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Nonequilibrium thermodynamics of driven amorphous materials. I. Internal degrees of freedom and volume deformation

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This is the first of three papers devoted to the nonequilibrium thermodynamics of amorphous materials. Our focus here is on the role of internal degrees of freedom in determining the dynamics of such systems. For illustrative purposes, we study a solid whose internal degrees of freedom are vacancies that govern irreversible volume changes. Using this model, we compare a thermodynamic theory based on the Clausius-Duhem inequality to a statistical analysis based directly on the law of increase of entropy. The statistical theory is used first to derive the Clausius-Duhem inequality. We then use the theory to go beyond those results and obtain detailed equations of motion, including a rate factor that is enhanced by deformation-induced noisy fluctuations. The statistical analysis points to the need for understanding how both energy and entropy are shared by the vacancies and their environments.

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I. INTRODUCTION

This is the first of three papers describing our efforts to develop a thermodynamically well-founded theory of nonequilibrium phenomena in amorphous materials. Specific goals of this project are to develop a thermodynamic understanding of the effective disorder temperature and the role that it plays in shear-transformation-zone (STZ) theories of amorphous plasticity [1–5]. While working toward these goals, we have encountered a number of fundamental questions. Those questions include: what is the most basic statement of the second law of thermodynamics? How can we reconcile the different approaches to nonequilibrium thermodynamics taken by engineers, applied mathematicians, and physicists? Are the dynamic roles played by internal degrees of freedom properly described by any of those theoretical approaches? Many recent developments in the physics of glassy materials, including the STZ theory, are based on the idea that the state of disorder in such systems is described by an effective temperature that is not necessarily the same as the ordinary temperature. In what sense is the effective temperature a well-defined thermodynamic concept?

In this first paper, we focus on questions regarding internal degrees of freedom. For illustrative purposes, we address that issue in the limited context of a simple model of a uniform, not necessarily glassy, solid in which vacancies govern irreversible volume changes. We originally developed this vacancy model as a way of studying irreversible changes in the volume of a glassy material subject to varying temperatures and pressures. We hope to return to such applications in the future, but, for the present, we use the model purely as an aid for exploring theoretical ideas. In the second paper [6], we use the insights gained here to define the effective disorder temperature and to write equations of motion for it. Finally, in the third paper [7], we reformulate the STZ theory in a way that is consistent with the thermodynamic analysis presented here and in [6].

Almost by definition, the irreversible responses of materials to applied forces are determined by internal degrees of freedom. Deforming amorphous solids are generally described in terms of internal entities such as flow defects or, of special interest here, STZs. Qualitatively similar internal structures appear in theories of dislocation motion in crystalline solids and in nonequilibrium theories of granular materials and complex fluids. Theories of these dissipative phenomena necessarily invoke the second law of thermodynamics at the very least as a constraint on the equations of motion for the internal variables.

There is a very large body of literature on this subject. For example, see monographs by Lubliner [8], Maugin [9], and Nemat-Nasser [10], which we have found to be especially useful. Essentially all of this literature is based on the postulate that the Clausius-Duhem entropy-production inequality is the fundamental statement of the second law of thermodynamics; therefore, we refer to that theoretical starting point as "conventional." We recognize, however, that the body of literature to which we are referring contains many different points of view and that these points of view have continued to evolve in recent decades, especially in the engineering and applied mathematics communities. Our motivation for developing a statistical approach based directly on the law of increase of entropy simply reflects the fact that we have not been able to take any version of the conventional approach far enough to answer the questions that we are asking.

In this paper, we look at the issues concerning the second law and internal degrees of freedom in a simple but physically realistic situation—the vacancy model mentioned earlier. We start in Sec. II by introducing the model and then, in Sec. III, by briefly summarizing a conventional analysis. The first-principles statistical theory and the resulting nonequilibrium equations of motion are presented in Secs. IV–VI. We conclude in Sec. VII with some remarks about the broader implications of our results.

II. VACANCY MODEL

We consider a uniform viscoelastic solid of total volume V, containing a small but extensive number of vacancies N_v. It may be easiest to visualize this solid as being noncrystalline, but that assumption is not essential for present purposes. To avoid the complications of position-dependent deformation, we assume that this system remains spatially uniform at all times and we work with extensive quantities rather than local densities. We further assume that the system is never too far from thermodynamic equilibrium, i.e., that we are not dealing with extremely rapid nonequilibrium phenomena for which local thermodynamic concepts would be invalid. This quasiequilibrium condition is essential for our arguments in Sec. IV.

