Statistical mechanics of time independent nondissipative nonequilibrium states

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We examine the question of whether the formal expressions of equilibrium statistical mechanics can be applied to time independent nondissipative systems that are not in true thermodynamic equilibrium and are nonergodic. By assuming that the phase space may be divided into time independent, locally ergodic domains, we argue that within such domains the relative probabilities of microstates are given by the standard Boltzmann weights. In contrast to previous energy landscape treatments that have been developed specifically for the glass transition, we do not impose an *a priori* knowledge of the interdomain population distribution. Assuming that these domains are robust with respect to small changes in thermodynamic state variables we derive a variety of fluctuation formulas for these systems. We verify our theoretical results using molecular dynamics simulations on a model glass forming system. Nonequilibrium transient fluctuation relations are derived for the fluctuations resulting from a sudden finite change to the system's temperature or pressure and these are shown to be consistent with the simulation results. The necessary and sufficient conditions for these relations to be valid are that the domains are internally populated by Boltzmann statistics and that the domains are robust. The transient fluctuation relations thus provide an independent quantitative justification for the assumptions used in our statistical mechanical treatment of these systems. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2780161]

I. INTRODUCTION

The formal expressions of equilibrium statistical mechanics strictly apply only to ergodic systems that are in thermodynamic equilibrium. Thus these expressions only strictly apply to systems which are at the global free energy minimum given the system Hamiltonian and the macroscopic thermodynamic state variables (number of particles, temperature and pressure, or density). For such systems Gibbsian equilibrium statistical mechanics provides an exact prescription for how to calculate the various thermodynamic quantities.[1] However, these prescriptions are routinely applied to systems that are not in true thermodynamic equilibrium (for example, to metastable liquids,[2] glasses,[3] polymorphs,[4] and allotropes). It is often observed empirically that within experimental uncertainties many expressions for thermodynamic quantities yield consistent results. In the present paper we provide arguments for why many of the results of equilibrium statistical mechanics can be applied to such time independent nondissipative nonequilibrium systems. We also point out some of the limits inherent in the application of the formulas of equilibrium statistical mechanics to such systems.

We choose to study the isothermal isobaric ensemble[5] (externally regulated pressure and temperature). The methods and reasoning we use here can be directly transferred to other ensembles such as the canonical (fixed volume and externally regulated temperature). The Gibbs free energy G,

which is the thermodynamic potential for the isothermal isobaric ensemble, is related to the partition function Δ by the equation

$$G(N, P_0, T) = -k_B T \ln \Delta(N, P_0, T), \tag{1}$$

and the partition function is given by the integral

$$\Delta = \int \int_D dV d\Gamma \exp[-\beta(H_0(\Gamma) + P_0 V)], \tag{2}$$

where $\Gamma = (\mathbf{q}, \mathbf{p})$ is the phase space vector describing the coordinates $\mathbf{q}$ and momenta $\mathbf{p}$, of all the N particles in the system, P_0 is the thermodynamic pressure, and $\beta = 1/k_B T$ where k_B is Boltzmann's constant and T is the temperature. The integration domain D provides limits for both integrals and extends over all the available phase space (Γ, V). This is $\pm \infty$ for every component of the generalized momentum, $0 \rightarrow \infty$ for the volume V, and over the volume for the Cartesian coordinates of the particles. Since the system Hamiltonian $H_0(\Gamma, V)$ is single valued, so too is the partition function and in turn the free energy.

If we require the distribution function of a single thermodynamic phase it is necessary that other phases do not contribute significantly to the partition function. The full integration domain D may include states that are characteristic of crystalline states or fluids states. In the thermodynamic limit this does not cause problems because, as we shall see, the partition function will be *completely* dominated by those microscopic domains that have the lowest free energy. However the application of these formulas to allotropes or metastable systems does present a problem. The standard equilib-

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rium statistical mechanical expressions for variables such as the enthalpy I, the average volume $\langle V \rangle$, and second order quantities such as the specific heat at constant pressure c_P may all be computed from a knowledge of the partition function [Eq. (2)] or equivalently the thermodynamic potential [Eq. (1)]. If other phases of lower free energy exist this computation [from Eq. (2) as written] will strictly speaking be incorrect.

It is well known that the formulas for thermal properties such as entropy, free energy, temperature, and specific heat do *not* hold for *dissipative* nonequilibrium systems outside the linear response regime.[6,7] In this paper we examine the question of whether they are correct for any *nondissipative* nonequilibrium systems such as allotropes, metastable systems, or history dependent glasses. We provide a statistical mechanical theory of time independent, nondissipative, nonequilibrium systems. The theory is based on the fact that these systems are nonergodic and individual sample systems comprise ergodic domains that do not span all of phase space. We show that if these domains are robust with respect to small changes in thermodynamic state variables, a successful statistical mechanical treatment of these nonequilibrium systems can be given. We provide direct evidence, from molecular dynamics simulations on a model glass former, that the resulting statistical mechanical formulas are satisfied within empirical errors. Finally we provide an independent test of the two key elements of our theory: Boltzmann weights within the phase space domains and the robustness of those domains. It happens that these two elements are the necessary and sufficient conditions for the application of the transient fluctuation relation to finite thermodynamic quenches (in temperature or pressure) for such systems.[8] While the application of thermodynamics to a single time averaged system is usually straightforward the application to an ensemble, whose members may be locked in different phase space domains, can require modification to the standard formulas.

In the case of glasses our treatment has some similarities with the energy landscape approach of Stillinger and Weber.[3,9,10] However, there are significant differences; our treatment makes no reference to the inherent structure and imposes no *a priori* knowledge of the interdomain relative population levels. The energy landscape approach has been extended to account for the phenomena of aging or history dependence by the addition of a fictive parameter.[11] Sciortino has convincingly shown that the addition of a single fictive parameter is inadequate to deal with glasses, which may have different properties at the same temperature and pressure if they are prepared by a different protocol (different history dependence) (Ref. 11) and poses the challenge to recover a thermodynamic description "by decomposing the aging system into a collection of substates." The treatment we present here succeeds in doing just that by providing a rigorous development of equilibrium statistical mechanics and thermodynamics for ensembles of systems where the phase space breaks up into ensembles of domains whose interdomain dynamics is nonergodic and whose interdomain population levels may not be Boltzmann weighted.

II. CONDITIONS FOR EQUILIBRIUM

A dynamical system in equilibrium has the properties that it is nondissipative and that its macroscopic properties are time independent. Thus the N-particle phase space distribution function $f(\mathbf{\Gamma}, V, t)$ must be a time independent solution to the Liouville equation,[7]

$$\frac{\partial}{\partial t} f(\mathbf{\Gamma}', t) = -\dot{\mathbf{\Gamma}}' \cdot \nabla f(\mathbf{\Gamma}', t) - f(\mathbf{\Gamma}', t) \Lambda = 0, \qquad (3)$$

where Λ is the phase space compression factor[7] obtained by taking the divergence of the equations of motion [see Eq. (5)] and $\mathbf{\Gamma}'$ is the extended phase space vector which consists of $\mathbf{\Gamma}$ and may include additional dynamical variables such as the volume V. Since the system is assumed to be nondissipative both the ensemble average $\langle \Lambda \rangle$ and the time average $\bar{\Lambda}$ of the phase space compression factor (which is directly proportional to the rate at which heat is exchanged with the fictitious thermostat) are zero. The time independent solution to Eq. (3) depends on the details of the equations of motion. Equilibrium solutions to Eq. (3) for the equations of motion, suitable for use in molecular dynamics simulations, are compatible with Gibbsian equilibrium statistical mechanics.[7]

Microscopic expressions for mechanical properties such as the pressure, the internal energy, the enthalpy, and the volume can be derived without reference to Gibbsian statistical mechanics and indeed can be proved to hold for nonequilibrium systems including nonequilibrium dissipative systems.

There are two ways in which the formulas derived from Gibbsian equilibrium statistical mechanics can break down. The most obvious way is that the relative weights of microstates may be non-Boltzmann and the exponential factor $\exp[-\beta H_0(\mathbf{\Gamma})]$, may be replaced by some other function [either the exponential function itself may be modified as in Tsallis statistics[12] or the Hamiltonian may be modified to some new function $H_0(\mathbf{\Gamma}) \rightarrow B(\mathbf{\Gamma}, t) H_0(\mathbf{\Gamma})$]. In either circumstance the standard expressions for the thermal quantities derived from equilibrium Gibbsian statistical mechanics will not be valid. This certainly happens in dissipative nonequilibrium systems where the distribution function is not a time independent solution to Eq. (3).

In deterministic nonequilibrium steady states the phase space may break down into ergodically separated domains (Each of which will be fractal and of lower dimension than the ostensible phase space dimension. This is a consequence of dissipation.) However for these steady states, the domains are always exquisitely sensitive to macroscopic thermodynamic parameters since they are strange fractal attractors.[13] Often a deterministic *nonequilibrium* steady state approaches a unique fractal attractor. As time progresses the distribution function collapses ever closer to (but never reaching) the steady state attractor.

