Master equation approach to the non-equilibrium negative specific heat at the glass transition

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Although glasses are disordered and complex systems, we show that important characteristics of the glass transition, such as a negative measured specific heat in the transition region, can be understood using a simple model of thermally activated hopping in a two-level system. The dynamics of the heating of a nonequilibrium state is modeled by a master equation. The calculation illustrates the connection between equilibrium and nonequilibrium, in particular, the determination of transition rates using the principle of detailed balance. © 2005 American Association of Physics Teachers. [DOI: 10.1119/1.1891173]

I. INTRODUCTION

The dynamics of systems far from equilibrium is important in many situations in physics, chemistry, and biology. Some systems, such as glasses, exist indefinitely in a nonequilibrium state. Also of interest is nonequilibrium steady states, which occur when a stationary flux is driven by an external field.

The master equation is an important tool for understanding systems in nonequilibrium. Zia, Praestgaard, and Mouritsen recently provided an introduction to the master equation and remarked on the appearance of a negative specific heat in certain model systems. Their model is a three-level system that is maintained in a nonequilibrium steady state driven by two thermal baths at different temperatures. In this paper we apply the master equation to a simpler, two-level system and discuss the behavior of the dynamic heat capacity when the system is heated from a quenched state. This process occurs in real systems and is the main experimental method of probing the properties of the glass transition with differential scanning calorimetry.

A “glass” refers to systems that have some degrees of freedom which fluctuate at a rate that depends strongly on temperature and pressure, and become so slow at low temperature or high pressure that the fluctuations become frozen during ordinary time scales. Upon cooling, many viscous liquids become solid-like, but neither crystallization nor long range ordering occurs. This liquid to solid transformation goes through a glass transition region where the liquid changes its properties to an out-of-equilibrium solid-like state. The glass transition is common in quite different and important classes of materials (for example, polymers, oxides, chalcogenides, metals, and molecular solids), and continues to attract much attention from a fundamental and a practical point of view.

A useful way to think about the glass transition is based on the energy landscape of the liquid. In a viscous liquid the atomic mobility is sufficiently high so that the system is able to sample different configurations of the energy landscape. The structure rearranges rapidly in response to changes of temperature and pressure. However, when the temperature is sufficiently low, atomic reorganization becomes too slow and near the glass transition temperature, $T_g$, the system is trapped in a local free energy minimum characterized by an energy greater than the equilibrium crystalline state. Below the glass transition structural rearrangements are kinetically arrested, and the response of the system to changes in temperature does not contain contributions from all of the configurational degrees of freedom. In short, a glass is a liquid that has lost its ability to flow.

A negative heat capacity is common in a calorimetric heating scan through the glass transition. While changing the temperature of the sample through the glass transition, the heat capacity shows a step change from $C_{\text{glass}}$ to that of the liquid, $C_{\text{liquid}}$, which is larger than $C_{\text{glass}}$ due to the release of the frozen configurations. That is, as the system is heated, the heat capacity usually first decreases and then increases with a pronounced spike before reaching its equilibrium value of $C_{\text{liquid}}$. The experimental behavior of $B_2O_3$ (a key ingredient of Pyrex) is shown in Fig. 1(b), and the negative feature is clearly observed at the faster cooling rate (bottom curve), which induces the largest nonequilibrium behavior in the glass. In Fig. 1 the heat capacity data are normalized so that the heat capacity is the temperature derivative of the fccive temperature (discussed in Sec. IV), and the change of $C_{\text{glass}}$ to $C_{\text{liquid}}$ is scaled to be from 0 to 1. The unnormalized data for the same material are reported in Ref. 10. This negative feature has been discussed recently.