Our model, like any model of a material subject only to volume and not shape deformations, is technically viscoelastic rather than elastoplastic. If it is allowed to equilibrate at a fixed temperature and pressure, it eventually returns to the same equilibrium volume with the same number of vacancies, whereas a true elastoplastic material would return to a permanently deformed shape if subjected to shear. A second difference is that a plastic material can undergo steady-state shear flow and usually exhibits a yield stress that marks the onset of that behavior. No such steady-state deformation can occur in the present case.

The fundamental differences between these kinds of inelastic deformation are important, but are not the central issues to be discussed here. Rather, the model of purely volumetric deformation is especially useful to us because there is no need for anything other than an additive decomposition of arbitrarily large elastic and inelastic volume changes. No special mathematical efforts are needed to compute the results of complex sequences of deformations, but the separation between elastic and inelastic deformations remains a nontrivial topic of interest as discussed, for example, in [11].

The volume V in this model consists of three additive components

$$V = V_0 + V_{el} + V_{in}. \tag{2.1}$$

Here, V_0 is a reference volume, determined by the entropy (or temperature). For simplicity, we neglect thermoelastic effects and assume that V_0 is just a constant. The elastic volume, V_{el}, is associated with reversible changes in the elastic energy. An increment δV_{el} is a change in the total volume at fixed entropy and fixed N_v; that is, it takes place with no change in the internal state of the system. Our central assumption is that the inelastic volume associated with the vacancies is simply $V_{in}=v_0 N_v$, where v_0 is the effective volume of a vacancy. V_{el} and V_{in} are independently "variable" but not independently "controllable." In equilibrium, V_{el} is controlled directly by the pressure. On the other hand, N_v is a "hidden" internal variable so long as the system is not coupled to a chemical-potential reservoir that controls the number of vacancies. Nevertheless, we must treat N_v as having its own dynamics and being able at any time to change in ways that are not directly constrained by concurrent changes in V_{el} or the entropy. Specifically, we assume that the rate of inelastic volume deformation is

$$\dot{V}_{in} = v_0 \dot{N}_v \tag{2.2}$$

and that N_v is a dynamical variable that satisfies its own equation of motion.

III. CONVENTIONAL THEORY

A conventional analysis of this model, described along lines laid out by Coleman, Noll, and Gurtin in the 1960s [12,13], starts by writing the first law of thermodynamics in the form

$$\dot{U} = -p\dot{V} + Q, \tag{3.1}$$

where U is the internal energy, p is the pressure, $-p\dot{V}$ is the work done on the system, and Q is the rate at which thermal energy is entering the system. The conventional theory then *postulates* that there exists an entropy S and a temperature θ defined by a continuity equation. For this spatially uniform system, that equation is simply

$$\dot{S} - \frac{Q}{\theta} = \Sigma. \tag{3.2}$$

Here, the temperature θ is expressed in energy units ($k_B=1$), Q/θ is the rate at which entropy is entering the system, and Σ is the entropy source, i.e., the rate at which entropy is being produced. The conventional statement of the second law, the Clausius-Duhem inequality, says that the entropy production rate is non-negative

$$\Sigma \geq 0. \tag{3.3}$$

These relations are taken to be axiomatic; they do not presuppose any statistical interpretation of S or θ.

Eliminating Q between Eqs. (3.1) and (3.2), we find

$$\theta\dot{S} - \dot{U} - p\dot{V} = \theta\Sigma \geq 0, \tag{3.4}$$

which is conveniently rewritten by transforming to the Helmholtz free energy $F(\theta, V_{el}, N_v) = U(S, V_{el}, N_v) - \theta S$ and then performing the partial differentiations

$$\left(\frac{\partial F}{\partial \theta} + S\right)\dot{\theta} + \left(\frac{\partial F}{\partial V_{el}} + p\right)\dot{V}_{el} + \left(\frac{\partial F}{\partial N_v} + v_0 p\right)\dot{N}_v = -\theta\Sigma \leq 0. \tag{3.5}$$

Here we have used Eqs. (2.1) and (2.2).

