}, \boldsymbol{r}_j^{\rm is}=\boldsymbol{r}+\boldsymbol{R}-\boldsymbol{w}), \tag{B1}$$

where quantities to be evaluated after deformation are indicated by an overbar and where we use the symbol $\rho_{\rm is}$ for the mass density in an inherent structure configuration (from a macroscopic perspective, $\rho_{\rm is}$ coincides with the mass density ρ). The relationship (B1) should be compared to the transformation behavior associated with the hindrance h under a small deformation $\tilde{\boldsymbol{\kappa}}$,

$$\bar{\rho}_{\rm is}(\boldsymbol{r})\bar{g}_{\rm is}(\boldsymbol{r},\boldsymbol{R}) = \rho_{\rm is}(\boldsymbol{r}-\tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{r})\, g_{\rm is}(\boldsymbol{r}-\tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{r},\boldsymbol{R}-(\boldsymbol{1} - h\boldsymbol{R}\boldsymbol{R}/R^2)\cdot\tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{R}). \tag{B2}$$

By evaluating suitable moments one could hence determine the hindrance function h in terms of transition probability densities p.

We here follow a different route. Also the correlations of the atomistic (i.e., fluctuating) inherent structure mass densities can be written in terms of transition probability densities,

$$\langle \hat{\rho}_{\rm is}(\boldsymbol{r})\hat{\rho}_{\rm is}(\boldsymbol{r}+\boldsymbol{R})\hat{\rho}_{\rm is}(\boldsymbol{r}-\boldsymbol{u})\hat{\rho}_{\rm is}(\boldsymbol{r}+\boldsymbol{R}-\boldsymbol{w})\rangle = \rho_{\rm is}(\boldsymbol{r}-\boldsymbol{u})\, g_{\rm is}(\boldsymbol{r}-\boldsymbol{u},\boldsymbol{R}+\boldsymbol{u}-\boldsymbol{w}) \times \frac{m^3}{NV}\sum_{i,j,k,l=1}^{N} p(\bar{\boldsymbol{r}}_k^{\rm is}=\boldsymbol{r},\bar{\boldsymbol{r}}_l^{\rm is}=\boldsymbol{r}+\boldsymbol{R}|\boldsymbol{r}_i^{\rm is}=\boldsymbol{r}-\boldsymbol{u}, \boldsymbol{r}_j^{\rm is}=\boldsymbol{r}+\boldsymbol{R}-\boldsymbol{w}). \tag{B3}$$

The occurrence of h in our phenomenological theory thus suggests to consider four-point correlation functions which we choose to study as objects in their own right. In order to focus on structural correlations rather than trivial averages, we consider only the fluctuating contributions to the mass density,

$$\rho_{\rm is}^{\rm f}(\boldsymbol{r}) = \hat{\rho}_{\rm is}(\boldsymbol{r}) - \rho_{\rm is}(\boldsymbol{r}), \tag{B4}$$

in the four-point correlation (B3). This step corresponds to a different normalization of the pair correlation so that average effects are eliminated. Finally, for large $|\boldsymbol{R}|$, two pairs of the four factors in Eq. (B3) become independent, and we hence introduce the correlation function (with conveniently shifted arguments)

$$G_4(\boldsymbol{r},\boldsymbol{R},\boldsymbol{u},\boldsymbol{w}) = \langle \bar{\rho}^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{u})\bar{\rho}^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{R}+\boldsymbol{w})\rho^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r})\rho^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{R})\rangle - \langle \bar{\rho}^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{u})\rho^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r})\rangle\langle \bar{\rho}^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{R}+\boldsymbol{w})\rho^{\mathrm{f}}_{\mathrm{is}}(\boldsymbol{r}+\boldsymbol{R})\rangle, \tag{B5}$$

which vanishes for large $|\boldsymbol{R}|$.

The introduction of the four-point correlation function G_4 is a natural consequence of studying the convection mechanism for the pair correlation function. The analogous object was studied before to identify cooperative dynamic length scales, where $\boldsymbol{u}=\boldsymbol{w}$ [see Eq. (1) of Ref. [56]] or $\boldsymbol{u}=\boldsymbol{w}=\boldsymbol{0}$ [see Eq. (9) of Ref. [64]] was used and the real time evolution was considered instead of given deformations. For a given time step Δt, a susceptibility has been introduced as [64]

$$\chi_4(\Delta t) = \int G_4(\boldsymbol{r},\boldsymbol{R},\boldsymbol{0},\boldsymbol{0})d^3R, \tag{B6}$$

which is actually expected to be independent of the absolute location $\boldsymbol{r}$ in space and can hence be averaged over $\boldsymbol{r}$. For the case of imposed deformations, only the rearrangements with respect to the imposed deformation taking place to minimize the energy should be compared to the actual motions in a glass. The natural generalization of Eq. (B6) would hence be

$$\chi_4(\tilde{\boldsymbol{\kappa}}) = \int G_4(\boldsymbol{r},\boldsymbol{R},\tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{r},\tilde{\boldsymbol{\kappa}}\cdot(\boldsymbol{r}+\boldsymbol{R}))d^3R. \tag{B7}$$