The second way that these expressions may fail is that the system may become nonergodic. In this case three things happen. (a) Most obviously time averages no longer equal full (domain D) ensemble averages. (b) If we take an initial microstate the subsequent phase space trajectory will span

some phase space domain D_α where the initial phase is labeled $\mathbf{\Gamma}'_\alpha(0)$. In this case for nondissipative nonequilibrium systems where the domains are robust (i.e., small changes in thermodynamic state parameters to leading order do not change the domain) the standard equations of equilibrium statistical mechanics may continue to be valid but in a slightly modified form. We will examine this in some detail below. (c) Given robust domains the population densities between each domain may well depend on the history of the system. The *macroscopic* history can be expected to condition the ensemble's set of initial *microstates* $\{\mathbf{\Gamma}'_\alpha(0)\}$ from which the macroscopic material is formed. This in turn can be expected to condition the set of nonergodic domains $\{D_\alpha\}$ that characterize the ensemble. For a macroscopic sample spanning a single ergodic domain D_α, the free energy G_α then satisfies only a local extrema principle and thus looses much of its thermodynamic meaning.

III. THEORY AND METHODS

A. Equations of motion

We use the constant pressure Nosé-Hoover equations of motion by combining the Nosé-Hoover feedback mechanism with the so-called SLLOD or DOLLS equations of motion,[7] which are equivalent for dilation. It is known that these equations of motion do not produce artifacts in the systems linear response to an external field and that to leading order the effect on the dynamical correlation functions is at most $O(1/N)$, where N is the number of particles.[7] The equations of motion are,

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \alpha_V \mathbf{q}_i,$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \alpha_V \mathbf{p}_i - \alpha_T \mathbf{p}_i,$$

$$\dot{\alpha}_V = \left(\frac{V(t)}{Nk_BT}(P(t) - P_0) + \frac{1}{N} \right) \Big/ \tau_V^2, \qquad (4)$$

$$\dot{\alpha}_T = \left(\frac{\sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{p}_i}{3mNk_BT} - 1 + \frac{1}{N} \right) \Big/ \tau_T^2,$$

$$\dot{V} = 3\alpha_V V,$$

where $\mathbf{q}_i$ is the position, $\mathbf{p}_i$ is the momentum, and $\mathbf{F}_i$ is the force on the ith particle, m is the particle mass, τ_V is the barostat time constant, τ_T is the thermostat time constant, T is the input temperature, P_0 is the input (thermodynamic) pressure, and the instantaneous (mechanical) pressure is given by $P(t) = (\sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{p}_i/m + \sum_{i=1}^N \mathbf{F}_i \cdot \mathbf{q}_i)/3V$. Because these equations of motion have additional dynamical variables the extended phase space vector is $\mathbf{\Gamma}' = (\mathbf{\Gamma}, V, \alpha_V, \alpha_T)$. In order to obtain the equilibrium distribution function we first define the Hamiltonian, in the absence of any external fields, dilation $\alpha_V(t) = 0$, or thermostats $\alpha_T(t) = 0$, as $H_0 = \Phi + \frac{1}{2}\sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{p}_i/m$, where Φ is the total interparticle potential energy. To proceed further we identify the extended Hamiltonian as $H_E = H_0 + \frac{3}{2}N\alpha_T^2\tau_T^2 k_BT + \frac{3}{2}N\alpha_V^2\tau_V^2 k_BT$ and then obtain the phase space compression factor

$$\Lambda \equiv \nabla \cdot \dot{\mathbf{\Gamma}}' = \sum_{i=1}^N \sum_{\gamma=1}^3 \frac{\partial \dot{q}_{i,\gamma}}{\partial q_{i,\gamma}} + \sum_{i=1}^N \sum_{\gamma=1}^3 \frac{\partial \dot{p}_{i,\gamma}}{\partial p_{i,\gamma}} + \frac{\partial \dot{V}}{\partial V} + \frac{\partial \dot{\alpha}_V}{\partial \alpha_V}$$

$$+ \frac{\partial \dot{\alpha}_T}{\partial \alpha_T} = \beta(\dot{H}_E + P_0\dot{V}), \qquad (5)$$

where the index γ sums over the components of the Cartesian position and momentum vectors. Using the Heisenberg streaming representation (rather than the more usual Schrödinger representation [Eq. (3)]) of the Liouville equation

$$\frac{d}{dt} \ln[f(\mathbf{\Gamma}'(t),t)] = -\Lambda(\mathbf{\Gamma}'(t)), \qquad (6)$$

we can obtain the particular time independent solution for the distribution function,

$$f(\mathbf{\Gamma}') \propto \exp(-\beta I_0)\exp(-\tfrac{3}{2}N(\alpha_T^2\tau_T^2 + \alpha_V^2\tau_V^2)), \qquad (7)$$

where $I_0(t) = H_0(t) + P_0V(t)$ is the instantaneous enthalpy. The second exponential on the right hand side of Eq. (7) with α_V and α_T in the argument, which has no dependence on the input temperature T or the input pressure P_0, is statistically independent from the rest of the distribution function, which is the standard equilibrium isothermal isobaric distribution. We can normalize Eq. (7) by integrating over all space to obtain the thermodynamic equilibrium distribution function,

$$f(\mathbf{\Gamma}') = \frac{3}{2}N\frac{\tau_V\tau_T}{\pi} \exp\left(-\frac{3}{2}N(\alpha_T^2\tau_T^2 + \alpha_V^2\tau_V^2)\right)f_0(\mathbf{\Gamma}, V), \qquad (8)$$

where the standard isothermal isobaric distribution function is

$$f_0(\mathbf{\Gamma}, V) = \frac{\exp(-\beta(H_0 + P_0V))}{\int_0^\infty dV \int_D d\mathbf{\Gamma} \exp(-\beta(H_0 + P_0V))}. \qquad (9)$$

It should be emphasized that the derivation of Eq. (7) says nothing about the existence or otherwise of any domains. These must be considered when normalizing Eq. (7), and thus Eqs. (8) and (9) are only valid in thermodynamic equilibrium. If we wish to use Eq. (7) outside thermodynamic equilibrium we must consider domains.

We can also use the so called SLLOD equations of motion[7] to apply strain rate controlled Couette flow (planar shear) to our equations of motion. The necessary modifications to the first two lines of Eq. (4) result in

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \alpha_V \mathbf{q}_i + \mathbf{i}\dot{\gamma}q_{yi},$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \alpha_V \mathbf{p}_i - \alpha_T \mathbf{p}_i - \mathbf{i}\dot{\gamma}p_{yi}, \qquad (10)$$

where $\dot{\gamma}$ is the strain rate and the last three lines of Eq. (4) remain unchanged.

B. Equilibrium statistical mechanics in a single domain

As we have stated in the introduction, the full phase space domain includes phase points from many different thermodynamic phases (gases, liquids, and crystals). In the thermodynamic limit this does not cause problems. To under-

stand this suppose we can label microstates to be in either of two possible thermodynamic phases 1 or 2 bound by two phase space domains D_1 and D_2. By assumption we are not presently considering the possibility of coexistence. The system is assumed to be ergodic: atoms in one thermodynamic phase can, in time, transform into the other phase. Assume that the two thermodynamic phases have different free energies: G_1 is the Gibbs free energy of the first phase and G_2 is that of the second phase. For a sufficiently large N the free energy [Eq. (1)] is an extensive variable. We may thus express the partition function as the sum of contributions from the two phases

$$\Delta = e^{-\beta G_1} + e^{-\beta G_2} = e^{-\beta N g_1} + e^{-\beta N g_2}, \quad (11)$$

where the lower case g on the second line is used to represent the intensive free energies which do not change with system size N in the thermodynamic limit. If g_1 is less than g_2 then in the thermodynamic limit, $N \to \infty$, the only significant contribution to the partition function Δ will be due to the "equilibrium" phase, namely, phase 1. Thus although the free energy defined in Eq. (2), is given by an integral over all of phase space D, in the thermodynamic limit this integral can be approximated to arbitrary precision, as an integral over the domain that includes the most stable phase. Suppose D_1 includes only crystalline phases and D_2 includes only amorphous phases and further suppose that a particular crystalline phase has a lower free energy than any amorphous phase. According to Eq. (2), we should calculate the free energy by integrating over all crystalline and all amorphous phases. In practice in the thermodynamic limit we can compute the free energy to arbitrary accuracy by integrating Eq. (2), only over that part of phase space within which the thermodynamically stable state resides.

If we consider a nonergodic system that according to different preparative protocols can be formed in either phase 1 or phase 2, after preparation, because the system is nonergodic both phases are kinetically stable indefinitely. By restricting the phase space integrals for the free energy to those domains that contain the kinetically stable phase we can compute the free energy of that phase. However, although it may be possible to formally assign free energies to nonergodic systems, these free energies clearly fail to satisfy any global extremum principle. As we will show these partition functions can be used formally to yield first and second order thermodynamic quantities by numerical differentiation. The metastable domain is a subset of the thermodynamic equilibrium domain which contains all possible atom positions including the ones belonging to the metastable phase.

Within a single domain the system is, by construction, ergodic. Thus for almost all microstates $\Gamma'_\alpha(0) \in D_\alpha$, ensemble averages, of some variable B, $\langle B \rangle$, equal time averages $\bar{B}$, for phase space trajectories that start at time zero,

$$\langle B \rangle_\alpha = \bar{B}_\alpha \equiv \lim_{t \to \infty} \frac{1}{t} \int_0^t ds B(\Gamma'(s); \Gamma'_\alpha(0)). \quad (12)$$

Microscopic expressions for mechanical variables may be used as a test of ergodicity in nondissipative systems which are out of equilibrium. (Note that a nondissipative system does not on average exchange heat with any thermal reservoir with which it has been in contact for a long time.) In the case of metastable fluids or allotropes we may introduce a single restricted domain and by construction the system remains ergodic within this domain.

