The Glass Transition and the Jarzynski Equality

Stephen R. Williams, Debra J. Searles, and Denis J. Evans

Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia
Nanoscale Science and Technology Centre, School of Biomolecular and Physical Sciences, Griffith University, Brisbane, QLD 4111, Australia

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A simple model featuring a double well potential is used to represent a liquid that is quenched from an ergodic state into a history dependent glassy state. Issues surrounding the application of the Jarzynski Equality to glass formation are investigated. We demonstrate that the Jarzynski Equality gives the free energy difference between the initial state and the state we would obtain if the glass relaxed to true thermodynamic equilibrium. We derive new variations of the Jarzynski Equality which are relevant to the history dependent glassy state rather than the underlying equilibrium state. It is shown how to compute the free energy differences for the nonequilibrium history dependent glassy state such that it remains consistent with the standard expression for the entropy and with the second law inequality.

I. INTRODUCTION

In many real chemical and physical systems the observed distribution of the components is not that expected by statistical mechanics for a system at thermodynamic equilibrium. This can occur in the absence of mechanical forces driving the system away from equilibrium. Many compounds exist as more than one polymorph at standard room temperature and pressure, despite one polymorph having a significantly lower free energy than the others. Fluids can be cooled below the temperature at which thermodynamics predicts that a solid phase would be thermodynamically more stable. Some components exist in different abundance than that predicted thermodynamically. These situations sometimes persist for timescales that are longer than human measurement allows or even for geological timescales. This behaviour might simply occur due to a slow transformation to the more stable state, or extreme rarity of necessary nucleating events might mean that the system is trapped in some nonergodic state for timescales that are incredibly long. Systems in these states are often considered as being in ‘metastable’ states, although it is perhaps inappropriate terminology for a polymorph like diamond (an allotrope of carbon that has higher free energy than graphite) which would normally be considered quite stable. Such systems are also often described as being in ‘nonequilibrium states’, but they are nondissipative and no mechanical force is applied to prevent relaxation to the equilibrium distribution. To simplify terminology we will refer to these history dependent, non-dissipative, nonergodic, time independent nonequilibrium states as quasiequilibrium states.

In the past it has often been assumed that subsets of the components will be equilibrated, and their relative distributions will be given by equilibrium, Boltzmann distributions. Such ideas have been exploited in the so called energy landscape picture of the glass transition. It has also been assumed that equilibrium thermodynamics can be applied to these systems, which requires that the phase space domains of the subsets do not change with small changes in the state point.

Quasiequilibrium states can be formed in various ways - e.g. by temperature quenching, changing the potential energy function or changing the pressure of a system so rapidly that the system is not given sufficient time to adjust to the new conditions and the inter-domain weights can therefore not be expected to be Boltzmann. If the barrier for transformation between two or more local minima is high, the non-equilibrium distribution between the phase space domains will persist. The relative distribution between the domains will depend on the way they are prepared and will therefore not be a Boltzmann distribution. Nevertheless, once trapped, there is ample time for the subsystems to become equilibrated within their restricted phase space subdomains. Williams and Evans produced convincing arguments that within these individual ergodic phase space sub-domains the internal distribution of states is given by a Maxwell-Boltzmann distribution and, using the fluctuation theorem as a sensitive test of aspects of the domain statistics, they confirmed that in aged glasses that are not too close to the glass transition, the intra-domain statistics are Boltzmann and the domains are robust with respect to small but finite changes in the external thermodynamic state variables (temperature, pressure etc.).

A particularly interesting example of a quasiequilibrium system is a glass. When a good glass former is prepared, it is not able to relax to true thermodynamic equilibrium for an extraordinarily long time, often many thousands of years and in the case of the natural glass obsidian, some hundred million years. The system remains in a very long lived, history dependent, quasiequilibrium state. Nevertheless, from a macroscopic point of view, the material appears to be an ordinary equilibrium solid. The fundamental thermodynamics and statistical mechanics of glass is a topic of active research.
Here we consider a simple model that could be used to represent a glass. Unlike some solids (e.g., allotropes of carbon), glasses have a structure which resembles that of a liquid. Because of the numerous long lived structures it is necessary to examine the distribution of states within the glassy system. However, the model presented below might also be considered to represent many other systems e.g. a protein might be frozen into a particular conformation, and we might be interested in the free energy of this conformation compared to the overall free energy.

In recent years the equality for determination of free energy differences introduced by Jarzynski has received considerable attention. This remarkable equality allows the difference in free energy between two states in thermodynamic equilibrium to be computed from an ensemble of nonequilibrium trajectories or pathways, of finite duration, which transform between the two equilibrium states. It is an interesting question as to whether this equality can be extended to treat these systems. Since the Jarzynski Equality relates the free energies of different canonical states at the same temperature, we consider the formation of a glass by changing the potential energy surface of the system while keeping temperature constant. This models the formation of glassy systems by, say, altering the molecular interactions by changing the pH, or increasing the mole fraction of free polymer in a dispersion to form a glassy colloidal system.

II. THEORY

A. Jarzynski Equality

Here we will outline a very general approach that can be applied to arbitrary ensembles and dynamics (deterministic or stochastic). It can be used to obtain the Jarzynski Equality (JE) under particular conditions, but is more general and will be useful in the study of the quasiequilibrium states in the next section. Consider two closed N-particle systems: (1) and (2) with arbitrary equilibrium distribution functions. A protocol and the corresponding time-dependent equations of motion are defined to transform system (1) to system (2). The dynamics may be thermostatted as in Eq. (3) below or it may be isoinertial or even unthermostatted. We define a generalised dimensionless “work” \( \Delta X_r(\Gamma; 0, \tau) \), that is evaluated for a trajectory of duration \( \tau \),

\[
\exp[\Delta X_r(\Gamma)] = \frac{P_{eq}^{(1)}(d\Gamma)}{P_{eq}^{(2)}(d\Gamma(\tau))} \frac{Z^{(1)}}{Z^{(2)}}
\]

where \( Z^{(i)} \) is the partition function for equilibrium system \( i \) and \( P_{eq}^{(i)}(d\Gamma) = f_{eq}^{(i)}(\Gamma)d\Gamma \) is the probability of observing the infinitesimal phase volume \( d\Gamma \), centred on the phase vector \( \Gamma \), according to the \( i^{th} \) equilibrium distribution function, \( f_{eq}^{(i)} \). The phase volume \( d\Gamma(\tau) \) is generated from \( d\Gamma \) using the equations of motion that take the system from equilibrium state (1) towards state (2) (using the forward protocol). For \( \Delta X_r(\Gamma) \) to be well defined requires that

(a) if \( f_{eq}^{(1)}(\Gamma) \neq 0 \) then \( f_{eq}^{(2)}(\Gamma(\tau)) \neq 0 \), and

(b) the converse, namely that if \( f_{eq}^{(2)}(\Gamma(\tau)) \neq 0 \), then \( f_{eq}^{(1)}(\Gamma) \neq 0 \).

The second condition is also required because if the numerator of Eq. (1) is zero, the “work” which is the logarithm of the right hand side of Eq. (1) will not be defined. We call these conditions the **ergodic consistency conditions for the generalised work**. They are analogous to the ergodic consistency condition for the Evans-Searles Fluctuation Theorem.

It is trivial to prove that the exponential average of \( -\Delta X_r \) satisfies the following relation:

\[
\langle \exp(-\Delta X_r) \rangle_{eq1} = \int_{\Gamma | f_{eq}^{(1)}(\Gamma) \neq 0} d\Gamma f_{eq}^{(1)}(\Gamma) \frac{f_{eq}^{(2)}(\Gamma(\tau)) \| \partial \Gamma(\tau)/\partial \Gamma \| Z^{(2)}}{f_{eq}^{(1)}(\Gamma)Z^{(1)}} = Z^{(2)} Z^{(1)}
\]

where the brackets \( \langle \ldots \rangle_{eq1} \) denote an ensemble average over the initial (i.e. \( f_{eq}^{(1)} \)) equilibrium distribution and \( d\Gamma(\tau)/d\Gamma = \| \partial \Gamma(\tau)/\partial \Gamma \| \). This relationship is very general and shows how free energy differences can be computed from path integral information taken from nonequilibrium paths. These paths do not need to be quasistatic. We call this equality Eq. (2) the **Generalised Jarzynski Equality (GJE)**.