In the spirit of Coleman and Noll [12], we recognize that this expression consists of three separate, independent inequalities because, as discussed above, the time derivatives are unconstrained by each other. We satisfy the first inequality by identifying $S=-\partial F/\partial\theta$, thus recovering the familiar thermodynamic relation. The second inequality usually is satisfied by identifying $p=-\partial F/\partial V_{el}$, i.e., using the equilibrium relation between p and V_{el}. However, if we were interested in thermoviscoelastic effects, then we would satisfy this inequality by writing a dissipative equation of motion for V_{el} of the form

$$\dot{V}_{el} = -\gamma_{el}\left(\frac{\partial \tilde{F}_{el}}{\partial V_{el}}\right)_{\theta,N_v}; \quad \tilde{F}_{el} = F + pV_{el}, \tag{3.6}$$

where γ_{el} is a non-negative dissipation coefficient. In this way, we would account for the energy dissipation that accompanies the relaxation of the "viscous pressure" $p + \partial F/\partial V_{el}$. Since thermoviscoelasticity is not the topic of primary interest here, we simply adopt the equilibrium relation from here on.

Finally, using Eq. (2.2), we write the third inequality in the form

$$-\left(\frac{\partial \tilde{F}_v}{\partial N_v}\right)_{\theta,V_{el}} \dot{N}_v \geq 0, \quad \tilde{F}_v = F + pv_0N_v. \tag{3.7}$$

This is a specific realization of the Clausius-Duhem inequality, Eq. (3.3). The same result was obtained in Rice's classic 1971 paper [14] where, however, the free energy F was assumed to be a function of the total deformation rather than the elastic part alone, so that the pressure was missing in the expression for $\tilde{F}_v$. The inequality of (3.7) is satisfied by

$$\dot{N}_v = -\gamma_v\left(\frac{\partial \tilde{F}_v}{\partial N_v}\right)_{\theta,V_{el}}, \tag{3.8}$$

where γ_v is again a non-negative dissipation coefficient. More generally, any monotonically increasing function of N_v that vanishes where $\partial\tilde{F}_v/\partial N_v = 0$ can be used on the right-hand side of Eq. (3.8).

Ever since Coleman and Noll introduced their axiomatic version of thermomechanics, physicists have been impressed by its mathematical elegance, but have worried that it might be incomplete because it does not start with a statistical definition of entropy. It is not clear what statistical interpretation of the entropy S is implied by the preceding equations or, conversely, how the internal energy U might depend on S. For example, it is not obvious in a conventional formulation how to evaluate the free energy $\tilde{F}_v$ in Eq. (3.7). More importantly, the Coleman-Noll postulates operationally define a temperature as well as an entropy. In the analysis presented here, we are looking ahead to an effective temperature theory in which there will be two different temperatures—a situation that seems to be beyond the scope of the conventional axiomatic formulation.

Lastly, we note that the axiomatic approach makes no mention of a thermal reservoir. It seems to us that any theory of this kind ought to include a specific mechanism by which the temperature is controlled. If that mechanism involves coupling to a thermal reservoir, then the theory ought to predict the rate at which heat is flowing between the system and the reservoir. Conversely, the theory should be able to predict what happens if that flow is constrained, as in an adiabatic process. But any coupling to a reservoir disappears when Q is eliminated in Eq. (3.4).

IV. STATISTICAL THEORY

The basic statistical statement of the second law is that the system as a whole, including any thermal reservoir to which the subsystem of primary interest may be coupled, must move toward states of higher probability, i.e., to states of higher entropy. Although the Coleman-Noll procedure assigns no *a priori* statistical significance to the entropy, this principle lies at its heart. In their formulation, however, the principal focus is on spatial heterogeneities. The entropy of the system as a whole increases as heat flows between spatially separated elements, each of which is always in a state of local equilibrium with its own local energy, entropy, and temperature. It is conceptually easy, albeit mathematically more complicated, to add spatial heterogeneity to the vacancy model. We do not do this explicitly here but, nevertheless, anticipate the need to reinterpret our uniform model as just one element of a larger, spatially inhomogeneous, coarse-grained system.