The heat capacity is related to the mean square fluctuation of the energy and is necessarily a positive quantity. However, we are concerned here with differential scanning calorimetry measurements (sometimes termed the dynamic specific heat), which is given by $C = (dE/dt)/(dT/dt)$. In this case the temperature changes at a finite rate and the system may or may not be in equilibrium. Odagaki et al. defined the heat capacity as the ratio of the increase of the energy to the temperature jump when the jump is infinitesimal. This heat capacity depends on the observation time in nonequilibrium systems. For such systems it is necessary to consider the time scale of the measurement, because the system has uncompensated fluxes that induce changes of the macroscopic variables with time, in contrast to systems in thermodynamic equilibrium. The existence of a negative heat capacitance might seem surprising, but the behavior of nonequilibrium systems can be counterintuitive from the point of view of equilibrium thermodynamics where the internal fluxes are strictly compensated.

A system is characterized by its density of states and the occupancies of the states determine a configuration that occurs with a certain probability. The master equation describes the evolution of the system by giving the rate of change of the configuration probabilities in terms of the rates of transi-
characteristics of glass relaxation that can be understood with this simple model, such as aging and the use of the fictive temperature to describe nonequilibrium states.

II. TWO-LEVEL SYSTEM EQUILIBRIUM PROPERTIES

In a two-level system, particles exhibit thermally activated transitions between two states separated by an energy barrier (see Fig. 2). In equilibrium the forward and backward transitions occur at the same rate. However, at low temperatures the time scale of the transition rates becomes longer than the cooling rate, and the transitions become rare, so that the system falls out of equilibrium. This picture reproduces the basic features of the kinetic arrest that occurs at the glass transition by the slowing down of relaxation modes involving diffusive motion and structural rearrangements. A two-level system has been applied to the residual energy of glasses after being slowly cooled to $T = 0$ K, and is the basis for more complex and realistic models that consider cooperative phenomena or intrabasin relaxation. In addition, two-level systems have been used to describe differential scanning calorimetry results for biological processes such as the unfolding of proteins.

In the two-level model sketched in Fig. 2, the bottoms of the potential wells differ by the energy $E_{1} - E_{0} = e$, and the height of the barrier between the two minima is $\Delta_{0} = E_{s} - E_{0}$ from configuration 0 and $\Delta_{1} = E_{s} - E_{1}$ from configuration 1, where $E_{s}$ is the energy at the top of the barrier (saddle point) and $e = \Delta_{0} - \Delta_{1}$. The two configurations are occupied with probabilities $f_{0}$ and $f_{1}$ with $f_{0} + f_{1} = 1$. We set the origin of energy at the bottom of the lowest state, so that the Boltzmann factors at temperature $T$ are $1$ and $e^{-e/k_{B}T}$, where $k_{B}$ is Boltzmann’s constant. The equilibrium distribution shown in Fig. 3(a) is

\begin{equation}
 f_{0e} = \frac{1}{1 + e^{-e/k_{B}T}},
 \end{equation}

\begin{equation}
 f_{1e} = \frac{1}{1 + e^{e/k_{B}T}}.
 \end{equation}

The energy of the system,

\begin{equation}
 \langle E(T) \rangle = f_{1}e,
 \end{equation}

is shown in Fig. 3(b) as a function of temperature. The equilibrium heat capacity $C = d\langle E \rangle/dT = e df_{1e}/dT$ is
III. THE MASTER EQUATION AND TRANSITION RATES

The master equation can be stated in terms of the loss-gain of the probabilities of the separate states in the system. These states are the result of a coarse graining procedure, and thus each state involves an average over a large number of microscopic degrees of freedom.\(^{35}\) Because it is not usually possible to determine the transition rates from basic principles, they are stated with the aid of the principle of detailed balance. Detailed balance implies that the distribution of probabilities governed by the master equation must reduce to the equilibrium distribution in an unbiased steady state. Detailed balance also requires that the frequencies of the forward and backward transitions between a pair of states be equal in equilibrium. This requirement implies that the ratio of probabilities for a transition and its reverse is given by the Boltzmann factor of the energy difference.\(^{28}\) It is commonly assumed that the same rates can be used for the dynamics of local transitions in nonequilibrium situations.