The restriction of the integral to those regions where \( f_{eq}^{(1)}(\Gamma) \neq 0 \) means that one completely avoids divergences in the function being averaged. The validity of Eq. (2) only requires:
(c) an integrable region in the phase space of the final equilibrium distribution for which \( f_{eq}^{(2)}(\Gamma(\tau)) \neq 0 \).

We call this the ergodic consistency condition for the GJE. This condition is more general than the corresponding ergodic consistency condition for the generalised work. The following example illustrates a case where this condition breaks down and where the GJE fails. Consider the adiabatic transformation of one Hamiltonian system into a different Hamiltonian for which \( H(\Gamma(\tau)) \neq H(\Gamma(0)) \) \( \forall \Gamma \). If the two equilibrium states are microcanonical and they have the same energy then we will have \( \forall \Gamma, \ f_{eq}^{(2)}(\Gamma(\tau)) = 0 \). So in this example ergodic consistency is violated for both the generalised work and for the GJE.

Of course we also make the usual physical assumptions that the dynamics is such that there are no singularities in the equations of motion so that the trajectories in phase space are well defined and that the Jacobian in Eq. (2) is non-divergent.

To obtain the Jarzynski Equality we consider the special case of transformations using thermostatted dynamics between canonical equilibrium states with the same temperature. In order to determine the free energy differences. This reservoir can be regarded as being in thermodynamic equilibrium because it is assumed to have many more degrees of freedom than the system of interest.

The equations of motion for the system during the time \( 0 < t \leq \tau \) are written as

\[
\begin{align*}
\dot{q}_i &= \frac{p_i}{m} \\
\dot{p}_i &= -\frac{\partial H_0(q, p, \lambda(t))}{\partial q_i} - \alpha S_i p_i \\
\alpha &= \frac{\sum_{i=1}^{N} S_i F_i \cdot p_i}{\sum_{j=1}^{N} S_j p_j \cdot p_j}
\end{align*}
\]

(3)

where \( F_i = -\frac{\partial H_0(q, p, \lambda(t))}{\partial q_i} \). In these equations \( \lambda \) is a parametric function such that \( H_0(\lambda(0)) = H_0^{(1)} \) and \( H_0(\lambda(\tau)) = H_0^{(2)} \) and the function \( \lambda(t) \) defines the transformation protocol. The switch, \( S_i \), is defined such that \( S_i = 1 \) for particles that form the thermostating reservoir and \( S_i = 0 \) when they are part of the system of interest. The variable \( \alpha \) is a Gaussian thermostat multiplier\(^{15,16}\) that fixes the kinetic energy of the reservoir particles. It is easy to see that for such a system \( H_{0,therm}(\Gamma, t) = -2K_{therm}\alpha(\Gamma, t) = \dot{Q} \) where \( K_{therm} = \sum_{i=1}^{N} S_i p_i^2 / 2m \) is the kinetic energy of the reservoir particles and \( \dot{Q} \) is the rate at which heat is exchanged with the synthetic thermostat.

In this case the Liouville equation states: \( \frac{df}{d\tau} = -\Lambda f = 3N_{therm}\alpha f \), where \( \Lambda = \frac{d}{d\tau} \Gamma \) is the phase space compression factor\(^{15,16}\). Hence

\[
\left\| \frac{\partial \Gamma(\tau)}{\partial \Gamma} \right\| = \frac{f_{eq}^{(1)}(\Gamma) \mid_{\Gamma(\tau)}}{f_{eq}^{(1)}(\Gamma(0)) \mid_{\Gamma(0)}} = \exp \left[ \int_{0}^{\tau} dt \Lambda(\Gamma(t)) \right] = \exp \left[ -3N_{therm} \int_{0}^{\tau} dt \alpha(\Gamma(t)) \right] = \exp \left[ \beta \int_{0}^{\tau} dt \dot{H}_{0,therm}(\Gamma(t)) \right],
\]

(4)

where \( f_{eq}^{(1)} \) denotes \( f_{eq}^{(1)} \) evolved for a period \( \tau \). In general \( f_{eq}^{(1)} \) is not an equilibrium distribution.

If the equilibrium distributions \( f_{eq}^{(1)}(\Gamma) \) and \( f_{eq}^{(2)}(\Gamma) \) are canonical and at the same temperature, it is trivial to show using Eq. (1), that \( \Delta X / \beta \) is the total energy change in the system minus the energy (i.e. the heat) gained by the system from the thermostat (usually a negative quantity), \(-\Delta Q(\Gamma; 0, \tau) = -\int_{0}^{\tau} dt \dot{H}_{0,therm}(\Gamma(t)) \). That is, using Eqs. (1) & (4), we see that

\[
\Delta X(\Gamma; 0, \tau) = \beta \int_{0}^{\tau} dt \left[ H_{tot}(\Gamma, t) - \dot{H}_{0,therm}(\Gamma, t) \right] = \beta \int_{0}^{\tau} dt \left[ \dot{H}_{0,therm}(\Gamma, t) - \beta \Delta Q(\Gamma; 0, \tau) \right]
\]
Here \( \dot{H}_0^{ad} \) is the adiabatic (unthermostatted) time-derivative of the internal energy\(^{[10]} \). The final equality is obtained by consideration of the First Law of Thermodynamics, and shows that in this case (thermostatted dynamics with canonical initial and final distributions), \( \Delta X_\tau \) is just the work performed on the system in the transformation multiplied by \( \beta \): \( \Delta X_\tau (\Gamma; 0, \tau) = \beta \Delta W_\tau (\Gamma; 0, \tau) \). Substitution of Eq. (5) into Eq. (2) then gives the well known Jarzynski Equality,

\[
\langle \exp(-\beta \Delta W_\tau) \rangle_{eq1} = \frac{Z^{(2)}}{Z^{(1)}} = \exp[-\beta \Delta A],
\]

where the partition functions \( Z^{(i)} \) are related to the Helmholtz free energy by the equation

\[
A = -k_B T \ln \left( \int d\Gamma \exp(-\beta H_0 (\Gamma)) \right) = -k_B T \ln Z.
\]

Eq. (6) provides a way of determining the difference in the Helmholtz free energy, \( \Delta A = A^{(2)} - A^{(1)} \), between two canonical equilibrium states with partition functions \( Z^{(1)} \) and \( Z^{(2)} \) by measuring the work, \( \Delta W_\tau \) done over a period \( \tau \), for an ensemble of nonequilibrium pathways starting in state “I” and moving towards but not actually reaching equilibrium state “2”.

The same result is obtained if the initial ensemble is canonical and the dynamics is either thermostatted by a Nosé-Hoover thermostat or the dynamics are adiabatic. For other ensembles Eq. (1) may not refer to work (see\(^{[19]} \)). For example the microcanonical ensemble with the same energy \( H_0 \) at times \( t = 0 \) and \( t = \tau \), the generalised “work” \( \Delta X_\tau \), is in fact the change in heat.

In the derivation of Eq. (6) it is assumed that the initial distribution is given by the full canonical ensemble. The initial distribution must be a fully relaxed ergodic equilibrium state. The identity is then a mathematical relation about how the free energy difference on the right hand side is related to various integrals on the left hand side. If at the end of the protocol for changing the Hamiltonian the system is not in true thermodynamic equilibrium, as long as the ergodic consistency conditions hold, subsequent relaxation to equilibrium does not matter. If ergodic consistency fails (because the observed phase density at time \( \tau \), has no overlap with the final equilibrium distribution) then the Jarzynski Equality fails. Also in any practical implementation of any GJE the generalised work needs to be properly defined, so the ergodic consistency condition for the generalised work takes precedence over that for the GJE itself.