Our strategy is to start with a statistical definition of entropy and to introduce a thermal reservoir, but otherwise to stay as close as possible to the conventional analysis. Therefore, in analogy to Eq. (3.1), we begin by writing the first law in the form

$$-p\dot{V} = \dot{U} + \dot{U}_R, \tag{4.1}$$

where $U_R = U_R(S_R)$ is the energy of the reservoir as a function of its entropy S_R. Similarly, in analogy to Eqs. (3.2) and (3.3), the second law is

$$\dot{S}_{neq} + \dot{S}_R \geq 0, \tag{4.2}$$

where S_{neq} is the entropy of a system that is not necessarily in thermal equilibrium.

The main question is what to use for S_{neq}. We propose, with several conditions to be listed below, that the correct choice of this entropy has the form

$$S_{neq}(U,V,\{\Lambda_\alpha\}) = \ln \Omega(U,V,\{\Lambda_\alpha\}), \tag{4.3}$$

where $\Omega(U,V,\{\Lambda_\alpha\})$ is a constrained measure of the number of states of the system with energy U, volume V, and specified values of a set of internal variables $\{\Lambda_\alpha\}$. The Λ_α's are out of equilibrium if their values are not the ones that maximize S_{neq}. When all of them do maximize S_{neq}, i.e., when $\Lambda_\alpha = \Lambda_\alpha^{eq}$, then we require that the equilibrium entropy $S_{eq}(U,V) = \ln \Omega(U,V)$ be accurately approximated by

$$\frac{1}{V}S_{eq}(U,V) \approx \frac{1}{V}S_{neq}(U,V,\{\Lambda_\alpha^{eq}\}). \tag{4.4}$$

This approximation must become an equality in the thermodynamic limit, $V \to \infty$. In general, $S_{neq} < S_{eq}$ because the constrained entropy S_{neq} counts fewer states than the unconstrained entropy S_{eq}. We require that the difference between these quantities per unit volume becomes negligibly small as $\{\Lambda_\alpha\} \to \{\Lambda_\alpha^{eq}\}$ and as the size of the system becomes indefinitely large. Without this condition, we would not have a single, well-defined entropy upon which to base a self-consistent thermomechanical theory.

Validity of Eq. (4.4) therefore requires that three conditions be satisfied:

(1) The set of variables $\{\Lambda_\alpha\}$ must be subextensive. If there are N_α such variables and there are N total degrees of freedom in the system, then N_α/N must vanish in the thermodynamic limit. Otherwise, the variations of the Λ_α's would produce an extensive entropic correction to the equilibrium free energy and Eq. (4.4) would not be correct. More explicitly, note that we can compute S_{eq} by integrating over each of the variables Λ_α in $\Omega(U,V,\{\Lambda_\alpha\})$, obtaining a correction to $\ln\Omega$ proportional to N_α. That correction must be negligibly small compared to $S_{neq}(U,V,\{\Lambda_\alpha^{eq}\})$, which is proportional to N.

(2) We must be working in the quasiequilibrium limit, where all the unconstrained degrees of freedom have rapidly come to equilibrium and where their fluctuations have been accounted for in computing S_{neq}.

(3) Condition (1) requires that the Λ_α's be coarse-grained variables. If there is only a subextensive number of these variables, then each of them must be a sum over a statistically large number of degrees of freedom. That is, the Λ_α themselves must be extensive. (Of course, nothing prevents us from interpreting them as spatial averages over a macroscopically large system.) It then follows that the entropies associated with each of the Λ_α must be included explicitly in S_{neq}. For example, our single internal variable N_v describes an extensive population of vacancies. The associated entropy, i.e., the logarithm of the number of ways in which the N_v vacancies can be arranged in the volume V, must be contained in S_{neq}.

Accordingly, the entropy appearing in Eq. (4.2) is

$$S_{neq}(U,V_{el},N_v) = \ln\Omega(U,V_{el},N_v). \tag{4.5}$$

For reasons discussed in Sec. II, we replace V by V_{el} as an independent argument of S_{neq}. We then invert $S_{neq}(U,V_{el},N_v)$ to obtain $U(S_{neq},V_{el},N_v)$. We identify

$$\left(\frac{\partial U}{\partial S_{neq}}\right)_{V_{el},N_v} = \theta \tag{4.6}$$

and, as stated following Eq. (3.6), we use the equilibrium thermodynamic relation for the pressure

$$\left(\frac{\partial U}{\partial V_{el}}\right)_{S_{neq},N_v} = -p. \tag{4.7}$$