The master equation gives the rate of variation of \(f_j\) in terms of the frequencies at which particles enter and leave a state:\(^{27,22}\)

\[
\frac{df_j}{dt} = w_0 f_0 - w_{10} f_j. \tag{5}
\]

There is a similar equation for \(f_0\) which changes as \(df_0/dt = -df_1/dt\). The quantity \(w_{ij}\) is the probability of a transition per unit time from state \(i\) to state \(j\) (the transition rate). To determine the form of the transition probabilities \(w_{ij}\), we note that the stationary solution of Eq. (5) must correspond to the equilibrium distribution, which implies that \(w_{ij}\) must satisfy

\[
\frac{w_{01}}{w_{10}} = \frac{f_1 e}{f_0 e} = e^{-\varepsilon/k_B T}. \tag{6}
\]

Equation (6) is the detailed balance condition. Only the ratio of the transition probabilities \(w_{ij}\) is specified, so there is considerable freedom to choose their form for a particular system.

In the simplest approach the transition rates are assumed to take the form \(w_{ij} = v_0 \phi(E_i, E_j)\), where \(v_0\) is a frequency that gives the time scale of the transitions and \(\phi\) is a function of the energies that satisfies

\[
\phi(E_i, E_j) = e^{-(E_j - E_i)/k_B T}. \tag{7}
\]

so that detailed balance is obeyed. We will use the Arrhenius form of the rates, in which the probability of a transition is determined by the height of the barrier. This form is widely used for chemical reactions\(^{29}\) and ion hopping in solids,\(^{30}\) and can be justified from transition state theory, which asserts that the probability of a transition is proportional to the concentration of the “activated complex” at the saddle point of the potential surface. Therefore

\[
\phi(E_i, E_j) = e^{-(E_j - E_i)/k_B T}. \tag{8}
\]

For the system of Fig. 2 we obtain

\[
w_{01} = v_0 e^{-\Delta_0/k_B T}, \quad w_{10} = v_0 e^{-\Delta_1/k_B T}. \tag{9}
\]

It is interesting to consider other forms of the transition rates. For example, the Miller-Abrahams rate\(^{31}\) is applicable to electron tunneling between defects in solids, and has the same form as the standard Metropolis rate\(^{32}\) often used in Monte Carlo simulations. A similar approach forms the basis for the Shockley-Read-Hall model\(^{33}\) of the recombination at defects in semiconductors. These transition probabilities are given by \(\phi(E_i, E_j) = 1\) if \(E_j < E_i\), else \(e^{-(E_j - E_i)/2k_B T}\), so that downward transitions occur with probability one. This rate is asymmetric. In other forms, the rate is symmetric, and the energy barrier for jumping is raised or lowered by half the energy change on hopping,

\[
\phi(E_i, E_j) = e^{-(E_j - E_i)/2k_B T}. \tag{10}
\]

Equation (10) is characteristic of hopping events that depend on thermal fluctuations of the environment of the particle, as in polaronic diffusion.\(^{34}\)
Note that both transition rates in Eq. (9) decrease for decreasing temperature, as shown in Fig. 3(d), which is an important requirement for the glass transition, because structural fluctuations become frozen at low temperatures. In contrast, Eq. (10) does not fulfill this requirement, because if one of the rates decreases at lower temperature, the other increases. For the Miller-Abrahams rate, the downward process is temperature independent.

IV. RELAXATION AND AGING

Equation (1) can be written as a function of \( f_1 \) as

\[
\frac{df_1}{dt} = -(w_{01} + w_{10})f_1 + w_{01}. \tag{11}
\]

Equations (9) and (11) constitute a complete kinetic model for the two-level system. The effect of the thermal bath enters the model through the transition probabilities. To describe a particular nonequilibrium process, it is necessary to determine an initial condition and the external perturbations on the system. If the system starts from a nonequilibrium configuration and is not perturbed, it will tend irreversibly to equilibrium. It is convenient to write Eq. (6) as

\[
f_{1,e} = \frac{w_{01}}{w_{01} + w_{10}}. \tag{12}
\]

Hence we may express Eq. (11) in the form

\[
\frac{df_1}{dt} = -(w_{01} + w_{10})(f_1 - f_{1,e}). \tag{13}
\]

The use of the equilibrium occupancy, \( f_{1,e}(T) \), in Eq. (13), which is applied far from equilibrium, is purely formal. The alternative formulation of Eq. (1) in Eq. (13) shows that the rate of relaxation of \( f_1 \) is proportional to the extent of the departure from equilibrium, \( f_1 - f_{1,e} \).