A *gedanken* experiment can be used to justify the Boltzmann weighting and the applicability of the zeroth law of thermodynamics for such systems. Consider a double well potential with an inner and outer potential well. If the barrier between the inner and outer wells is much greater than $k_B T$, so that over the duration of observation (which is much greater than any relaxation time in the ergodically restricted subsystem) no particles cross the barrier, then the system considered as a double well system will be, by construction, nonergodic. For systems composed of particles that are solely found in the inner potential well, our hypotheses are that the distribution of states in the inner well will be given by a Boltzmann distribution taken over the inner domain only and that, if such a system is in thermal contact with a body in true thermodynamic equilibrium, then the temperature of the ergodically restricted system must equal that of the system in true thermodynamic equilibrium. We can justify these hypotheses by considering a fictitious system that only has the inner potential well and in which the potential function is positive infinity for all separations that are greater than the inner well (this includes the position of the outer well). In accord with Gibbsian statistical mechanics the distribution of states is canonical over this (single well) potential. Furthermore the zeroth law of thermodynamics will apply to this single well system. Now if we dynamically generate the outer well, all the particles locked inside the inner well cannot "know" that the outer well has been formed so their dynamics will be completely unchanged by the time dependent generation of the new outer well. The generation of an inaccessible outer well will not alter the distribution of states in the inner well nor will it cause any flow of heat to the equilibrium heat bath surrounding the system. This provides a compelling physical justification for our domain hypotheses over a single ergodic subdomain of phase space.

In order to recover many of the basic relationships of Gibbsian statistical mechanics it is also necessary that the system appears to be in dynamical equilibrium, i.e., $|f(\Gamma_\alpha, t) - f(\Gamma_\alpha, t + \tau_o)| < \varepsilon, \forall \Gamma_\alpha, \in D_\alpha$, for some small ε, over the longest observation time τ_o. We use the definition of the partition function [Eq. (2)] as before but now the domain D_α in the integral is over a single contiguous hypervolume in the configuration space of the generalized position coordinate $\mathbf{q}$ and volume V. The domain over the generalized momentum $\mathbf{p}$ and multipliers α_V and α_T remains unchanged. We then obtain the Gibbs free energy by use of Eqs. (1) and (2). Thus far all we have altered is our definition of the domain. In changing the definition of the domain we have opened a potential problem for Gibbsian statistical mechanics. If we change the temperature or the pressure of the system the domain may also change. If the domain changes this may make a contribution to the derivatives of the partition function, Eq. (2), and the direct connection with the standard

outcomes of macroscopic thermodynamics will be lost. Thus the domains need to be robust with respect to changes in thermodynamic state variables.

There are three means by which a system could have robust domains. The first and most obvious is that the domain does not change when the pressure or the temperature changes, $\partial D_\alpha(X,Y)/\partial X=0$, where X is a thermodynamic state variable and Y is the other thermodynamic state variables. When we lower the temperature only the inverse temperature β in Eq. (7) changes and when we change the pressure only the parameter P_0 changes. If the domain's boundary is determined by a surface on which $I_0(\Gamma')$ always has a very high value it will remain unchanged under infinitesimal changes in P_0 or β. We will refer to a surface domain that doesn't change with the state variables as completely robust. The second way is that the distribution function is always identically zero on the domain boundary,

$$f_0(\Gamma,V)=0 \ \forall \ \Gamma \in S_\alpha, \tag{13}$$

where S_α is the surface of the domain D_α. Because the domain is contiguous (required for it to be ergodic) it must have a single connected surface. Such a domain will be robust. The third way the domain can be robust is less restrictive and allows for the possibility that the domain does change when the thermodynamic variables are changed substantially. If δX is an infinitesimal change in a thermodynamic state variable, then

$$\delta D_\alpha(X+\delta X,Y)=\delta D_\alpha(X,Y)+\mathcal{O}(\delta X)^n, \tag{14}$$

where Y denotes the other thermodynamic state variables; we require that $n \geq 2$ for first order thermodynamic property formulas to be correct, $n \geq 3$ for second order property formulas to be correct, etc. Obviously this third way will be satisfied in the first two cases as well.

Later in the paper we will introduce an independent test of domain robustness. However, if a system was not robust then we would expect that small changes in the state variables would change the macroscopic properties of the sample permanently—it would be as though the preparation history of the sample was continuing even for small changes in the state variable. Quite obviously if we produce huge changes in the state variables we will of course permanently change the properties of the system because we permanently deform the ergodic domain. Experience shows, however, that very many nondissipative nonequilibrium systems are quite robust with respect to small changes in state variables. All that is required for fluctuation formulas for first, second, and third order thermodynamic quantities to be valid is that the domains be unchanged, to first, second, or third order, by infinitesimal changes in the state variables. Obviously a robust domain is an ideal construct. However, on the typical time scale of interest, which is usually orders of magnitude less than the time scale on which the system will change to a new phase of lower free energy, this can be a very good approximation.

We are now able to recover most of the standard results of Gibbsian equilibrium statistical mechanics. For example, we may calculate the enthalpy $\langle I \rangle_\alpha$ from the partition function Δ, Eq. (2), as

$$\langle I \rangle_\alpha = k_B T^2 \left(\frac{\partial \ln \Delta_{D_\alpha}}{\partial T} \right)$$
$$= \frac{\int \int_{D_\alpha} dV d\Gamma I_0(\Gamma,V) \exp(-\beta I_0(\Gamma,V))}{\int \int_{D_\alpha} dV d\Gamma \ \exp(-\beta I_0(\Gamma,V))} = \bar{I}_\alpha. \tag{15}$$

Here we are considering an ensemble of systems which occupy a single ergodic domain D_α. Since this domain is self-ergodic the ensemble average is equal to the corresponding time average.

The term on the right hand side of the second line is obviously the average value of the instantaneous enthalpy $I_0(\Gamma,V)=H_0(\Gamma,V)+P_0 V$, obtained by using the equilibrium distribution function, Eq. (9) or equivalently Eq. (8), with the integration limits restricted to the domain D_α, where P_0 is the externally set thermodynamic pressure. We can also obtain expressions for the average volume $\langle V \rangle$ and the constant pressure specific heat c_P by taking the appropriate derivatives of the partition function, Eq. (2). In other ensembles we can use the same procedure to find other variables, e.g., the internal energy, the average pressure, and the constant volume specific heat in the canonical (N,V,T) ensemble.

An important outcome is that this description remains compatible with macroscopic thermodynamics. Here the Gibbs free energy is defined as

$$G \equiv U - TS + P_0 \langle V \rangle, \tag{16}$$

where $U = \langle H_0 \rangle$ is the internal energy and S is the entropy. If we take the derivative of Eq. (16) with respect to one of the isobaric isothermal ensemble conjugate variables (N,P_0,T) while keeping the others fixed we obtain

$$\left(\frac{dG}{dT} \right)_{N,P_0} = -S,$$
$$\left(\frac{dG}{dP_0} \right)_{N,T} = \langle V \rangle. \tag{17}$$

We now write down the microscopic equilibrium equation for the Gibbs entropy,

$$S = -k_B \int \int_{D_\alpha} dV d\Gamma f_0(\Gamma,V) \ln f_0(\Gamma,V). \tag{18}$$

It is an easy matter to show that Eqs. (1), (2), and (18) are consistent with the two derivatives given in Eq. (17). Given our condition of a robust boundary we thus have a form of Gibbsian statistical mechanics for metastable states which remains in agreement with macroscopic thermodynamics.

C. Multiple domains and nonergodicity

We now wish to consider an ensemble of systems which is prepared from an initial ergodic (usually high temperature) equilibrium ensemble. There is some protocol P, which involves a temperature quench or a sharp pressure increase, etc., which breaks the ensemble into a set of subensembles characterized by different macroscopic properties. After the protocol P has been executed we allow all the ensemble members to relax to states which are macroscopically time

independent, to within experimental tolerances. We assume that the ensemble can be classified into a set of subensembles $\{\alpha, \alpha=1, N_D\}$ whose macroscopic properties take on N_D distinct sets of values. For the longest observation times available a macroscopic system classified as an α system is not observed to transform into a β system, and vice versa. The full ensemble of systems is thus nonergodic. However, in each individual subensemble, say, subensemble α, the constituent members are ergodic (by construction). Thus we can partition the full phase space into a set of domains $\{D_\alpha\}$.