Therefore,

$$\dot{U} = -p\dot{V}_{el} + \left(\frac{\partial U}{\partial N_v}\right)_{S_{neq},V_{el}}\dot{N}_v + \theta\dot{S}_{neq}. \tag{4.8}$$

The first law, Eq. (4.1), becomes

$$-p\dot{V}_{in} - \left(\frac{\partial U}{\partial N_v}\right)_{S_{neq},V_{el}}\dot{N}_v - \dot{U}_R = \theta\dot{S}_{neq}, \tag{4.9}$$

where we have used $\dot{V}=\dot{V}_{el}+\dot{V}_{in}$ to eliminate $\dot{V}_{el}$.

At this point, we depart from the strategy that led to Eq. (3.4). Instead of eliminating the coupling to the thermal reservoir as was done there, we use Eq. (4.9) to evaluate $\dot{S}_{neq}$ in the second law, Eq. (4.2), and we identify $\dot{S}_R=\dot{U}_R/\theta_R$, where $\theta_R=\partial U_R/\partial S_R$ is the reservoir temperature. We also use Eq. (2.2) to eliminate $\dot{V}_{in}$ in favor of $\dot{N}_v$. The result is

$$\mathcal{W}(p,N_v,\dot{N}_v) - \left(1-\frac{\theta}{\theta_R}\right)\dot{U}_R \geq 0, \tag{4.10}$$

where

$$\mathcal{W}(p,N_v,\dot{N}_v) = -\left[pv_0 + \left(\frac{\partial U}{\partial N_v}\right)_{S_{neq},V_{el}}\right]\dot{N}_v \tag{4.11}$$

is the rate at which inelastic work is done on the system minus the rate at which energy is stored by the vacancies. As will be seen, $\mathcal{W}$ is a dissipation rate that appears in various forms throughout this series of papers.

The appearance of $\dot{U}_R$ in this inequality is important because we control the temperature of the system by controlling the reservoir temperature. Thus the inequality in Eq. (4.10) must be satisfied for arbitrary variations of U_R, independent of whatever else is happening in the system. We also must satisfy this inequality for arbitrary variations of N_v. For example, the vacancy population could be relaxing toward an equilibrium value while U_R remains constant. Therefore, in the spirit of Coleman and Noll, we argue that the only way to satisfy this combined inequality for all possible variations of the system is to enforce two separate, independent inequalities

$$\mathcal{W}(p,N_v,\dot{N}_v) \geq 0 \tag{4.12}$$

and

$$-\left(1-\frac{\theta}{\theta_R}\right)\dot{U}_R \geq 0. \tag{4.13}$$

The first of these relations is essentially identical to the Clausius-Duhem inequality in Eq. (3.7). The differences are that we have derived Eq. (4.12) from statistical first principles rather than postulated it and that we know exactly what energy and entropy are involved in it.

The second inequality is satisfied by requiring that $\dot{U}_R$ be a function of θ that changes sign only when $\theta=\theta_R$; therefore we write

$$-\dot{U}_R = A(\theta,\theta_R)(\theta_R-\theta) \equiv Q, \tag{4.14}$$

where $A(\theta,\theta_R)$ is a non-negative function of its arguments. Here, Q has the same meaning that it had in Eq. (3.1)—the rate at which heat is flowing into the system, in this case, from the reservoir—but now, Q is a well-defined function of θ and Eq. (4.14) is an equation, not an inequality. With this definition of Q, Eq. (4.9) becomes

$$\theta\dot{S}_{neq} = \mathcal{W}(p,N_v,\dot{N}_v) + Q. \tag{4.15}$$

V. SPECIFICS OF THE VACANCY MODEL

Because we have an unambiguous definition of the total entropy and because we know that the entropy of the vacancies must be included in it, we can write $S_{neq}(U,V_{el},N_v)$ in the form

$$S_{neq}(U,V_{el},N_v) = S_0(N_v) + S_1(U_1) = S_0(N_v) + S_1[U - e_0N_v - U_{el}(V_{el})]. \tag{5.1}$$

Equivalently, we can invert this relation and write it as an expression for the internal energy U,

$$U(S_{neq},V_{el},N_v) = U_0(N_v) + U_1(S_1) + U_{el}(V_{el}) = e_0N_v + U_1[S_{neq} - S_0(N_v)] + U_{el}(V_{el}). \tag{5.2}$$