After integrating over $\boldsymbol{R}$ and averaging over $\boldsymbol{r}$, we find

$$\chi_4(\tilde{\boldsymbol{\kappa}}) = \frac{m^4}{V}\sum_{i,j,k,l=1}^{N}[\langle \delta(\bar{\boldsymbol{r}}^{\mathrm{is}}_k - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_i)\delta(\bar{\boldsymbol{r}}^{\mathrm{is}}_l - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_j)\rangle - \langle \delta(\bar{\boldsymbol{r}}^{\mathrm{is}}_k - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_i)\rangle\langle \delta(\bar{\boldsymbol{r}}^{\mathrm{is}}_l - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_j)\rangle]. \tag{B8}$$

In evaluating the averages, the δ function clearly needs to be discretized.

In computer simulations, we can also study correlations of the type represented by Fig. 3(a). As an alternative option, we hence introduce the displacement-displacement correlation function

$$G_{\mathrm{dd}}(\boldsymbol{r},\boldsymbol{R},\boldsymbol{u},\boldsymbol{w}) = \sum_{\substack{i,j=1\\ i\neq j}}^{N}[\langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_i - \boldsymbol{r}^{\mathrm{is}}_i - \boldsymbol{u}||\bar{\boldsymbol{r}}^{\mathrm{is}}_j - \boldsymbol{r}^{\mathrm{is}}_j - \boldsymbol{w}|\delta(\boldsymbol{r}^{\mathrm{is}}_i - \boldsymbol{r}) \times \delta(\boldsymbol{r}^{\mathrm{is}}_j - \boldsymbol{r} - \boldsymbol{R})\rangle - \langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_i - \boldsymbol{r}^{\mathrm{is}}_i - \boldsymbol{u}|\delta(\boldsymbol{r}^{\mathrm{is}}_i - \boldsymbol{r})\rangle \times\langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_j - \boldsymbol{r}^{\mathrm{is}}_j - \boldsymbol{w}|\delta(\boldsymbol{r}^{\mathrm{is}}_j - \boldsymbol{r} - \boldsymbol{R})\rangle], \tag{B9}$$

which is closely related to the quantity G_u introduced in Ref. [55] (for $\boldsymbol{u}=\boldsymbol{w}=\boldsymbol{0}$, G_u is obtained by integrating G_{dd} over $\boldsymbol{r}$). By further integration over $\boldsymbol{R}$, we obtain a susceptibility that is proportional to the quantity κ_u investigated in Ref. [55]. In analogy to Eqs. (B6) and (B7), we actually define the susceptibility as

$$\chi_{\mathrm{dd}}(\Delta t) = \int G_{\mathrm{dd}}(\boldsymbol{r},\boldsymbol{R},\boldsymbol{0},\boldsymbol{0})d^3R, \tag{B10}$$

for the time-evolving system and as

$$\chi_{\mathrm{dd}}(\tilde{\boldsymbol{\kappa}}) = \int G_{\mathrm{dd}}(\boldsymbol{r},\boldsymbol{R},\tilde{\boldsymbol{\kappa}}\cdot\boldsymbol{r},\tilde{\boldsymbol{\kappa}}\cdot(\boldsymbol{r}+\boldsymbol{R}))d^3R, \tag{B11}$$

for the deformed system. After integrating over $\boldsymbol{R}$ and averaging over $\boldsymbol{r}$, we find

$$\chi_{\mathrm{dd}}(\tilde{\boldsymbol{\kappa}}) = \frac{1}{V}\sum_{\substack{i,j=1\\ i\neq j}}^{N}[\langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_i - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_i||\bar{\boldsymbol{r}}^{\mathrm{is}}_j - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_j|\rangle - \langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_i - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_i|\rangle\langle |\bar{\boldsymbol{r}}^{\mathrm{is}}_j - (\boldsymbol{1}+\tilde{\boldsymbol{\kappa}})\cdot\boldsymbol{r}^{\mathrm{is}}_j|\rangle]. \tag{B12}$$

Simulations to study the susceptibilities (B8) and (B12) for binary Lennard-Jones systems are in progress [65].

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