From the arguments given above (in Sec. B), after the relaxation of initial transients, we expect to observe a Boltzmann distribution of states within an individual domain which is therefore independent of the quench protocol. However the distribution between domains cannot be expected to be Boltzmann distributed and will instead be dependent on the quench protocol. Within a given ensemble the proportion of ensemble members ultimately found in domain D_α is given by a weight $w_\alpha(P)$ which is subject to the constraint

$$\sum_{\alpha=1}^{N_D} w_\alpha = 1. \tag{19}$$

We can calculate the full *ensemble* average of some macroscopic property B as

$$\langle B \rangle = \sum_{\alpha=1}^{N_D} w_\alpha \frac{\int\int_{D_\alpha} dV d\mathbf{\Gamma} B(\mathbf{\Gamma}, V) \exp(-\beta I_0)}{\int\int_{D_\alpha} dV d\mathbf{\Gamma} \exp(-\beta I_0)}. \tag{20}$$

Since the full ensemble of states is nonergodic the phase space breaks up into disjoint domains which in themselves are ergodic. Thus each domain may be identified by any point in phase space $(\mathbf{\Gamma}, V)$ that is a member of it so the subscript α is a function of the phase vector $\alpha(\mathbf{\Gamma}, V)$ allowing the following expression for the distribution function:

$$f(\mathbf{\Gamma}, V) = \sum_{\alpha=1}^{N_D} w_\alpha s(\mathbf{\Gamma}, D_\alpha) f_\alpha(\mathbf{\Gamma}, V), \tag{21}$$

where $s(\mathbf{\Gamma}, D_\alpha) = 1$ if $\mathbf{\Gamma} \epsilon D_\alpha$ and $s(\mathbf{\Gamma}, D_\alpha) = 0$, otherwise, and

$$f_\alpha(\mathbf{\Gamma}, V) = \frac{\exp(-\beta I_0(\mathbf{\Gamma}, V))}{\int_0^\infty dV \int_{D_\alpha} d\mathbf{\Gamma} \exp(-\beta I_0(\mathbf{\Gamma}, V))}. \tag{22}$$

The entropy is given by $S = -k_B \int_0^\infty dV \int_D d\mathbf{\Gamma} f \ln(f)$ and using Eq. (21) we have the following expressions for the multidomain entropy:

$$S = -k_B \sum_{\alpha=1}^{N_D} w_\alpha \left[\int\int_{D_V} dV d\mathbf{\Gamma} f_\alpha \ln(f_\alpha) + \ln(w_\alpha) \right]$$

$$= \sum_{\alpha=1}^{N_D} w_\alpha S_\alpha - k_B \sum_{\alpha=1}^{N_D} w_\alpha \ln(w_\alpha). \tag{23}$$

The term $-\sum_{\alpha=1}^{N_D} k_B w_\alpha \ln(w_\alpha) \equiv S_D$ is the interdomain entropy, which is maximized by an even distribution of ensemble members over all domains, while S_α is the intraentropy of domain α considered as a single N-particle system.

If we substitute Eq. (22) into Eq. (23) we find that

$$S = S_D + T^{-1} \sum_{\alpha=1}^{N_D} w_\alpha \langle I_0 \rangle_\alpha$$

$$+ k_B \sum_{\alpha=1}^{N_D} w_\alpha \ln \int\int_{D_\alpha} dV d\mathbf{\Gamma} \exp(-\beta I_0(\mathbf{\Gamma}, V))$$

$$= S_D + T^{-1} \langle I_0 \rangle$$

$$+ k_B \sum_{\alpha=1}^{N_D} w_\alpha \ln \int\int_{D_\alpha} dV d\mathbf{\Gamma} \exp(-\beta I_0(\mathbf{\Gamma}, V)), \tag{24}$$

where $\langle B \rangle_\alpha = \int\int_{D_\alpha} dV d\mathbf{\Gamma} B(\mathbf{\Gamma}) f_\alpha(\mathbf{\Gamma}, V)$. Combining Eq. (16) with Eq. (24) we obtain the following expression for the Gibbs free energy:

$$G = -k_B T \sum_{\alpha=1}^{N_D} w_\alpha \left[\ln \int\int_{D_\alpha} dV d\mathbf{\Gamma} \exp(-\beta I_0) - \ln(w_\alpha) \right]$$

$$= \sum_{\alpha=1}^{N_D} w_\alpha G_\alpha - S_D T. \tag{25}$$

It is easy to verify that if we hold the local domain weights fixed and then vary the temperature or the pressure Eqs. (23) and (25) are compatible with Eqs. (17). This means that if we have a fixed number of robust domains, whose population levels or weights are non-Boltzmann distributed, Eqs. (25) and (23) provide a direct microscopic link to standard macroscopic thermodynamics. On the extremely long time scale the weighting functions w_α may vary and the system will tend towards the direction where the free energy [Eq. (25)] is reduced. Without the interdomain entropy term S_D, Eq. (25) would be minimized when the domain with the lowest free energy has all the ensemble members in it. It turns out that Eq. (25) is minimized when all the domain weights are Boltzmann distributed, i.e., when

$$w_\alpha = \frac{\int\int_{D_\alpha} dV d\mathbf{\Gamma} \exp(-\beta I_0)}{\sum_{\beta=1}^{N_D} \int\int_{D_\beta} dV d\mathbf{\Gamma} \exp(-\beta I_0)}. \tag{26}$$

Here [i.e., upon obeying Eq. (26)] the entropy and free energy given by Eqs. (23) and (25) coincide with the standard equilibrium expressions so the free energy must be a minimum. To prove this we use Eq. (25) and we remove the first weight $w_1 = 1 - \sum_{\alpha=2}^{N_D} w_\alpha$, so that the constraint [Eq. (19)] is respected while the remaining weights are independent. This means that the free energy can be written as $G(1 - \sum_{\alpha=2}^{N_D} w_\alpha, w_2, w_3, \ldots w_{N_D})$. The constrained partial derivatives are then

$$\frac{\partial G}{\partial w_\alpha}\bigg|_c = \frac{\partial G}{\partial w_1} \frac{\partial w_1}{\partial w_\alpha} + \frac{\partial G}{\partial w_\alpha}$$

$$= -\frac{\partial G}{\partial w_1} + \frac{\partial G}{\partial w_\alpha}, \quad \alpha \geq 2$$

$$= -G_1 - kT \ln(w_1) - k_B T + G_\alpha + k_B T \ln(w_\alpha)$$

$$+ k_B T, \quad \alpha \geq 2. \tag{27}$$

Using the fact that for Boltzmann weights, Eq. (26),

$$w_\alpha = \exp[\beta(G_{eq} - G_\alpha)], \qquad (28)$$

where $G_{eq} = -k_B T \ln \Sigma_{\alpha=0}^{N_D} \int \int_{D_\alpha} dV d\Gamma \exp(-\beta I_0)$ is the equilibrium free energy, we find that at equilibrium,

$$\left. \frac{\partial G}{\partial w_\alpha} \right|_c = 0, \quad \alpha \geqslant 2. \qquad (29)$$

It remains to be proven that this is indeed a minimum. Using the same approach for treating the constraint, we continue making the first weight a function of all the others and obtain

$$\left. \frac{\partial^2 G}{\partial w_\alpha \partial w_\gamma} \right|_c = \frac{\partial^2 G}{\partial w_1^2} - \frac{\partial^2 G}{\partial w_\gamma \partial w_\alpha} - \frac{\partial^2 G}{\partial w_\gamma \partial w_1} - \frac{\partial^2 G}{\partial w_1 \partial w_\alpha}. \qquad (30)$$

Using the Boltzmann weights it is easy to show that

$$\frac{\partial^2 G}{\partial w_1^2} = \frac{kT}{w_1} = k_B T \exp[\beta(G_1 - G_{eq})],$$

$$\frac{\partial^2 G}{\partial w_1 \partial w_\alpha} = \frac{\partial^2 G}{\partial w_\gamma \partial w_1} = 0, \qquad (31)$$

$$\frac{\partial^2 G}{\partial w_\gamma \partial w_\alpha} = \delta_{\gamma\alpha} \frac{k_B T}{w_\alpha} = \delta_{\gamma\alpha} k_B T \exp[\beta(G_\alpha - G_{eq})].$$

From these results it is easy to see that the Hessian matrix $(\partial^2 G / \partial w_\alpha \partial w_\gamma)|_c$ is positive definite, thus we have proven the free energy to be a minimum for the case of equilibrium.

We can use a knowledge of the multiple domain thermodynamic potential, Eq. (25), to compute averages. As an example we consider the average enthalpy again,

$$\langle I_0 \rangle = -k_B T^2 \left. \frac{\partial \beta G}{\partial T} \right|_{w_\alpha, P_0, N}. \qquad (32)$$

Equation (32) can easily be derived from Eq. (16) and is in essence the same as the first line of Eq. (15). It is straightforward to see that upon using Eq. (25) to calculate the derivative in Eq. (32) one obtains the average enthalpy as given by Eq. (20). One can do the same for other quantities such as the specific heat, etc.

D. Application to molecular dynamics simulation

We are now in a position to test various outcomes, using computer simulation, which may be derived by drawing on the previous material. If we start with an ensemble of systems which are initially in equilibrium at temperature $T = T_0$ and then at time $t = 0$ we quench them by setting $T = T_1$, we can solve the Liouville equation [Eq. (6)] to obtain

$$f(\Gamma(t), \alpha_V(t), \alpha_T(t), t) = f(\Gamma(0), \alpha_V(0), \alpha_T(0), 0)$$
$$\times \exp[\beta_1(I_0(0) - I_0(t))], \qquad (33)$$

where $\beta_1 = 1/k_B T_1$. This nonequilibrium distribution function, valid for $t > 0$, explicitly requires the solution of the equations of motion and is of limited utility. However, it allows the identification of a formal condition to identify the amount of time, which must elapse after the quench, before Eqs. (7), (9), and (20), or (21) can be applied to the en-

semble. That is, the quantity $I_0(t) = H_0(t) + P_0 V(t)$ must be statistically independent of $I_0(0)$. Thus we are interested in the correlation function

$$C_1(I_0(t), I_0(0)) = \frac{\langle I_0(t) I_0(0) \rangle - \langle I_0(t) \rangle \langle I_0(0) \rangle}{C_{1,0}}, \qquad (34)$$

where

$$C_{1,0} = \sqrt{(\langle I_0(t)^2 \rangle - \langle I_0(t) \rangle^2)(\langle I_0(0)^2 \rangle - \langle I_0(0) \rangle^2)}. \qquad (35)$$

This function will equal 1 for a perfectly correlated system, -1 for a perfectly anticorrelated system, and 0 for an uncorrelated system. When we consider an ensemble of systems, occupying the various domains to different degrees, we see that Eq. (34) may not decay to zero given that the trajectories are unable to leave their domains. If the transients, due to the quench, fully decay Eq. (34) will decay to zero and Eqs. (7) and (9) will become valid for the ensemble.