Here, $U_0(N_v)$ is the energy of the vacancies, e_0 is the formation energy of a vacancy, $S_0(N_v)$ is the entropy of the vacancies, $U_{el}(V_{el})$ is the elastic energy, and S_1 and U_1 are, respectively, the entropy and energy of all the other configurational, kinetic, and vibrational degrees of freedom in the system. The structure of these relations, i.e., the arguments of U_1 and S_1 in their second versions, describes the way the energy and entropy are shared between the vacancies and the other degrees of freedom. Note that the total entropy and energy in Eqs. (5.1) and (5.2) are assumed to have very simple forms. For example, we have omitted a standard thermoelastic term proportional to S_1V_{el} in Eq. (5.2).

For specificity, we assume that the vacancies are very dilute so that

$$S_0(N_v) = -N_v \ln\left(\frac{N_v}{N_0}\right) + N_v, \tag{5.3}$$

where N_0 is the number of sites at which vacancies might occur. Then, using Eq. (5.2), we find that

$$\left(\frac{\partial U}{\partial N_v}\right)_{S_{neq},V_{el}} = \frac{d}{dN_v}[U_0(N_v) - \theta S_0(N_v)] = e_0 + \theta \ln\left(\frac{N_v}{N_0}\right). \tag{5.4}$$

If we write

$$\left(\frac{\partial U}{\partial t}\right)_{V_{el},N_v} = \theta \dot{S}_{neq} \equiv C_V\dot{\theta} \tag{5.5}$$

and interpret the extensive quantity C_V to be the heat capacity at constant volume, then Eq. (4.15) becomes

$$C_V\dot{\theta} + \left[e_0 + pv_0 + \theta \ln\left(\frac{N_v}{N_0}\right)\right]\dot{N}_v = C_V\dot{\theta} + \left(\frac{\partial G_v}{\partial N_v}\right)_{\theta,p}\dot{N}_v = Q, \tag{5.6}$$

where the vacancy-related Gibbs free energy G_v is

$$G_v(\theta,p,N_v) = e_0N_v - \theta S_0(N_v) + pv_0N_v. \tag{5.7}$$

The Clausius-Duhem inequality, Eq. (4.12), is

$$-\left(\frac{\partial G_v}{\partial N_v}\right)_{\theta,p}\dot{N}_v \geq 0. \tag{5.8}$$

Clearly, this term in Eq. (5.6) is a non-negative rate of heat production associated with the relaxation of the internal variable N_v toward an equilibrium value.

VI. EQUATION OF MOTION FOR N_v

At this point in the analysis, the standard procedure is to postulate a general form for an equation of motion for N_v and to use the Clausius-Duhem inequality in Eq. (5.8) to constrain the parameters that appear in it. In the present case, there is no reason why N_v should do anything more complicated than relax toward a stable equilibrium value. Therefore, for small departures from equilibrium, we write

$$\tau_0\dot{N}_v = \tilde{\Gamma}(N_v)[N_v^{eq}(\theta,p) - N_v], \tag{6.1}$$

where τ_0 is a time scale, $\tilde{\Gamma}$ is a positive, dimensionless rate factor that we anticipate will be a function of N_v (as well as θ and p), and $N_v^{eq}(\theta,p)$ is the equilibrium value of N_v at the given temperature and pressure. A convenient alternative form of this equation is

$$\tau_0\frac{\dot{N}_v}{N_v} = \tilde{\Gamma}(N_v)\left[\frac{N_v^{eq}}{N_v} - 1\right] \cong -\tilde{\Gamma}(N_v)\ln\left(\frac{N_v}{N_v^{eq}}\right). \tag{6.2}$$

Having no information about nonlinear corrections to Eq. (6.1), we can use the second expression on the right-hand side of Eq. (6.2) just as well as the first and will do so from here on. Other nonlinear equations of motion for N_v can easily be incorporated into this analysis when justified by some physical mechanism.