A necessary condition for Eq. (6) or Eq. (2) to yield correct results in practise is that in the ensemble averaging process the time reversed path of the most probable path, must be observed. If the averaging process is not sufficiently exhaustive for the initial points of these possibly extremely rare events to be sampled from the initial equilibrium distribution, numerical evaluation of Eq. (6) or Eq. (2) will give misleading results. One can easily see that this is the case. Write the work (or the generalised work) as the sum of the reversible work and the purely irreversible work. As the reversible work is just the free energy difference it can be taken through the average of the negative exponential. The average of the negative exponential of the purely irreversible work must now average to unity. This is just the Nonequilibrium Partition Identity\(^{[11,22]} \). It is well known from the Evans Searles Fluctuation Theorem\(^{[23]} \) that the necessary condition for this to hold in sampled data is to see the anti trajectories of the most probable trajectories for the process considered. This observation has an immediate impact on the calculation of free energy differences in the thermodynamic limit. These differences must be calculated for finite systems for a series of system sizes and then extrapolation must be employed in order to take the thermodynamic limit.

### B. Quasiequilibrium free energies from the quasiequilibrium partition function

Consider an ensemble of glass-forming systems at equilibrium at \( t = 0 \). We then quench the system to a quasiequilibrium glass state by changing \( H_0 \) over a period \( 0 < t \leq \tau \). After the relaxation of transients, at \( t = \tau_{qe} \geq \tau \), we assume that the ensemble remains in the glass state for a prolonged period of time during which the average properties of the system seem constant on the time scale of observation. The effect of this process on the phase space distribution is shown schematically in Fig. 1. If the time scale over which the system relaxes to equilibrium is very slow \( (t \gg \tau_{qe}) \) we may accurately model the ensemble’s distribution function at \( t = \tau_{qe} \) by treating it as consisting of a set of non-overlapping phase space domains \( \{ D_{\alpha}; \alpha = 1, N_p \} \). These domains partition the phase space available to any individual sample. By definition any sample belongs to one and only one phase space domain. Within individual domains the samples are ergodic (by definition) and time averaged properties are equal to ensemble averages over
where the partition function

\[ Z = \sum_{\alpha=1}^{N_D} a_\alpha \int_{D_\alpha} d\Gamma \exp[-\beta H_0(\Gamma)] \]

Figure 1: A schematic diagram showing how the phase space density (represented by shading) and the location of a phase space volumes centered at \( \Gamma(0) \) evolve with time from an equilibrium state at \( t = 0 \) through a period, \( \tau \) where the Hamiltonian is changing with time, and then as the system relaxes to a quasiequilibrium state at long times.

sets of samples belonging to the same phase space domain. The domains have zero overlap - otherwise they would not be ergodic. When viewed separately each of these domains appears to be in equilibrium with internal weights given by the relative Boltzmann weights. However the relative number of ensemble members in each of these domains is not consistent with an equilibrium Boltzmann distribution. Instead these relative populations are influenced by the details of the quench and subsequent ageing process that was used to prepare the ensemble of samples - they are history dependent. We call this ensemble a quasiequilibrium ensemble. The phase space distribution function for this ensemble has been derived by Williams and Evans.

Following reference, for \( t = \tau_{qe} \) we can write the distribution function of a single occupied domain, \( D_\alpha \), as

\[ f_\alpha(\Gamma) = \frac{s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]}{\int_{D_\alpha} d\Gamma \exp[-\beta H_0(\Gamma)]} = \frac{s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]}{Z_\alpha} \]

where the switch, \( s_\alpha(\Gamma) \), is equal to unity when \( \Gamma \in D_\alpha \) and zero otherwise, and

\[ Z_\alpha = \int d\Gamma s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]. \]

We note that \( f_\alpha(\Gamma) \) is the phase space density at \( \Gamma \) normalised over \( D_\alpha \) only. Only in the case of an equilibrium state will \( f_\alpha(\Gamma) = f(\Gamma) \) for all \( \Gamma \). We now write the distribution function for the quasiequilibrium ensemble,

\[ f_{qe}(\Gamma) = \frac{\sum_{\alpha=1}^{N_D} a_\alpha s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]}{\sum_{\gamma=1}^{N_D} a_\gamma \int_{D_\gamma} d\Gamma \exp[-\beta H_0(\Gamma)]} = \frac{\sum_{\alpha=1}^{N_D} a_\alpha s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]}{Z_Z} = \frac{\sum_{\alpha=1}^{N_D} a_\alpha f_\alpha(\Gamma) Z_\alpha}{Z_Z}, \]

where the partition function

\[ Z_Z = \sum_{\alpha=1}^{N_D} a_\alpha \int_{D_\alpha} d\Gamma \exp[-\beta H_0(\Gamma)]. \]
The value of \( a_{\alpha} \) gives the contribution of the domain \( \alpha \) to the partition function, relative to its contribution in an equilibrium state. If the domain \( \alpha \) is unoccupied, \( a_{\alpha} = 0 \). If we consider an equilibrium distribution of states that is arbitrarily partitioned into domains then we see that if the same partition function is to be obtained by summing over the arbitrary domains as was obtained without partitioning, then

\[
a_{\alpha} = 1, \: \forall \alpha.
\]

This in turn implies the quasiequilibrium normalisation condition:

\[
\sum_{\alpha=1}^{N_D} a_{\alpha} = N_D.
\]

We can define a partition function weighted free energy of an ensemble of glass samples, \( A_Z \), as

\[
\exp[-\beta A_Z] = Z_Z = \sum_{\alpha=1}^{N_D} a_{\alpha} \int_{D_{\alpha}} d\Gamma \exp[-\beta H_{0}(\Gamma)]
\]

\[
= \sum_{\alpha=1}^{N_D} a_{\alpha} \int d\Gamma s_{\alpha}(\Gamma) \exp[-\beta H_{0}(\Gamma)]
\]

\[
= \sum_{\alpha=1}^{N_D} a_{\alpha} Z_{\alpha} = \sum_{\alpha=1}^{N_D} a_{\alpha} \exp[-\beta A_{\alpha}]
\]

where the local domain free energy is \( A_{\alpha} = -k_B T \ln Z_{\alpha} \). For ease of reference we will refer to \( A_Z \) as the quasi-Helmholtz free energy. We will show later that (except at equilibrium) this free energy is not the Helmholtz free energy.

Replacing the equilibrium distribution function in the definition Eq. (1) with the quasiequilibrium distribution functions, Eq. (10), and using \( Z_Z \) for the partition functions, it is straightforward to show that for an ensemble of glass samples,

\[
\exp[\Delta X_{Z,\tau_{qe}}(\Gamma)] = \frac{f_{qe}^{(1)}(\Gamma) \| \partial \Gamma / \partial \Gamma(\tau_{qe}) \| Z_{Z}^{(1)}}{f_{qe}^{(2)}(\Gamma(\tau_{qe})) Z_{Z}^{(2)}}
\]

\[
= \frac{\sum_{\alpha=1}^{N_D} a_{\alpha}^{(1)} s_{\alpha}^{(1)}(\Gamma) \exp[-\beta H_{0}(\Gamma)] \| \partial \Gamma / \partial \Gamma(\tau_{qe}) \|}{\sum_{\gamma=1}^{N_{D_{\gamma}}} a_{\gamma}^{(2)} s_{\gamma}^{(2)}(\Gamma(\tau_{qe})) \exp[-\beta H_{0}(\Gamma(\tau_{qe}))]} \frac{\sum_{\alpha=1}^{N_D} a_{\alpha}^{(1)} s_{\alpha}^{(1)}(\Gamma)}{\sum_{\gamma=1}^{N_{D_{\gamma}}} a_{\gamma}^{(2)} s_{\gamma}^{(2)}(\Gamma(\tau_{qe}))}
\]

\[
= \exp \left[ \beta \Delta W_{\tau_{qe}}(\Gamma) \right] \frac{\sum_{\alpha=1}^{N_D} a_{\alpha}^{(1)} s_{\alpha}^{(1)}(\Gamma)}{\sum_{\gamma=1}^{N_{D_{\gamma}}} a_{\gamma}^{(2)} s_{\gamma}^{(2)}(\Gamma(\tau_{qe}))}
\]