If the correlation function, Eq. (34), decays to a plateau then we may have a situation where Eqs. (20) and (21) are valid. It may be that the material can still slowly age, due to processes, that occur on a time scale which is longer than the one we are monitoring. For a glass we expect that correlation function, Eq. (34), will not fully decay on a reasonable time scale. If we give the system time to age, such that it appears to be time translationaly invariant and then compute the following correlation function,

$$C_2(I_0(\tau), I_0(0)) = \frac{\Sigma_{\alpha=1}^{N_t} \langle I_0(t) I_0(0) \rangle_\alpha - \langle I_0(t) \rangle_\alpha \langle I_0(0) \rangle_\alpha}{C_{2,0}}, \qquad (36)$$

where

$$C_{2,0} = \sum_{\alpha=1}^{N_t} \sqrt{(\langle I_0(t)^2 \rangle_\alpha - \langle I_0(t) \rangle_\alpha^2)(\langle I_0(0)^2 \rangle_\alpha - \langle I_0(0) \rangle_\alpha^2)}, \qquad (37)$$

we may observe a full decay. If this occurs Eqs. (20) and (21) will be valid. To compute this correlation function N_t trajectories are produced and for each of these the averages, $\langle \bar{B} \rangle_\alpha$ [where B is an arbitrary dynamical variable, appearing in Eqs. (36) and (37)] are approximately obtained by time averaging. When the system is ergodic and time translationaly invariant these two correlation functions, Eqs. (34) and (36), will give the same result. However, for a nonergodic system C_2 will decay to zero on a reasonable time scale while C_1 will not. Rather C_1 may decay to some plateau on a reasonable time scale and then decay on a much slower time scale. The preceding sections then rest on this clear separation of time scales in the correlation function, Eq. (34). For metastable fluids and allotropes this separation is so extreme that we probably cannot observe, even the early stages of, the later slow decay on any reasonable experimental time scale. Further for these systems there will only be a single domain and thus they appear ergodic. For glasses some signs of the later decay can often be observed; however, it is still very much slower than the initial decay. In the field of glassy dynamics the initial decay is often called the β decay and the slower long time decay is often called the α decay. As the

glass is further aged this second stage decay is observed to slow down dramatically while the early decay does not change very much.[14]

To allow the hypothesis of local phase space domains to be tested we will now introduce several relations whose derivation draws upon the equilibrium distribution function, Eq. (9). We will also discuss the effect of the phase space domains on these relations.

First we introduce the configurational temperature,

$$k_B T = - \frac{\langle \mathbf{F} \cdot \mathbf{F} \rangle}{\langle \nabla \cdot \mathbf{F} \rangle}, \tag{38}$$

where $\mathbf{F}$ is a $3N$ dimensional vector representing the interparticle forces on each atom $\mathbf{F} = -\nabla \Phi$. This relation is easily derived from Eq. (9) (set B to $\nabla \cdot \mathbf{F}$, integrate by parts, and drop the boundary terms) and will remain valid for nonergodic systems where Eq. (26) is not obeyed. The relation involves the spatial derivative of the force, which is not zero at the cutoff radius for the potential we use in our simulations (see below). This along with finite size effects can result in a small disagreement between Eq. (38) and the kinetic temperature for our system when in equilibrium.

Equilibrium fluctuation formulas may be easily derived from Eq. (20); see Refs. 1 and 5 for some examples of how this is done. We consider how the average enthalpy changes with the temperature at constant pressure,

$$C_{P_0} = \langle V \rangle c_{P_0} = \left. \frac{d}{dT} \right|_{N, P_0} \langle I_0 \rangle = \frac{\beta}{T} [\langle I_0^2 \rangle - \langle I_0 \rangle^2], \tag{39}$$

where c_{P_0} is the constant pressure specific heat. The calculation of the right hand side of Eq. (39) using the ensemble average given by Eq. (20) is subtle. If we simply calculate $\langle I_0 \rangle$ and $\langle I_0^2 \rangle$ with the use of Eq. (20) and then plug the results into Eq. (39) we obtain, what we will refer to as, a *single domain average* which does not give us the correct change in the average enthalpy for a history dependent equilibrium ensemble. This is because the average $\langle I_0^2 \rangle$ superimposes across the different domains while the quantity $\langle I_0 \rangle^2$ contains spurious cross terms. If we derive the heat capacity by taking the second derivative of the Gibbs free energy for the multiple domain distribution function, Eqs. (25) and (32), with respect to the temperature,

$$C_{P_0} = - \left. \frac{\partial}{\partial T} \right|_{N, P_0, w_\alpha} k_B T^2 \left. \frac{\partial \beta G}{\partial T} \right|_{N, P_0, w_\alpha}, \tag{40}$$

we obtain the following:

$$C_{P_0} = \langle V \rangle c_{P_0} = \frac{\beta}{T} \sum_{\alpha=1}^{N_D} w_\alpha [\langle I_0^2 \rangle_\alpha - \langle I_0 \rangle_\alpha^2], \tag{41}$$

where the quantity $\langle I_0^2 \rangle_\alpha - \langle I_0 \rangle_\alpha^2$ is obtained for each domain separately (here $\langle \ldots \rangle_\alpha$ represents an average taken where all ensemble members are in the αth domain). We will refer to this as a *multidomain average* which is consistent with the nonergodic statistical mechanics and thermodynamics that we have introduced here. It is obvious that both a single and multiple domain average will give the same result in the case of thermodynamic equilibrium and metastable equilibrium

(single domain). The transition from the single domain average producing the correct result to an anomalous result is symptomatic of an ergodic to a history dependent nonergodic transition. If we consider a large macroscopic system (the supersystem) to be made of N_s independent subsystems the multidomain average remains self-consistent. To see this we apply Eq. (41) to fluctuations in the supersystem and then we inquire how this relates to fluctuations in the subsystem. The enthalpy of one instance of the supersystem will be given by $I_s = \Sigma_{\alpha=1}^{N_s} I_\alpha$. In principle, an ensemble of supersystems can be prepared by applying the same history dependent macroscopic protocol to all members of this ensemble. Due to the statistical independence of the subsystems, upon taking an ensemble average of supersystems, we have $\langle I_\alpha I_\beta \rangle_S = \langle I_\alpha \rangle_S \langle I_\beta \rangle_S$ for all $\alpha \neq \beta$. Here the average $\langle \ldots \rangle_S$ is taken over the ensemble of supersystems and the αth subsystem in each supersystem is identified by its location. It is then easy to show that the specific heat obtained from the ensemble average, Eq. (41), of the supersystem is equivalent to that obtained from the subsystem due to the two quantities $\langle I_s^2 \rangle_S = \langle (\Sigma_{\alpha=1}^{N_s} I_\alpha)^2 \rangle_S$ and $\langle I_s \rangle_S^2 = \langle \Sigma_{\alpha=1}^{N_s} I_\alpha \rangle_S^2$ possessing identical cross terms which cancel each other out (as a result of the independence of the subsystems) upon applying Eq. (41).

If we ignore finite size effects, due to assuming the equivalence of ensembles, the constant volume specific heat is related to the constant pressure specific heat by the equation

$$C_V = \langle V \rangle c_V = C_P - P \left. \frac{dV}{dT} \right|_T - \left(\left. \frac{\partial H}{\partial P} \right|_T \middle/ \left. \frac{\partial V}{\partial P} \right|_T \right) \left. \frac{\partial V}{\partial T} \right|_P. \tag{42}$$

We may also obtain an expression for the constant volume specific heat c_V by deriving equilibrium fluctuation formula for each of the derivatives appearing in Eq. (42) in lieu of directly measuring them. We may then obtain a single domain expression for c_V which does not work for the history dependent glass and also a correctly weighted ensemble average (multidomain average) which does. This is completely analogous to what has been shown in detail for c_P. As the equations are unwieldy and their derivation (given an understanding of the c_P case) is straightforward, we will not reproduce them here.