To satisfy the inequality in Eq. (5.8), we require that both $\partial G_v/\partial N_v$ and the expression for $\dot{N}_v$ on the right-hand side of either Eq. (6.1) or Eq. (6.2) vanish at the same point, i.e., at $N_v = N_v^{eq}(\theta,p)$. Thus, $N_v^{eq}(\theta,p)$ is the solution of

$$\left(\frac{\partial G_v}{\partial N_v}\right)_{\theta,p,N_v=N_v^{eq}} = e_0 + pv_0 + \theta \ln\left(\frac{N_v^{eq}}{N_0}\right) = 0 \tag{6.3}$$

and the equilibrium number of vacancies is proportional to a Boltzmann factor

$$N_v^{eq}(\theta,p) = N_0 \exp\left(-\frac{e_0 + pv_0}{\theta}\right). \tag{6.4}$$

The inequality in Eq. (5.8) is always satisfied so long as $\dot{N}_v$ is a monotonically decreasing function of N_v, which is required for dynamic stability, and is true for both Eqs. (6.1) and (6.2).

Retaining Q explicitly in this analysis has the added benefit of allowing us to deduce an expression for the rate factor $\tilde{\Gamma}(N_v)$. The equation of motion for N_v, as shown in Eq. (6.1), is a detailed-balance relation in which the vacancy creation rate is proportional to $N_v^{eq}(\theta,p)$. Therefore, according to Eq. (6.4), the creation rate automatically contains the appropriate Arrhenius activation factor and $\tilde{\Gamma}/\tau_0$ can be interpreted as a dimensionless attempt frequency or, equivalently, a noise strength.

Our experience with the STZ theory of plasticity leads us to write $\tilde{\Gamma}$ as the sum of two terms

$$\tilde{\Gamma} = \rho(\theta) + \Gamma(N_v), \tag{6.5}$$

where $\rho(\theta)$ is the strength of the noise generated solely by thermal fluctuations in the absence of mechanical deformation and $\Gamma(N_v)$ is the noise strength associated with irreversible deformations, i.e., with nonzero $\dot{N}_v$. For present purposes, we could simply set $\rho(\theta)=1$ and let τ_0 be temperature dependent, but we will need the explicit factor $\rho(\theta)$ for discussing glassy systems in the following papers.

A hypothesis (originally due to Pechenik [15]) that has worked well for the STZ theory is that Γ is proportional to the total rate per vacancy at which heat is generated by the work done on the system. In the present case, this means that

$$\frac{\theta_0}{\tau_0}N_v\Gamma(N_v) = \theta\dot{S}_{neq} - Q = \mathcal{W}, \tag{6.6}$$

where θ_0 is an energy and $\mathcal{W}$ is the same non-negative dissipation rate that was defined in Eq. (4.11). With this assumption and with the second form of $\dot{N}_v$ given in Eq. (6.2), Eq. (5.6) becomes

$$-\theta N_v \ln^2\left(\frac{N_v}{N_v^{eq}}\right)(\rho+\Gamma) + \theta_0\Gamma N_v = 0. \tag{6.7}$$

Solving for $\rho+\Gamma$ (a necessarily non-negative noise strength), we find

$$\tilde{\Gamma} = \rho + \Gamma = \frac{\rho(\theta)}{1-(\theta/\theta_0)\ln^2(N_v/N_v^{eq})}. \tag{6.8}$$

Thus, the mechanically generated noise enhances the rate factor, possibly quite substantially. The feature that $\tilde{\Gamma}$ diverges when N_v is sufficiently far from its equilibrium value simply means that the system is dynamically driven away from such values of N_v and that $\tilde{\Gamma}$ remains positive at all times.

Putting these pieces of the theory together, we have

$$\frac{\dot{N}_v}{N_v} = -\frac{\rho(\theta)}{\tau_0}\frac{\ln(N_v/N_v^{eq})}{1-(\theta/\theta_0)\ln^2(N_v/N_v^{eq})}. \tag{6.9}$$

Equation (5.6) becomes

$$C_V\dot{\theta} + \theta\ln\left(\frac{N_v}{N_v^{eq}}\right)\dot{N}_v = Q = A(\theta,\theta_R)(\theta_R-\theta). \tag{6.10}$$

The combination of Eqs. (6.9) and (6.10) allows us to compute time-dependent functions $\theta(t)$ and $N_v(t)$ given any driving force $p(t)$ and reservoir temperature $\theta_R(t)$. The simplest case is the limit in which the coupling to the reservoir is so strong that $\theta=\theta_R$ and the heat capacity of the reservoir is so large that θ_R remains a constant independent of how much heat is flowing to or from the system. This assumption, that the temperature is fixed by coupling to the reservoir, is implicit in most thermodynamic theories, but it is actually a bit subtle. The quantity Q on the right-hand side of Eq. (6.10) is undefined in the limit $A\to\infty$, $\theta\to\theta_R$, which means that it can assume whatever value is needed in order to keep $\theta=\theta_R$ =constant. With $\dot{\theta}=0$, Eq. (6.10) is just the Clausius-Duhem inequality again, now telling us that $Q<0$ and that—as in the Kelvin-Planck statement of the second law [16]—we are not allowed to convert heat directly into work.