We note that \( \Delta W_{\tau}(\Gamma) = \Delta W_{\tau_{qe}}(\Gamma) \) since no work is done during the relaxation period \( \tau < t < \tau_{qe} \), and \( \Delta W_{\tau}(\Gamma(0)) \) is the work given by Eq. (5). In Eq. (15) \( a_{\alpha}^{(1)} \) and \( a_{\alpha}^{(2)} \) are the weights for the relaxed quasiequilibrium state which, by choice of \( \tau_{qe} \), are the domain weights at that same finite time. Note at this same time the intra-domain weights may not yet be Boltzmann. Therefore,

\[
\Delta X_{Z,\tau_{qe}}(\Gamma) = \beta \Delta W_{\tau}(\Gamma) + \ln \left[ \sum_{\alpha=1}^{N_D} a_{\alpha}^{(1)} s_{\alpha}^{(1)}(\Gamma) \right] - \ln \left[ \sum_{\gamma=1}^{N_{D_{\gamma}}} a_{\gamma}^{(2)} s_{\gamma}^{(2)}(\Gamma(\tau_{qe})) \right].
\]
The expression Eq. (15) was obtained from Eq. (1) and therefore $\Delta X_{Z,\tau_{qe}}(\Gamma(0))$ also satisfies a modified version of Eq. (2):

$$\langle \exp(-\Delta X_{Z,\tau_{qe}}) \rangle_1 = \frac{Z_{Z}^{(2)}}{Z_{Z}^{(1)}} = \exp[-\beta \Delta A_{Z}].$$

(17)

Due to its resemblance to the GJE, Eq. (2), we refer to this as the GJE for quasiequilibrium ensembles, or simply the quasiequilibrium GJE. In the derivation of this relationship we have assumed:

(d) The occupancy of the domains in the final state at $t = \tau_{qe}$ is the same occupancy as in the relaxed quasiequilibrium state.

(e) For every $\Gamma$ where $f_{q_e}^{(1)}(\Gamma) \neq 0$ we require that $f_{q_e}^{(2)}(\Gamma(\tau_{qe})) \neq 0$ and vice versa. Translating this into domain weights, if $s_{\alpha}^{(1)}(\Gamma) \neq 0$ then we require that $s_{\alpha}^{(2)}(\Gamma(\tau_{qe})) \neq 0$, and vice versa.

The first assumption arises because although $\Delta W_{\tau}(\Gamma(0))$ does not change beyond $t = \tau$, the weights $a_{\alpha}^{(2)}$ and $s_{\alpha}^{(2)}(\Gamma(t))$ do continue to change for $t > \tau$. This is very different to the usual circumstance for ergodic systems. We also note that a necessary condition for the intra-domain weights to be Boltzmann is that they relax on a time scale which is much shorter than that for the inter-domain weights. This implies that although the inter-domain weights do not significantly change for $t \geq \tau_{qe}$, at the time $\tau_{qe}$ the intra-domain weights may not yet be Boltzmann.

For an aged glass where the observable rate of change for any macroscopic property relative to the relaxation time of the intra-domain weights approaches infinity, we have given a proof that if the phase space domains are robust with respect to small changes in macroscopic parameters, the phase space distribution within any domain is distributed in a Maxwell-Boltzmann distribution. Such distributions always satisfy assumption (d) above.

We note that if there is only one occupied domain, (e.g. $a_{1} = 1$ and $a_{2}, \ldots , a_{N_{D}} = 0$) then $A_{Z} = A_{1} - k_{B}T \ln(1) = A_{1}$ where $A_{1}$ is defined as in Eq. (14).

If the initial and final states are both at equilibrium, $\Delta A_{Z} = \Delta A$ since $a_{i} = 1 \forall i$. However, in general this is not the case. In order to determine the relationship between the Helmholtz free energy difference between quasiequilibrium states and $\Delta A_{Z}$, we consider its thermodynamic definition. The Gibbs expression for the entropy is

$$S = -k_{B} \int d\Gamma \ f(\Gamma) \ln[f(\Gamma)],$$

(18)

where the integral is over all space. Once the nonequilibrium process has finished, and the system slowly relaxes towards equilibrium ($t > \tau$), we have every expectation that Eq. (18) obeys the second law inequality, that is

$$T \frac{dS}{dt} \geq \frac{d}{dt} \langle Q \rangle,$$

(19)

When the transformation process finishes no more work is done on the system and the only way the average energy can change is through the transfer of heat, in our case through thermostats. Given the fundamental thermodynamic relation for the Helmholtz free energy,

$$A = \langle H_{0} \rangle - TS,$$

(20)

and the equation for the entropy, Eq. (18), the Helmholtz free energy is uniquely defined. In reference, it was shown that quasiequilibrium states can be treated using standard macroscopic thermodynamics. So by use of the distribution function, Eq. (10), we obtain the Helmholtz free energy of a quasiequilibrium state

$$A_{qe} = \langle H_{0} \rangle_{qe} + k_{B}T \langle \ln[f_{qe}(\Gamma)] \rangle_{qe}$$

$$= \langle H_{0} \rangle_{qe} + k_{B}T \left\langle \ln \left[ \sum_{\alpha=1}^{N_{D}} a_{\alpha} s_{\alpha}(\Gamma) \exp[-\beta H_{0}(\Gamma)]/Z_{Z} \right] \right\rangle_{qe}$$

$$= \langle H_{0} \rangle_{qe} - k_{B}T \left\langle \ln \left[ \sum_{\alpha=1}^{N_{D}} s_{\alpha}(\Gamma) a_{\alpha} \right] \right\rangle_{qe} + k_{B}T \langle -\beta H_{0}(\Gamma) - \ln[Z_{Z}] \rangle_{qe}$$

$$= \langle H_{0} \rangle_{qe} + k_{B}T \left\langle \ln \left[ \sum_{\alpha=1}^{N_{D}} s_{\alpha}(\Gamma) a_{\alpha} \right] \right\rangle_{qe}.$$
\[ = -k_B T \left\langle \ln \sum_{\alpha=1}^{N_D} s_\alpha(\Gamma) a_\alpha \right\rangle_{\text{eq}} + AZ \] 

(21)

where the notation \( \langle B(\Gamma) \rangle_{\text{qe}} \equiv \int_D d\Gamma f_{\text{qe}}(\Gamma) B(\Gamma) \) where \( D \) is all the available phase space in the glass state. Therefore, calculation of \( AZ \) which is an ensemble average of \( \Delta X_{ze} \) calculated along nonequilibrium trajectories, and use of Eq. (21) allows the Helmholtz free energy of a quasiequilibrium state to be determined:

\[ \Delta A_{\text{qe}} = \Delta A_Z + k_B T \left\langle \ln \left[ \sum_{\alpha=1}^{N_D} a^{(1)}_\alpha s^{(1)}_\alpha(\Gamma) \right] \right\rangle - k_B T \left\langle \ln \left[ \sum_{\gamma=1}^{N_D} a^{(2)}_\gamma s^{(2)}_\gamma(\Gamma(\tau_{\text{qe}})) \right] \right\rangle. \]  

(22)

In Eq. (27) of reference 6 it was shown (for Gibbs free energies rather than Helmholtz) that the free energy was minimised when all the domain weights were Boltzmann, that is \( \int_{D_\alpha} d\Gamma a_\alpha \exp(-\beta H_0(\Gamma)) = \int_{D_\alpha} d\Gamma \exp(-\beta H_0(\Gamma)). \) This implies that \( A(a_1, a_2, \ldots a_{N_D}) \) is minimised when \( a_i = 1 \ \forall \ i \), which coincides with thermodynamic equilibrium. We make the standard observation of macroscopic thermodynamics that when the system is not acted on externally Eqs. (19) & (20) give \( dA/dt \leq 0 \). Thus we have proved the following: as the system’s distribution function moves towards the equilibrium state, which is at the point \( a_\alpha = 1 \ \forall \ alpha, \) Eq. (19) is obeyed. By towards we mean the direction the system is moving has a component in the direction given by \( -\nabla A_{\text{qe}} + ([\nabla A_{\text{qe}} \cdot \nabla g]/(\nabla g \cdot \nabla g)]\nabla g \) where \( g = \sum_{\alpha=1}^{N_D} a_\alpha - N_D \) and \( \nabla \) acts on the \( N_D \) dimensional space given by the coordinate set \( a_\alpha \). In contrast \( A_Z \) might not be a minimum in equilibrium.