E. Test of domain robustness: Transient fluctuation theorem

The application of the Evans-Searles transient fluctuation theorem[8,15,16] to the systems treated in this paper provides a sharp test of the assumptions used to develop the theory given in this paper. The theorem describes a time reversal symmetry satisfied by a generalized entropy production, namely, the so-called dissipation function. The precise mathematical definition of this function requires a knowledge of the dynamics and also of the initial distribution function. The three necessary and sufficient conditions for the fluctuation theorem to be valid are that the initial distribution is known (here we assume the distribution is Boltzmann weighted over some initial domain of phase space), that the dynamics is time reversible (all the equations of motion used

here are time reversible), and lastly that the system satisfies the condition known as ergodic consistency. When applied to the systems studied here this requires that the phase space domains should be robust with respect to the sudden changes imposed on the system and that the number of interdomain transitions remain negligible on the time over which the theory is applied. If any one of these three conditions fail then the theorem cannot be applied to the system and the corresponding fluctuation relation will not be satisfied.[8]

We can use the fluctuation theorem to obtain relations for how the system responds upon suddenly changing the input temperature or pressure for a system, which is initially in equilibrium as specified by Eq. (7) or (8). Firstly we consider a change in the pressure, while holding the temperature fixed, by changing the input variable P_0 in Eq. (4) (thermodynamic pressure) to $P_0 = P_2$ at time $t = 0$ for a system initially in equilibrium with $P_0 = P_1$. The probability density $p(\Delta V = A)$ of observing a change in volume of $\Delta V(t) = V(t) - V(0)$ relative to a change of equal magnitude but opposite sign is then given by

$$\frac{p(\Delta V(t) = A)}{p(\Delta V(t) = -A)} = \exp(\beta(P_2 - P_1)A). \tag{43}$$

To derive this expression we have had to assume that the intradomain populations are Boltzmann distributed according to Eq. (7). Ergodic consistency requires that, for any initial phase space point $\mathbf{\Gamma}(0)$ that can be initially observed with nonzero probability, there is a nonzero probability of *initially* observing the time reversal map M^T of the end point $\mathbf{\Gamma}(t)$, [i.e., $\forall \mathbf{\Gamma}(0)$ such that $f(\mathbf{\Gamma}(0), 0) \neq 0, f(M^T(\mathbf{\Gamma}(t)), 0) \neq 0$]. This condition obviously requires that the phase space domains remain robust and the number of interdomain transitions remain negligible for at least a time t, after the pressure (or temperature) quench.

If we sample all or our initial $t = 0$, $P_0 = P_1$ configurations from the one trajectory which remains locked in a single domain even after the quench, we expect Eq. (43) to be valid. If we prepare an ensemble of initial configurations using the same protocol we still expect Eq. (43) to remain valid even with different domain weightings w_i, as defined in Eqs. (20) and (21), provided that the domains are robust over the time t appearing in Eq. (43). Note that suddenly reducing the pressure by a very large amount could result in a breakdown of the robustness condition. Equation (43) may be partially summed to obtain what is referred to as the integrated fluctuation theorem,

$$\frac{p(\Delta V(t) > 0)}{p(\Delta V(t) < 0)} = \langle \exp(\beta(P_2 - P_1)\Delta V) \rangle_{\Delta V < 0}. \tag{44}$$

For the case where we change the input temperature T in Eq. (4) while holding the input pressure P_0 fixed we obtain a relation for fluctuations in the extended instantaneous enthalpy $I_E(t) = H_E(t) + P_0 V(t)$. We start with a system initially in equilibrium at temperature $T = 1/(k_B \beta_1)$ and we then subject it to a temperature quench by changing the input temperature in Eq. (4) to $T = 1/(k_B \beta_2)$, at time $t = 0$, while holding the input pressure fixed. The probability density $p(\Delta I_E(t) = A)$ of observing a change in instantaneous enthalpy $\Delta I_E(t) = I_E(t) - I_E(0)$ relative to a change of equal magnitude but opposite sign is then given by

$$\frac{p(\Delta I_E(t) = A)}{p(\Delta I_E(t) = -A)} = \exp((\beta_1 - \beta_2)A). \tag{45}$$

Note that if we suddenly increase the temperature by a very large amount we could expect to violate the robustness or the negligible interdomain transition condition. In common with Eq. (43) we expect that this expression will be valid when all initial configurations are sampled from a single common domain and also when sampled from multiple arbitrarily populated domains under the assumption that the domains are robust and the number of transitions are negligible over time t. This equation may also be partially summed to obtain

$$\frac{p(\Delta I_E(t) > 0)}{p(\Delta I_E(t) < 0)} = \langle \exp((\beta_2 - \beta_1)\Delta I_E) \rangle_{\Delta I_E < 0}. \tag{46}$$

IV. SIMULATION DETAILS

For our simulations we use a variation on the Kob-Andersen glass former[17] featuring a purely repulsive potential.[18] The pairwise additive potential is

$$u_{ij}(r_{ij}) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6} + \frac{1}{4}\right],$$

$$\forall r_{ij} < \sqrt[6]{2}\sigma_{\alpha\beta},$$

$$u_{ij}(r_{ij}) = 0, \quad \forall r_{ij} > \sqrt[6]{2}\sigma_{\alpha\beta}, \tag{47}$$

where the species identities of particles i and j, either A or B, are denoted by the subscripts α and β. The energy parameters are set $\epsilon_{BB} = 0.5\epsilon_{AA}$, $\epsilon_{AB} = 1.5\epsilon_{AA}$ and the particle interaction distances $\sigma_{BB} = 0.88\sigma_{AA}$, $\sigma_{AB} = 0.8\sigma_{AA}$. The energy unit is ϵ_{AA}, the length unit is σ_{AA}, and the time unit is $\sqrt{m\sigma_{AA}^2/\epsilon_{AA}}$ with both species having the same mass m. The composition is set at $X = N_B/N_A = 0.2$, the number of particles are $N = N_A + N_B = 108$, the pressure is set to $P_0 = 14\epsilon_{AA}/\sigma_{AA}^3$, and the temperature unit is ϵ_{AA}/k_B. The time constants are set at $\tau_V = 5\sqrt{N}$ and $\tau_T = \sqrt{N}$. Note that the energy parameters are slightly different to the potential we used in Ref. 18 The equations of motion were integrated using a fourth order Runge-Kutta method.[19] The time step used was $dt = 0.002$ and sometimes $dt = 0.004$ for very low temperatures.

From previous work on binary mixtures we know the basic reason why this system is vary reluctant to crystallize.[20–23] The chosen nonadditivity of the species A-B interaction makes the mixture extremely miscible; consider the present value of $\sigma_{AB} = 0.8\sigma_{AA}$ relative to the additive value of $\sigma_{AB} = 0.94\sigma_{AA}$. This effect dominates over the choice of the energy parameters. Due to this extreme miscibility the relatively large composition fluctuations necessary, about the average composition of $X = 0.2$, to form the crystal phases (either the pure species A, $X = 0$, fcc crystal or the binary, $X = 0.5$, CsCl crystal) are strongly suppressed and crystallization is strongly frustrated.

We identify the nominal glass transition by calculating the diffusion coefficient as a function of temperature. This is
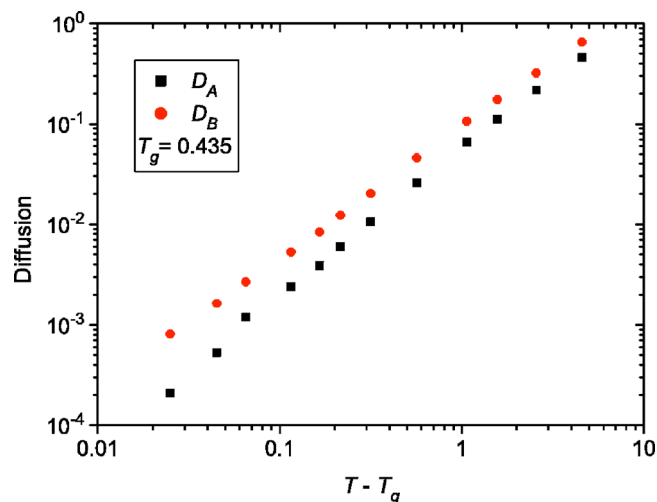
FIG. 1. (Color online) A logarithmic plot of the self-diffusion coefficient for both species A and species B particles as a function of the separation parameter $T-T_g$ with $T_g=0.435$.

shown for both species in Fig. 1 on a logarithmic plot demonstrating how the diffusion coefficient approaches zero critically, $D_\alpha(T) \propto (T-T_g)^b$; where b is the critical exponent, with a nominal glass transition temperature of $T_g=0.435$. It would be, perhaps, more customary to obtain a nominal glass transition temperature by analyzing the critical divergence of the viscosity. Given that the Stokes-Einstein relation is strongly violated upon approaching the glass transition one might be concerned that this would give a very different result. However, the violation of the Stokes-Einstein relation can largely be attributed to the exponent b being different between the viscosity and the diffusion coefficient rather than the nominal glass transition temperature T_g.[24]