Alternatively, suppose that the process is adiabatic, i.e., $A=0$. Then Eq. (6.10) determines how the temperature rises as the external work is converted into internal heat. In the following paper, we will encounter an intermediate case in which A is small but nonzero.

VII. CONCLUDING REMARKS

Although the statistical analysis described here has been developed primarily for use in the effective-temperature theory of amorphous materials presented in the following paper [6], the present results already point toward some general conclusions. We have shown that the Clausius-Duhem entropy-production inequality, when applied to the dynamics of internal degrees of freedom, can be derived directly from a statistical interpretation of the second law of thermodynamics—but only if the conditions listed following Eq. (4.4) are satisfied. Perhaps the most important of these conditions is that the internal variables must be a small set of extensive quantities in order that the statistical entropy be well defined for nonequilibrium situations. This condition, in turn, means that entropies as well as energies associated with the internal variables must be included in any dynamical description of the system.

The quantity appearing in the Clausius-Duhem inequality in Eq. (5.8) is interpreted by Lubliner [17] as the "dissipation associated with the internal variables and their conjugate forces." Our analysis suggests a sharper and more physically intuitive interpretation that the rate of energy dissipation $\mathcal{W}$ is the difference between the inelastic power $-p\dot{V}_{in}$ $=-pv_0\dot{N}_v$ and the rate of change of the *free* energy $U_0(N_v)$ $-\theta S_0(N_v)$ that is stored in the internal degrees of freedom.

One example of this difference occurs in Rice's 1971 paper [14], where he suggests that his internal variables represent an extensive set of slips on slip planes distributed throughout a polycrystalline material. However, he does not calculate the number of ways in which the total slip can be realized as the sum of many individual slips and therefore does not include the entropy associated with his internal "averaging variables" in dynamical formulas analogous to Eqs. (5.7) and (5.8).

These issues persist in the more recent literature and, in our opinion, are quite serious. For example, Anand and Su [18] implement something like Rice's picture of frictional slips on multiple slip planes by using a phenomenological, nonlinear, rate-dependent relation between local flow and resolved stresses. Some memory of past deformation is carried by a "plastic volumetric strain" and by a related cohesion parameter that appears in the flow equation, but these are scalar quantities that cannot contain information about the directional history of shear flow. There is no dynamical yield stress as in STZ theory, nor—so far as we can tell—is there any way of using the theory to predict what happens when the loading stresses are removed or reversed, partly because the plastic volumetric strain and the cohesion parameter are scalars, but more importantly because neither are properly constituted internal state variables. The STZ theory has been developed explicitly to overcome such difficulties. It is the topic of the third paper in this series [7].

A related question, which is sometimes raised but not answered in the conventional literature, is what happens when the internal degrees of freedom do not relax in a simple manner. In the present case, our irreversible process can be described by a variational principle; that is, our single internal variable N_v moves downhill in the one-dimensional free-energy landscape defined by $G_v(N_v)$ in Eq. (5.7). This picture is generalized in the conventional literature by assuming that a system with multiple internal variables moves downhill in a multidimensional inelastic potential. The resulting fluxes obey what is called a "normality condition" or sometimes a "generalized normality condition" [8] because they are assumed to be perpendicular to surfaces of constant (generalized) potential.

We already know that the picture cannot be so simple for the STZ theory, where increasing shear stress drives the system through an exchange of stability between jammed and flowing steady states. This behavior is discussed in detail in the third paper in this series [7]. More generally, we know that no such energy-minimization principles exist for many open situations, where the system is being persistently driven away from equilibrium and where there are multiple, coupled, internal state variables. It seems to us that it will be hard to predict a form for a generalized Clausius-Duhem inequality without starting from a first-principles, fully statistical and dynamical description of such systems.

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