C. Quasiequilibrium free energies from a weighted sum of local domain free energies.

A nonequilibrium free energy relation can also be obtained for systems that are quenched from an equilibrium state to a quasiequilibrium state by considering the average of \( \exp(-\beta \Delta W_\tau) \) over trajectories that are in domain \( D_\alpha \) of a quasiequilibrium system at time \( \tau \). These can then be combined to obtain a difference in free energy of the initial equilibrium state and the final quasiequilibrium state. In this case it is convenient to work using a weighted sum of distributions that are normalised over sub-domains as introduced by Williams and Evans (9)

\[ f_{\text{qe}}(\Gamma) = \sum_{\alpha=1}^{N_D} w_\alpha f_\alpha(\Gamma) \]

\[ = \sum_{\alpha=1}^{N_D} \frac{w_\alpha s_\alpha(\Gamma) \exp[-\beta H_0(\Gamma)]}{\int_{D_\alpha} d\Gamma \exp[-\beta H_0(\Gamma)]}. \]

(23) 

Here \( N_D \) is the number of domains, and \( w_\alpha \) represents the relative weights of these domains under the constraint \( \sum_{\alpha=1}^{N_D} w_\alpha = 1 \), see reference 6. As above, we assume conditions \( \text{(a) \& (c)} \) hold. The relationship between \( w_\alpha \) and \( a_\alpha \) can be obtained by considering Eqs. (10) & (23) and is given by:

\[ w_\alpha = \frac{a_\alpha \int_{D_\alpha} d\Gamma \exp[-\beta H_0(\Gamma)]}{\sum_{\gamma=1}^{N_D} a_\gamma \int_{D_\gamma} d\Gamma \exp[-\beta H_0(\Gamma)]} = \frac{a_\alpha Z_\alpha}{Z}. \]

(24)

In order to develop free energy relations, we consider two possibilities: we first consider the reverse process where the work is monitored as a prepared quasiequilibrium system is relaxed towards the ergodic equilibrium state by varying \( H_0 \) over a period \( 0 < t \leq \tau \); in the second case we consider the reverse process where the work is monitored as a prepared quasiequilibrium system is relaxed towards the ergodic equilibrium state by varying \( H_0 \) over a period \( 0 < t \leq \tau \) using the reverse protocol. In the first case we can use the relationships between the work and equilibrium canonical distribution functions, Eqs. (2) & (5), to show for any domain, \( D_\alpha \), of a quasiequilibrium state,

\[ \langle s_\alpha(\Gamma(\tau_{\text{qe}})) \exp(-\beta \Delta W_{\tau-\text{qe}}(\Gamma(\tau_{\text{qe}}))) \rangle_{\text{qe}} = \int d\Gamma f_{\text{qe}}^{(1)}(\Gamma) \frac{s_\alpha(\Gamma(\tau_{\text{qe}})) f_{\text{eq}}^{(2)}(\Gamma(\tau_{\text{qe}})) \| \partial \Gamma(\tau_{\text{qe}}) / \partial \Gamma \| Z^{(2)}_{\text{eq}}}{f_{\text{eq}}^{(1)}(\Gamma) Z^{(1)}_{\text{eq}}}. \]

\[ = \int d\Gamma(\tau_{\text{qe}}) \frac{s_\alpha(\Gamma(\tau_{\text{qe}})) f_{\text{eq}}^{(2)}(\Gamma(\tau_{\text{qe}})) Z^{(2)}_{\text{eq}}}{Z^{(1)}_{\text{eq}}} = \exp[-\beta \Delta A_{2\alpha,1}] \]

(25)
where we have used the fact that \( \Delta W^{e\rightarrow qe}_r(\Gamma) = \Delta W^{e\rightarrow qe}(\Gamma) \) and \( \Delta A_{qeq} = A_{qeq}^{(2)} - A_{qeq}^{(1)} \). Note that only trajectories that are in \( D_a \) at time \( \tau_{qe} \) will have a non-zero contribution to the ensemble average on the left. Using this and the Schrödinger-Heisenberg equivalence for phase space averages (see Section 3.3 of reference [13]) we may write \( \langle s_\alpha(\Gamma(\tau_{qe})) \rangle _{eq} = \langle s_\alpha(\Gamma) \rangle _{qe} = w_\alpha \). By only averaging over trajectories that are in \( D_a \) at time \( \tau \), we form a conditional ensemble average \( \langle B(\Gamma) \rangle _{eq1,qe} = \frac{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe})) \Gamma(\tau_{qe})}{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe}))} = \langle s_\alpha(\Gamma(\tau_{qe}))B(\Gamma) \rangle _{eq1} \). By only averaging over trajectories that are in \( D_a \) at time \( \tau \), we form a conditional ensemble average \( \langle B(\Gamma) \rangle _{eq1,qe} = \frac{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe})) \Gamma(\tau_{qe})}{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe}))} = \langle s_\alpha(\Gamma(\tau_{qe}))B(\Gamma) \rangle _{eq1} \). By only averaging over trajectories that are in \( D_a \) at time \( \tau \), we form a conditional ensemble average \( \langle B(\Gamma) \rangle _{eq1,qe} = \frac{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe})) \Gamma(\tau_{qe})}{\int d\Gamma f^{(1)}_{eq}(\Gamma) s_\alpha(\Gamma(\tau_{qe}))} = \langle s_\alpha(\Gamma(\tau_{qe}))B(\Gamma) \rangle _{eq1} \).

We emphasise that by \( \langle \cdot \cdot \rangle _{eq1,qe} \) we imply that the condition is on the domain that the trajectory is in when it reaches the quasiequilibrium state, and not on the domain in which it starts.

Note that in Eqs. (16) & (25), we have assumed that \( w_\alpha \) and \( a_\alpha \) do not vary with time (they remain equal to their value at \( t = \tau_{qe} \)). Of course this does not allow for the extremely slow relaxation to the final equilibrium state that might occur, on a much larger timescale. Therefore it is more accurate to say that they are constant on the accessible timescales.

Conditions [a] & [d] specified above for the quasiequilibrium GJE are also required in this case. However, as discussed above, these restrictions are not likely to be of any significance for cases of practical interest, certainly not from the energy landscape point of view.

From Eq. (26), and the fact that the Helmholtz free energy \( A = \sum_{\alpha=1}^{N_D} [w_\alpha A_\alpha + k_B T w_\alpha \ln(w_\alpha)] \) (see Eq. (25) of reference [5]), we obtain,

\[
\Delta A^{e\rightarrow qe} = -k_B T \sum_{\alpha=1}^{N_D} w_\alpha^{(2)} \ln \left[ \langle \exp(-\beta \Delta W^{e\rightarrow qe}_r(\Gamma)) \rangle _{eq1,a} \right]
\]  

(27)

where \( \Delta A^{e\rightarrow qe} = A_{qe}^{(2)} - A_{qe}^{(1)} \) is the difference between the initial equilibrium Helmholtz free energy \( A_{qe}^{(1)} \) and the Helmholtz free energy of the nonergodic quasiequilibrium state \( A_{qe}^{(2)} \).

Alternatively, we can develop an expression for the ensemble average over a single domain of the quasiequilibrium state, by considering the reverse process when the initial state (state (2)) is a relaxed quasiequilibrium state and the final state (state (1)) is an ergodic equilibrium state. Since each domain in the quasiequilibrium state is locally canonical, the same arguments in Section A can be used to show that for any trajectory starting at \( \Gamma \) in domain \( D_a \) and subject to a change in \( H_0 \) over a period \( 0 < t < \tau \), (rather than the longer period \( 0 < t \leq \tau_{qe} \)),

\[
\exp(\beta \Delta W_{qe}^{e\rightarrow qe}(\Gamma)) = \frac{f_{eq}^{(2)}(\Gamma) ||\partial \Gamma / \partial \Gamma(\tau)|| Z_{eq}^{(2)}}{f_{eq}^{(1)}(\Gamma(\tau)) Z_{eq}^{(1)}}
\]  

(28)

The ensemble average over domain \( D_a \) is given by

\[
\langle \exp(-\beta \Delta W_{qe}^{e\rightarrow qe}(\Gamma)) \rangle _{eq1,a} = \int d\Gamma s_\alpha(\Gamma) f_{eq}^{(1)}(\Gamma) \frac{f_{eq}^{(2)}(\Gamma(\tau)) ||\partial \Gamma(\tau) / \partial \Gamma|| Z_{eq}^{(1)}}{f_{eq}^{(2)}(\Gamma)} Z_{eq}^{(2)}
\]

(29)

where the Schrödinger-Heisenberg equivalence for phase space averages is used to give \( \int d\Gamma s_\alpha(\Gamma) f_{eq}^{(1)}(\Gamma(\tau)) = \langle s_\alpha(\Gamma) \rangle _{qe} = w_\alpha \).