V. RESULTS AND DISCUSSION

The correlation functions given in Eqs. (34) and (36) were calculated from ensembles of 100 independent simulations at the two temperatures given in Fig. 2 ($T=1$ and $T=0.4$). In all cases the systems were subject to an instantaneous quench, from an initial equilibrium at $T=5$, by changing the value of the input temperature in Eq. (4). The system was then run for a significant time, in the case of the glass ensemble $\tau_{age} > 8 \times 10^5$, in an attempt to age it. Of course the longest time that can be accessed in a molecular dynamics simulation is rather short, and so the system is not very well aged, but we are still able to meaningfully treat it as a time invariant state. Each of the 100 independent simulations was interpreted as being stuck in its own domain D_α and the correlation functions were calculated for each of these domains using time averaging. The time averaging was approximately 100 times longer than the longest time $t=800$ that the correlation functions were calculated out to. Obviously in the limit of an infinite number of independent simulations and the case where the domains are robust we will obtain the exact multidomain average given by Eq. (20). We assume that our limited ensemble of simulations is representative of this. The data from each domain (independent simulation) was then used to obtain the correlation functions, Eqs.
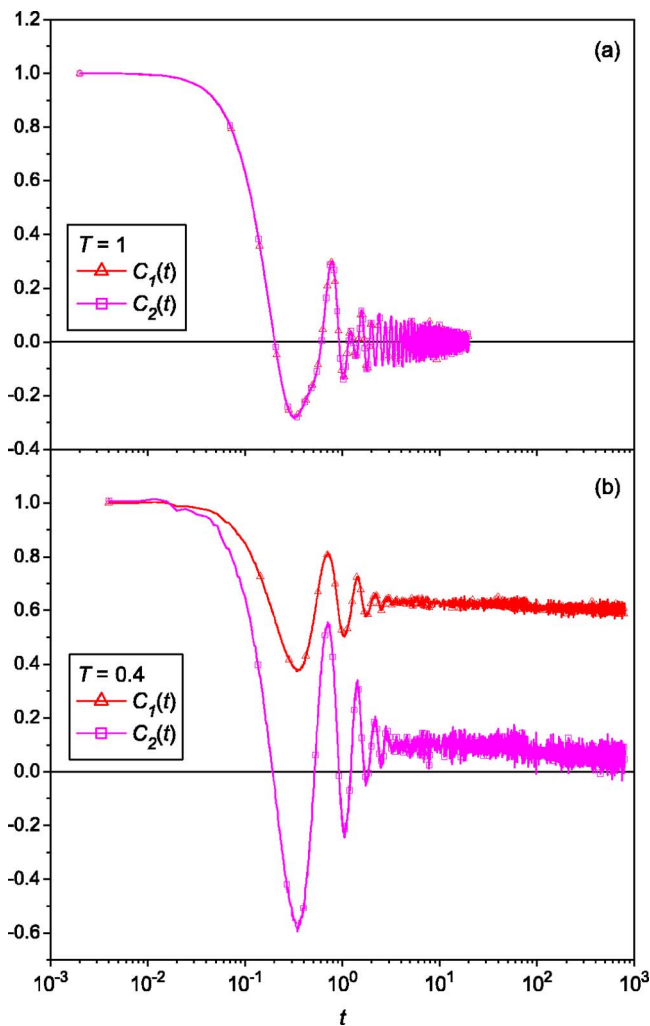

FIG. 2. (Color online) (a) The instantaneous enthalpy correlation functions as defined by Eqs. (34) and (36) as a function of logarithmic time for the temperature $T=1$. The calculation of the function was started after the fluid had been given time to equilibrate. The strong agreement between the two correlation functions is indicative of ergodicity. (b) The instantaneous enthalpy correlation functions as defined by Eqs. (34) and (36) as a function of logarithmic time for the temperature $T=0.4$. The calculation of the correlation function was started at various times after the quench, all approximately at $t=8 \times 10^5$, in an attempt to age the system. The difference between the correlation functions is indicative of nonergodicity. Notice that C_2 reaches a near full decay between $t=1$ and 10, while C_1 reaches a nondecaying plateau.

(34) and (36), as seen in Fig. 2. At the higher temperature $T=1$ it can be seen that the two functions are equivalent, demonstrating how the system is ergodic. It can also be seen that the correlation function has decayed on a time scale of $t \sim 10$ which is therefore [by Eq. (33)] the time scale on which the ensemble becomes accurately represented by Eq. (9) with only one domain D which does not necessarily extend over all phase space. The oscillations, which can be seen in the correlation function, are due to both ringing in the feedback mechanisms of Eq. (4) and the frequency dependent storage component of the bulk viscosity. The statistical uncertainty in the correlation function becomes larger than these oscillations somewhere between a time of $t=1$ and 10. If we constructed an experiment where the pressure was regulated by a piston and a spring, the correlation functions,

Eqs. (34) and (36), would depend on the details of the piston and spring parameters in a similar way to the simulation dependence on the details of the feedback mechanism.

When the system is quenched to the lower temperatures ($T=0.4$) ergodicity is lost and we obtain a glass. The complete decay of the first correlation function C_1, Eq. (34), may no longer occur because the individual trajectories remain stuck in local domains which have different average values for $\langle I_0 \rangle_\alpha$. This is similar to the much studied density correlation function[25] (the intermediate scattering function) which decays to a finite plateau for a glass or more generally a solid material. On the other hand there is nothing to stop the second correlation function C_2, Eq. (36); from fully decaying when the system is nonergodic. If the second correlation function fully decays while the first is only able to decay to a plateau then we have a situation where Eqs. (21) and (20) are valid as can be seen from Eq. (33). In Fig. 2 it can be seen that C_1 does indeed fail to decay while C_2 comes very close to fully decaying at the time where C_1 reaches the plateau. The reason C_2 does not fully decay here is due to the fact that the interdomain transition rates, while small, are not exactly zero. If the system had been aged more extensively this problem would be significantly reduced. This effect is exacerbated by the time averaging, used to form the averages for each trajectory, being two orders of magnitude longer than the longest time the correlation function was calculated to. The effect of the state slowly evolving due to finite interdomain transition rates is too small to seriously compromise the modeling of the system as obeying Eqs. (20) and (21) and thus we have obtained direct evidence for the validity of these equations. The height of the plateau for C_1 will depend on the history of the system, i.e., the protocol used to prepare the ensemble.

We move on to a comparison between the kinetic temperature and the configurational temperature, the results of which may be seen in Fig. 3(a). The input temperature ranges from $T=3$ to $T=0.3$. Also shown are results for the system, undergoing constant planar shear, Eq. (10), with a strain rate of $\dot{\gamma}=0.5$. At the higher temperatures we see a very small relative discrepancy between the two types of temperatures, which we attribute to the discontinuity in the first spatial derivative of the interparticle force at the cutoff radius and to finite size effects. These effects appear to diminish a little at lower temperatures. For temperatures above T=1.5 the chosen strain rate has no significant effect on the configurational temperature, indicating that our system is in the linear response domain.[18] At the lowest temperatures, well below the glass transition temperature, we observe good agreement between the configurational and input temperatures for the system without shear. This provides further evidence of our assertion that the system obeys Boltzmann statistics in the glass, Eqs. (20) and (21). However, at low temperatures, the system that is undergoing shear shows an increasing relative discrepancy between the two temperatures. At low temperatures the system leaves the linear response domain,[18] demonstrating the fundamental difference between the nonequilibrium distribution of the history dependent glassy state and that of a strongly driven steady state. If we drive the system hard enough, at any given temperature, we can always make
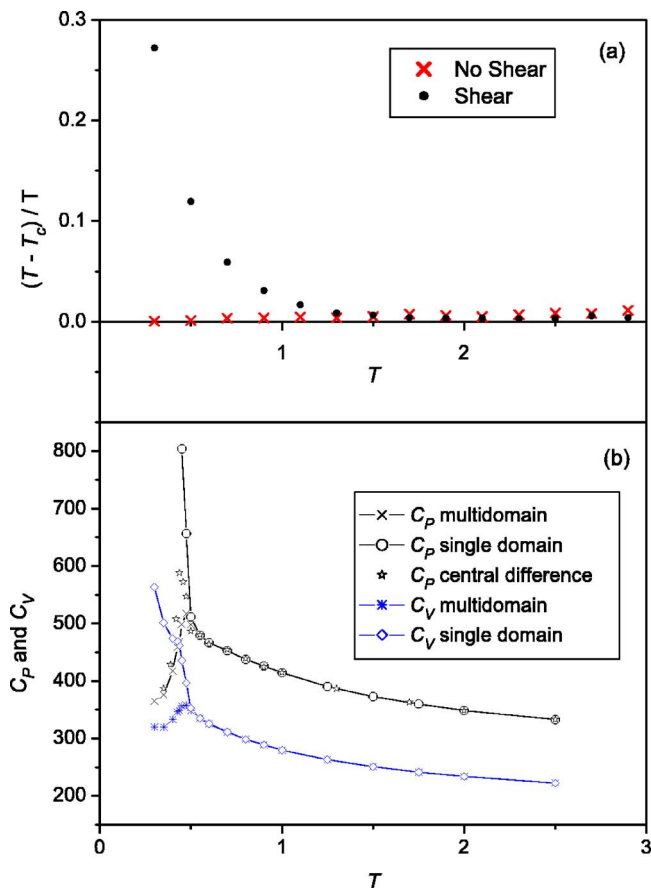

FIG. 3. (Color online) (a) The relative difference between the kinetic temperature T (controlled directly by the Nosé-Hoover thermostat) and the configurational temperature given by Eq. (38) as a function of the kinetic temperature. The results for the system undergoing Couette flow (shear) are for a constant strain rate of $\dot{\gamma}=0.5$. (b) The heat capacity calculated using the equilibrium fluctuation formula by the single domain averaging method, Eq. (39), and the multidomain method, Eq. (41). Also shown are data obtained by numerically differentiating the enthalpy by central difference. At the temperatures above the peak the three types of averages give very similar results. Also shown are equivalent equilibrium fluctuation formula data for the constant volume specific heat, Eq. (42).

a disagreement between the two types of temperature due to the steady state no longer being accurately represented by a Boltzmann distribution, i.e., due to a breakdown in local thermodynamic equilibrium. When the system is not driven by an external field we have been unable to observe any difference in the two temperatures by deeply supercooling a glass forming mixture apart from the initial transient decay immediately following the quench, which falls off surprisingly rapidly.

In Fig. 3(b) results are presented for the heat capacities (the specific heat multiplied by the volume) at both constant pressure C_P and constant temperature C_V. Details of the protocol used to obtain these data are given in the end note.[26] The estimates from the multidomain average are compared with those from the single domain average. The results from the multidomain averages exhibit the well-known peak, which is a signature of the onset of the glass transition, and has been observed directly by calorimetry in many experiments on real glass forming materials.[2] The temperature, where the peak is observed, depends on the history of the

system. No peak is observed for the single domain averages which continue to increase as the temperature is lowered. While the two methods for forming averages give the same results at temperatures above the peak, they diverge at temperatures below the peak. It is the multidomain average that gives results consistent with the actual calorimetric behavior of the system. This may be seen in the figure by comparing the data which has been computed by numerically differentiating the enthalpy using central difference. At the peak neither the central difference (due to rapid rate of change) nor the multidomain average data (due to a lack of domain robustness) are reliable and they show significant differences. However, below the peak they once again show quantitative agreement, providing strong evidence that the domains are robust in this region. If we substantially increase the duration the time averages (for each domain) are constructed on, the peak will be shifted to lower temperatures as previously shown.[27] This requires the time average to be constructed over some two orders of magnitude more time than the decay time for the correlation function in Eq. (34). This is necessary in order to obtain enough independent samples for a meaningful estimate of the variance of the instantaneous enthalpy appearing in Eq. (39). For a large macroscopic system we would expect that the specific heat measured over the entire ensemble would differ very little to that measured from any one of its members. We are now in a position to make an unambiguous interpretation of the peak in the specific heat. The peak is observed at the temperature where the system leaves metastable equilibrium and enters a history dependent state that requires averages to be computed by Eq. (20) rather than by direct use of Eq. (9). The calculation of both $\langle I_0 \rangle_\alpha$ and $\langle I_0^2 \rangle_\alpha$ will be different for each domain. If we use time averaging to calculate these variables on a time scale that falls within the plateau region for Eq. (34), see Fig. 2(b), then the amount of time chosen to form the average is not critical. The peak occurs because the various ensemble members have become locked in local domains on the time scale that we are able to access. Near the peak itself these domains are not expected to be robust.

The multidomain average, Eq. (41), gives the heat capacity for a glass with robust domains. At the lowest temperatures the heat capacity reaches the beginning of a plateau, Fig. 3(b). For the constant volume heat capacity C_V this plateau (within uncertainties due to finite size effects) has a value that is consistent with the Dulong-Petit law,[28] as would be expected for an amorphous solid where the potential energy surface can be modeled as harmonic upon transformation to the orthogonal independent basis set. This is exactly what we would expect from our local domain model at low temperatures.

Testing the integrated transient fluctuation theorem (ITFT) for a sudden pressure change, Eq. (44), and a sudden temperature change, Eq. (46), provides further evidence that the Boltzmann distribution may be used to accurately describe intradomain statistics in the glassy state and also that in a properly aged glass, the domains are robust with respect to the pressure and temperature changes studied here, Fig. 4. These equations remain valid whether we subject an ensemble of simulations (multidomain) to a quench or we
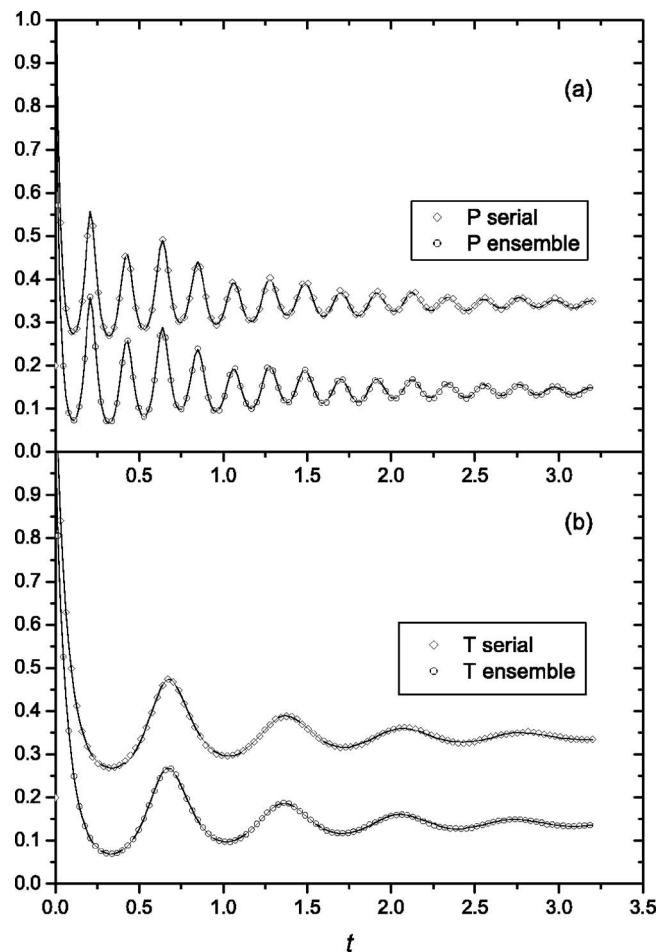

FIG. 4. (Color online) Results from applying the fluctuation theorem to the glass (T=0.3) for (a) a sudden pressure change of ΔP=1, where the symbols are $p(\Delta V>0)/p(\Delta V<0)$ and the solid line is $\langle \exp(\beta(P_2-P_1)\Delta V) \rangle_{\Delta V<0}$ and (b) a sudden temperature change of ΔT=−0.025, where the symbols are $p(\Delta I_E>0)/p(\Delta I_E<0)$ and the solid line is $\langle \exp((\beta_2-\beta_1)\Delta I_E) \rangle_{\Delta I_E<0}$. Results from an ensemble of independent initial systems and in addition from a single initial trajectory (with a time of t=5 being computed between each transient trajectory) are shown for a total of 10^5 pressure or temperature changes. The serial results have been shifted up, for clarity, by adding 0.2 to the data.

sample from a single trajectory (single domain), which remains stuck in a single domain. The accuracy with which these relations are satisfied is a powerful independent evidence for the applicability of our assumptions to the systems studied here. The fact that over the times shown in Fig. 4, the ITFT does indeed yield correct results directly implies that, within experimental tolerance of the data, the phase space domains must be robust and the number of interdomain transitions must be negligible. Unlike the specific heat fluctuation formula this requires that the domains are robust to finite changes of the state rather than infinitesimal changes. Thus, given that we have aged the glass sufficiently that domains are robust and the number of transitions are negligible over the longest time the fluctuation formulas are computed, we expect Eqs. (44) and (46) to be correct. If we wished to apply the steady state fluctuation theorem matters become more difficult.[18]

VI. CONCLUSIONS

We have presented a rigorous development of statistical mechanics and thermodynamics for nonergodic systems where the macroscopic properties are sensibly time independent and the phase space for the ensemble is partitioned into robust domains. Using computer simulation we have carried out various tests on a glassy system and shown that apart from the immediate vicinity of the glass transition, the computed results are consistent with our theory. While the intradomain populations are individually Boltzmann distributed, the interdomain populations are not.

A correlation function whose decay to zero requires global Boltzmann weighting has been derived and it has been shown that it decays on a reasonable time scale for ergodic systems but not for nonergodic systems. A second correlation function which decays to zero if the intradomain populations are Boltzmann distributed, but globally the interdomain populations are not, has also been defined. We have developed expressions for obtaining averages in a multiple domain ensemble and shown how single domain averages, which always give correct results in metastable equilibrium, can give spurious results in a history dependent nonergodic ensemble. The statistical mechanics and thermodynamics developed here allow the derivation of expressions for multi-domain ensemble averages which give the correct results for time nondissipative nonequilibrium ensembles. The fundamental origin of the peak in the specific heat near the glass transition has been unambiguously shown to be a signature of a transition from metastable equilibrium to a nonergodic multidomain ensemble.

We have shown that the transient fluctuation relations for temperature and pressure quenches provide independent tests of the fundamental hypotheses used in our theory: that intra-domain populations are individually Boltzmann distributed, that except in the immediate vicinity of the glass transition the domains are robust with respect to small but finite variations in thermodynamic state variables, and that the interdomain transition rates are negligible.

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[26] An ensemble of 100 simulations was used to obtain the specific heat data starting from an initial equilibrium at $T=5$. The ensemble was sequentially quenched to the next lower temperature at the completion of each cycle. For each cycle the ensemble was equilibrated for a duration of $t=2\times10^3$ before computing a production run of duration $t=1\times10^4$. The temperatures were $T=5, 4, 3, 2, 1.75, 1.5, 1.25, 1, 0.9, 0.8, 0.7, 0.6, 0.55, 0.5, 0.475, 0.45, 0.4375, 0.425, 0.4, 0.35$, and 0.3. Some of the central difference data in Fig. 3(b) was computed at different temperatures; however, all the nonergodic data was computed by strictly adhering to the above protocol.
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