As above, we can then show that

\[
\Delta A^{e\rightarrow qe} = -k_B T \sum_{\alpha=1}^{N_D} w_\alpha^{(2)} \ln \left[ \langle \exp(-\beta \Delta W_{qe}^{e\rightarrow qe}(\Gamma)) \rangle _{eq1,a} \right]
\]  

(30)

In this section and Section B, we have described three approaches for determination of the free energy of the quasiequilibrium state that involve exponential averages of nonequilibrium path integrals, in the same way the Jarzynski Equality is applied to equilibrium states. In the next section we will consider practical issues regarding their application.
III. MODEL AND SIMULATION DETAILS

In order to examine the ability of the Jarzynski Equality and the new free energy expressions Eqs. (21) & (30) to probe the free energy of a quasiequilibrium state, we consider a model of a system which may be quenched into a glass state. We employ a dynamical model originally developed by Hoover and coworkers\cite{14,15} for other purposes. This simple dynamical system is ergodic and mixing and samples phase space canonically despite there only being a single particle in a one dimensional Cartesian space. To achieve this two Nosé-Hoover thermostats are employed giving the following equations of motion

\[
\begin{align*}
\dot{q} &= \frac{p}{m}, \\
\dot{p} &= F(q) - \zeta_1 p - \zeta_3 p^3, \\
\dot{\zeta}_1 &= \left( \frac{\beta p^2}{m} - 1 \right) / \tau_1^2, \\
\dot{\zeta}_3 &= \left( \frac{\beta p^4}{m} - 3p^2 \right) / \tau_3^2,
\end{align*}
\]

where \( q \) is the particle’s position, \( p \) is its momentum, \( \beta = 1/(k_B T) \) where \( T \) is the average temperature regulated by the two thermostats and \( F(q) = -d\Phi(q)/dq \) is the force acting on the particle. The variables \( \tau_1 \) and \( \tau_3 \) are time constants for the thermostat’s feedback mechanism.

Using the Liouville theorem, the distribution function of this system can be derived, and is given by\cite{23}

\[
f(q, p, \zeta_1, \zeta_3) = \frac{\tau_1 \tau_3}{(2\pi)^{3/2}(mk_BT)^{1/2}} \frac{\exp(-\beta H_e(q, p, \zeta_1, \zeta_3))}{\int_{-\infty}^{\infty} dq' \exp(-\beta \Phi(q'))}.
\]

Here \( H_e(q, p, \zeta_1, \zeta_3) = H_0(q, p) + \frac{1}{2}k_B T(\tau_1^2 \zeta_1^2 + \tau_3^2 \zeta_3^2) + \Phi(q) + \frac{1}{2}p^2/m + k_B T(\tau_1^2 \zeta_1^2 + \tau_3^2 \zeta_3^2) \) where \( H_0 \) is the Hamiltonian and internal energy of the unthermostatted oscillator. The partition function is

\[
Z_e = \frac{(2\pi)^{3/2}(mk_BT)^{1/2}}{\tau_1 \tau_3} \int_{-\infty}^{\infty} dq' \exp(-\beta \Phi(q')) = \frac{2\pi}{\tau_1 \tau_3} Z,
\]

where \( Z_e \) is the partition function in the extended phase space. We use a double well potential to form a simple model of a glass. This forms a very simplistic representation of the complicated energy landscape of a real glass. It features a local minimum that can be separated from the global minimum on quenching. The potential, shown in Fig. 2 is given by the equation

\[
\Phi(q) = \epsilon \left( b_0 + b_1 q/\sigma + b_2 q^2/\sigma^2 + b_4 q^4/\sigma^4 \right),
\]

where \( b_0 = 12.04541125, b_1 = 1.5, b_2 = -5.25 \) and \( b_4 = 0.75 \). We use reduced units throughout this section, where the length unit is \( \sigma \), the mass unit is \( m \) and the energy unit is \( k_B T \), resulting in the time unit \( \sigma \sqrt{m/k_BT} \). The thermostat time constants have fixed values of \( \tau_1 = \tau_3 = 0.5 \). The potential has a global minimum of \( \Phi = 0 \) at \( q = 1.9483214 \), a local minimum at \( q = -1.9385372 \) and a local maximum at \( q = 0.14370505 \). In Fig. 2 the potential is plotted for two different values of \( \epsilon \) (in units of \( k_BT \)). When \( \epsilon = 0.1 \), the two local minima are separated by a barrier of the order of 1 (i.e. 2\( k_BT \)), a barrier that the system readily traverses. At the lower temperature, when \( \epsilon = 1.0 \), (i.e. 2\( k_BT \)) a system in the local minimum is separated from the global minimum by a barrier of the order of 5 (i.e. 6\( k_BT \)). This is a significant energy barrier and the crossing of it constitutes a rare event. After quenching a large ensemble of systems to this low temperature, the higher energy local minimum is populated by a larger proportion of the ensemble than it would be when fully equilibrated. Due to the high energy barrier this situation persists for a long time.

In the quenching experiment considered above, the initial state can be divided into two non-intersecting domains with \( q < 0.14370505 \) and \( q \geq 0.14370505 \), and both are occupied according to their equilibrium distributions: \( a_1 = a_2 = 1 \). For this state \( Z_Z = Z \) is the usual equilibrium partition function and \( A_Z = A \) is the usual free energy. In the final state we expect that, due to our selection of the initial potential, after the quench the second domain \( (q \geq 0.14370505) \) will have an occupancy that is much higher than its Boltzmann occupancy and the first will have a lower than Boltzmann occupancy. The equilibrated occupancy for domain 2 is nearly zero so the change relative to the Boltzmann level is very large.

Here we have deliberately selected an initial distribution that leads to \( a_2 \ll a_1 \), so that we can clearly demonstrate the difference in information provided by the Jarzynski Equality and the new free energy expressions Eqs. (21) &
Figure 2: Potential energy function, defined by Eq. (34) with the blue dashed line corresponding to $\epsilon = 0.1$ and the red solid line corresponding to $\epsilon = 1$.

(27). The treatment described above can be readily applied to systems where the values of the weights for more than one domain are significant.

In order to compare the Jarzynski Equality and the new relations, ensembles of $10^5$ independent simulations were carried out starting from an initial equilibrium ensemble with $\epsilon = 0.1$ in Eq. (34). At time $t = 0$ the parameter $\epsilon$ was linearly increased to a final value of $\epsilon = 1$ at time $t = \tau = 200$. A second set of simulations was computed with duration of $\tau = 2000$ rather than $\tau = 200$. These times were chosen to be sufficiently short that a quasiequilibrium state develops, yet sufficiently long that within the domains the distribution is sufficiently close to Boltzmann at the end of the trajectory, that no further relaxation is required to develop the quasiequilibrium distribution. That is, for our model we can take $\tau = \tau_{qe}$. If a more rapid protocol was used, this might not be the case and the system would need additional time to relax before generating the quasiequilibrium distribution. The probability distribution was then separated into two domains with any configuration where the position of the particle was in the range $-\infty < q < 0.14370505$ being designated as in the first domain and all other configurations $0.14370505 \leq q < \infty$ being designated as in the second domain. Recall that the value 0.14370505 is the position of the local maximum in the potential Eq. (34).

IV. RESULTS AND DISCUSSION

A. Distribution Functions

The first point to be tested is whether Eq. (10) is able to accurately represent our simulations and to what degree they are out of equilibrium at time $\tau = 200$ with $\epsilon = 1.0$. In order to examine this, Fig. 3 shows $f(q)$ obtained from the equilibrium distribution function, Eq. (32), and the distribution found in the simulations. Eq. (10) was then used to fit the data, and it was found that the best fit was obtained with the single free parameter set to $a_1/a_2 = 0.03627$. Using the normalisation condition gives $a_1 = 0.07000; a_2 = 1.930$.

It can be seen that Eq. (10) fits the data very well despite $a_1$ and $a_2$ being very different, which means the system is a long way from equilibrium by this measure. In the vicinity of the local minima in the energy (at $q = 1.79483214$), the equilibrium distribution function can be seen to have a value which is very close to zero. The observed quasiequilibrium distribution function has a significant value here, approximately 25 times larger than the equilibrium value. As time progresses, after the nonequilibrium process has finished, this difference between the two distribution functions follows a very slow exponential decay which will depend on the barrier height in the potential (see Fig. 2) along with the choice of time constants $\tau_1$ and $\tau_3$ in Eq. (31). We will not pursue the details of this further in this paper.

The ergodic consistency conditions for the application of the Jarzynski Equality and the quasiequilibrium GJE for the two quasiequilibrium states are satisfied. Firstly there is only a very slow relaxation of the weights after the transformations. The second condition namely that if $s_1^1(\Gamma) \neq 0$ then we require that $s_2^2(\Gamma(\tau_{qe})) \neq 0$, and vice versa is also satisfied. Although it is hard to see in the figure the final equilibrium distribution does have measurable
density in both domains and rather more obviously in the final quasiequilibrium state there is density in both domains. There is also density in both domains in the initial (ergodic) equilibrium distribution function.

B. Standard Jarzynski Equality

By employing the standard Jarzynski Equality, Eq. (6), we are able to compute the difference in free energy between the equilibrium states for $\epsilon = 0.1$ and $\epsilon = 1.0$. Of course, for the simple model under consideration, the difference in free energy may be readily computed using Eqs. (7), (33) & (34) for both values of $\epsilon$. Thus the partition function was evaluated numerically, and a value of $\Delta A_{eq} = 1.7219$ was obtained, where we add the subscript ‘eq’ to indicate that both states were at equilibrium. The value obtained from applying the Jarzynski Equality, Eq. (6), to the ensemble of simulations of duration $\tau = 200$, was $\Delta A = 1.7229$ and for the ensemble of duration $\tau = 2000$ it was $\Delta A = 1.7231$. This strong agreement with the equilibrium value in both cases gives a clear demonstration of how the Jarzynski Equality gives the free energy difference between the two equilibrated states. This might seem surprising. Despite the fact that the period over which the work is measured is too short to generate the final equilibrium state, the Jarzynski Equality refers to the state that would be reached after infinite relaxation time. Therefore, although there may be a long-lasting glassy state, the Jarzynski Equality does not refer to that.

Provided ergodic consistency is satisfied, the Jarzynski Equality gives the difference between the initial equilibrium free energy and the free energy of the final equilibrium state. However, if there are phase space domains in the final state that are not sampled at all, the Jarzynski Equality gives the free energy difference between the two equilibrium states subject to the constraint that the weights are zero in the excluded domains. The proof follows from a simple gedanken experiment. Suppose that the reason why those excluded domains are not sampled at all is that the potential energy is actually infinite for all states in those excluded domains. Then clearly the Jarzynski Equality gives the free energy difference between the two equilibrium states defined using the modified potential energy function for the final system. In this final equilibrium system all the nonzero weights are Boltzmann.

In a real glassy state, the relaxation of the fluid is so slow that the crystalline states are never reached and rather the glass remains in a history dependent state for time scales beyond human experience. Applying the Jarzynski Equality to glass forming systems where all crystalline phases are never sampled, gives the free energy difference between the initial equilibrium system and the “ideal” or equilibrium glass where the weights of all the glassy phases are Boltzmann - both intra and inter domain weights.

If the time over which $\epsilon$ varied was infinitely slow, the system would be quasistatic and the process would be thermodynamically reversible. The amount of work, Eq. (5), done by every trajectory would then be the same and equal to the change in Helmholtz free energy and the instant the process finishes the system would be in equilibrium. However in the final state, when $\epsilon$ is high, our system is not ergodic on the time scale of our simulations. By ergodic we mean that a single trajectory is able to sample a sufficient representation of phase space to be accurately representative
Figure 4: The distribution functions for the work done, Eq. (5), for an ensemble of simulations where the quench was carried out over period $\tau = 200$. The distributions are shown for the work done from when the quench states for times of a) 50, b) 100, c) 150 and d) 200. Curve e) corresponds to distribution of the work done for an ensemble of simulations when a quench was carried out over a period $\tau = 2000$. It shows the work done at the end of the quench (at a time of 2000).

of the entire phase space. Recalling the measured distribution function shown in Fig. 3, this would require that $\epsilon$ does not change significantly during the time it takes a single trajectory to sample a sufficient representation of the two peaks seen in the figure. Here the occurrence of a trajectory crossing from one peak to the other is a rare event and as $\epsilon$ is increased these events become much rarer. Thus as $\epsilon$ increases, the minimal time scale on which the system may not change significantly, in order to obtain something representative of a quasistatic process, diverges.

As the process is not thermodynamically reversible it is interesting to consider the distribution functions for the work done by the trajectories at different times, Fig. 4. The distributions are highly skewed towards large values of the work by trajectories where the particle remains trapped in the local minimum of the potential through the quench. By comparing the distribution of the more rapidly and slowly quenched ensembles, $\tau = 200$, and $\tau = 2000$ respectively, at the instant the quench finishes, $\epsilon = 1$, we gain some insight as to how the Jarzynski Equality works for this process. The distribution for the slower quench is much sharper and less skewed, with only a single peak, due to the process being significantly closer to the quasistatic limit. Thus during the slower quench many trajectories sample both the local minimum and the global minimum in the potential energy. In contrast to this, the more rapid quench is highly skewed with a second broad peak which can be observed at high values of $\Delta W/\beta$. This is due to many of the trajectories becoming stuck in either the local or global minima for prolonged times during the quench, i.e. loosely speaking, a break down in ergodicity. Due to the form of the exponential average in Eq. (6) the long skewed wing and broad second peak, for the more rapid quench, make only a small contribution to the average. This is exactly compensated for by the trajectories which remain trapped in the global minimum and have comparatively little work done on them, but make a large contribution to the average. Thus the Jarzynski Equality gives the same change in free energy that would be obtained from a single trajectory that is quenched quasistatically. Clearly these distributions are not Gaussian yet it is readily apparent that the distribution will approach a Dirac delta function as the quench time is extended towards infinity.

C. Quasiequilibrium free energy expressions

1. Quasiequilibrium free energy from the quasiequilibrium partition function

As seen in Fig. 4 the distribution function of the more rapidly quenched data is fitted very well at the time of $\tau = 200$, with $\epsilon = 1$, by Eq. (10) with $a_1/a_2 = 0.03627$ ($a_1 = 0.07000$; $a_2 = 1.930$). Using these values of $a_\alpha$ and numerical integration to evaluate the local partition functions, $(Z_\alpha = \int d\Gamma s_\alpha(\Gamma) \exp[-\beta H_\alpha(\Gamma)])$, Eq. (14) can be used to find that $\Delta A_Z = 4.276$ when $\epsilon$ is changed from $\epsilon = 0.1$ to $\epsilon = 1$ over this period. We can then compare this result with the value obtained using averages over nonequilibrium paths, Eq. (17) where $\Delta X_{Z,\tau}$ is given by Eq. (16). This method gives $\Delta A_Z = 4.281$, and the values are obviously in good agreement. It is worth noting that if we waited
long enough for the system to equilibrate and then calculated $\Delta X_{Z,\tau}$, at this time $\tau$ (which is much longer than 200), we would once again obtain the standard change in free energy, $\Delta A = \Delta A_{\text{eq}}$. The large difference between $\Delta A_{\text{eq}} (1.7219)$ and $\Delta A_Z (4.276)$ we find here shows how far the system is out of equilibrium at time $\tau = 200$ by this measure.

We can now use $\Delta A_Z$ and Eq. (22) to determine the difference in Helmholtz free energy of the equilibrium and quasiequilibrium states. With $a_1 = 0.07000$, $a_2 = 1.930$ and using numerical integration we find $\Delta A = 1.960$, which is significantly different from $\Delta A_{\text{eq}}$. This shows the importance of using the new expressions for the quasiequilibrium free energy if it is necessary to find the free energy of the glass state. In cases where $a_1Z_1/a_2Z_2 \ll 0$, it would be possible to obtain a good approximation to this free energy by approximating the potential energy of the glass state with Eq. (34) and $\epsilon = 1$ for $q \geq 0$. However, for the data presented here $a_1Z_1/a_2Z_2 \approx 8.657$ and this is not appropriate.

In order to demonstrate that the Helmholtz free energy, $A$, given by Eq. (21) is minimised when $a_1 = a_2 = 1$, as discussed in Section III C, we plot $A$ as a function of $a_1 = 2 - a_2$ for the potential, Eq. (34), with $\epsilon = 1$ in Fig. 5. The numerical data clearly support the theoretical result.

2. Quasiequilibrium free energy from a weighted sum of local domain free energies

Above we have shown that the free energy can be computed using Eqs. (17) & (21). However the approach has a serious drawback. If we wish to compute the free energy of a realistic model glass former using molecular dynamics simulations on a many body system, there will be a huge number of ergodic domains that must be considered. The number of domains will simply be too large to handle by these relations since it is necessary to identify what domain each trajectory belongs to, and to determine $a$ and various averages involving $a$ for each domain. A similar problem will occur, in general, with use of Eqs. (26) & (27).

Here we devise an algorithm based on Eqs. (29) & (30) that avoids this. We rewrite Eq. (30) as the following average:

$$\Delta A^{\text{qe-\text{eq}}} = -k_B T \ln \left[ \langle \exp(\beta \Delta W_{\tau}^{\text{qe-\text{eq}}}(\Gamma)) \rangle_{\alpha_{\text{qe}}} \right]$$

(35)

The over bar means that we sample master points in the phase space from the relaxed $f^{(2)}(\Gamma)$ distribution formed from an ensemble of quenched systems. These master points will belong to the various domains and will by definition populate those domains according to the weights appearing in Eq. (30) namely $w^{(2)}_{\alpha}$. For each master point we calculate the average $\langle \exp(\beta \Delta W_{\tau}^{\text{qe-\text{eq}}}(\Gamma)) \rangle_{\alpha_{\text{qe}}}$ over the domain that each master point resides in. This is done by generating daughter points from their master. These daughter points are guaranteed to belong to the same domain as their master, because they are generated either by fixing the configuration from the master point and sampling
the momenta from the appropriate Maxwell-Boltzmann distribution or by simply using the equations of motion to ergodically generate points in that same domain. In this Monte-Carlo like procedure for correctly averaging within and between domains we never need to know how many domains there are, or what their explicit weights are. The weights occur naturally and we know how to perform averages over each ergodic subdomain.

In the numerical work considered above, a quench time of $\tau = 200$ is sufficiently long that the numerical distribution is well approximated by the quasiequilibrium distribution when the quench is complete, and no additional relaxation time is required. This is demonstrated by the fact that the quasiequilibrium distribution function gave an excellent fit to the numerical data. Therefore Eq. (35) could be applied using states generated at the end of the quench. The free energy difference between the quasiequilibrium and equilibrium states was determined using $N_q = 5 \times 10^4$ trajectories or master points generated using the $\tau = 200$ quench. From each of these, an ensemble of 5000 trajectories was spawned in reverse by sampling the appropriate Gaussian distributions for the momentum $p$ and the trajectory weights $a_\alpha = 1, 0 \forall \alpha$, and for the occupied domains both the intra and inter domain weights are Boltzmann distributed.

By studying a simple model we have shown that subject to the ergodic consistency condition, that by performing nonequilibrium path integrals, the Jarzynski Equality can be used to predict free energy differences between states that are either in thermodynamic equilibrium or constrained thermodynamic equilibrium. We have shown that subject to this condition this equality can even be used in systems where after the change protocol between the two states has completed, the final relaxation to the new equilibrium state is exceedingly slow. Our example also confirms the correctness of a new statistical mechanical treatment of time independent, nonergodic, nondissipative nonequilibrium systems - so-called quasiequilibrium systems.

In systems where certain phase space domains are totally unsampled in the final observed distribution of states ($a_\alpha = 0$), the Jarzynski Equality gives the free energy difference between the equilibrium states and the final constrained equilibrium state.

We have derived three variations of the Jarzynski Equality (Eqs. (22), (27) & (30)) which calculate free energy differences between the initial equilibrium state and the final quasiequilibrium state. Due to the intractably large number of trajectories to be considered, the first two of these new expressions would be very difficult to use on a more realistic examples of a glass. The third result can be restated as Eq. (35), which allows these problems to be overcome by providing the free energy of the quasiequilibrium state directly in terms of averages, without it being necessary to explicitly enumerate and characterise the domains. Combined, these results provide a concise illustration of how thermodynamics relates to glasses, polymorphs or similar arrested systems.

The approach we have described in the main text above considers ensembles of quenched states, which in general will produce a number of different ergodic domains, (e.g. glasses with different physical properties or different polymorphs of a material). The free energies calculated therefore generally refer to the free energy of this ensemble. From a practical perspective, it is often of more interest to obtain the free energy of a single ergodic state (e.g. a single glass sample). The free energy of this system would be equal to that of a quasiequilibrium state where only one of the domains is populated. We note that Eqs. (22) & (27) could not strictly be applied under these conditions, since ergodic consistency would be violated - points in the initial equilibrium state might lead to points in the final state that are not within the required domain. However, Eqs. (30) & (35) meet the required conditions, and $N_D = 1, w_1^{(2)} = 1$. Eq. (35) takes on the particularly simple form $\Delta A^\alpha_{eq} = -k_B T \ln \left[ \langle \exp(-\beta \Delta W^\alpha_{eq}(\Gamma)) \rangle^\alpha \right]$ where $\alpha$ refers to the phase space domain that characterises the sample. This approach allows the free energy of individual ergodic subdomains to be determined relative to an ergodic equilibrium state.

V. CONCLUSIONS

In this paper we have considered a number of different states:

- time dependent nonequilibrium states;
- ergodic equilibrium states where there is only one phase space domain, say domain 1, for this domain, $a_1 = 1$ and within this single domain phases are Boltzmann distributed;
- nonergodic quasiequilibrium states where the domain weights $a_\alpha$ are time independent but essentially arbitrary and the intra-domain weights are Boltzmann distributed; and finally
- constrained equilibrium states where $a_\alpha = 1, 0 \forall \alpha$, and for the occupied domains both the intra and inter domain weights are Boltzmann distributed.

We have also shown that in systems where certain phase space domains are totally unsampled in the final observed distribution of states ($a_\alpha = 0$), the Jarzynski Equality gives the free energy difference between the equilibrium states and the final constrained equilibrium state.

We have derived three variations of the Jarzynski Equality (Eqs. (22), (27) & (30)) which calculate free energy differences between the initial equilibrium state and the final quasiequilibrium state. Due to the intractably large number of domains to be considered, the first two of these new expressions would be very difficult to use on a more realistic examples of a glass. The third result can be restated as Eq. (35), which allows these problems to be overcome by providing the free energy of the quasiequilibrium state directly in terms of averages, without it being necessary to explicitly enumerate and characterise the domains. Combined, these results provide a concise illustration of how thermodynamics relates to glasses, polymorphs or similar arrested systems.

The approach we have described in the main text above considers ensembles of quenched states, which in general will produce a number of different ergodic domains, (e.g. glasses with different physical properties or different polymorphs of a material). The free energies calculated therefore generally refer to the free energy of this ensemble. From a practical perspective, it is often of more interest to obtain the free energy of a single ergodic state (e.g. a single glass sample). The free energy of this system would be equal to that of a quasiequilibrium state where only one of the domains is populated. We note that Eqs. (22) & (27) could not strictly be applied under these conditions, since ergodic consistency would be violated - points in the initial equilibrium state might lead to points in the final state that are not within the required domain. However, Eqs. (30) & (35) meet the required conditions, and $N_D = 1, w_1^{(2)} = 1$. Eq. (35) takes on the particularly simple form $\Delta A^\alpha_{eq} = -k_B T \ln \left[ \langle \exp(-\beta \Delta W^\alpha_{eq}(\Gamma)) \rangle^\alpha \right]$ where $\alpha$ refers to the phase space domain that characterises the sample. This approach allows the free energy of individual ergodic subdomains to be determined relative to an ergodic equilibrium state.
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