The transition rates \( w_{ij} \) are defined only as a function of the instantaneous temperature. Hence Eq. (12) lets us express \( f_{1,e}(T) \) as a function of \( w_{ij}(T) \). It is important to recognize that the transition probabilities assume quasi-equilibrium, that is, their form is not affected by the system being out of equilibrium. One goal of recent research is to determine more general criteria that will specify the transition rates far from equilibrium.\[35\]

From Eq. (13) it follows that if the system is kept at constant temperature, \( f_1 \) will decay to its equilibrium value exponentially with time, with the relaxation time\[22\]

\[
\tau = \frac{1}{w_{01} + w_{10}}. \tag{14}
\]

How can we prepare a nonequilibrium initial state? We have already mentioned that a main characteristic of glasses is that they are out of equilibrium and are obtained by cooling the viscous melt rapidly. Consider the two-level system whose equilibrium properties are shown in Fig. 3. The system is quenched rapidly from the initial temperature \( T_a \) to the final temperature \( T_g \), which must be chosen so that \( \tau(T_b) \) is larger than available observation times. That is, if we cool the system from \( T_a \) at a rate \( dT/dt = -b \) to temperatures below \( T_g \), the remaining time of cooling will be much less than the time to overcome the barrier, \( b^{-1}T_b \ll \tau \). As a result, the equilibrium distribution corresponding to \( T_g \) is “frozen” on experimentally accessible time scales, and the system is in nonequilibrium in which the occupation of the higher level is significantly enhanced. The two-level system becomes a glass.

At the glass transition temperature, \( T_g \), the system departs from equilibrium during cooling. The glass transition is not a thermodynamic phase transition that is sharply defined at a certain temperature. The transition from solid to liquid occurs over a range of temperatures, and this range depends on the time of observation. One definition of \( T_g \) is when the viscosity (and hence the relaxation time) exceeds a certain value,\[10^{12}\] Pa s, but this definition is not convenient for all glass materials. Due to the simplicity of detection of the glass transition by calorimetry techniques, a generally accepted criterion for determining \( T_g \) is that it is the temperature at which the specific heat takes on its average value between \( C_{\text{glass}} \) and \( C_{\text{liquid}} \).

By quenching, the system at 50 K, say, may be in the configuration that it would have had in equilibrium at 150 K. This remark suggests a useful way of describing the nonequilibrium state of the system, which is given by the fictive temperature,\[37\] \( T_f \), defined as the temperature at which the nonequilibrium value of a property would be the equilibrium one, that is,

\[
f_{1,e}(T_f) = f_1(T). \tag{15}
\]

Because a two-level system has a single degree of freedom, the fictive temperature uniquely characterizes any nonequilibrium state.\[22\] In real glasses, all nonequilibrium states need not coincide with an equilibrium state,\[37\] but nonetheless \( T_f \) is widely used as a measure of the departure of the macroscopic properties from equilibrium.\[19,38,39\]

At temperatures that are not too much below \( T_g \), the relaxation time \( \tau(T) \) is not too long, and the glass with \( T_f > T \) will relax to equilibrium \( T_f = T \). This change in a glass by slow relaxation below \( T_g \) is known as aging.

V. NONEQUILIBRIUM DYNAMICS AND NEGATIVE HEAT CAPACITY

Another important class of nonequilibrium processes consists of externally driving a system either in steady-state or in time-varying situations. Reference 2 discusses an example where heat flow is maintained by having two transition rates coupled to different baths. The model of Fröhlich for ion hopping in solids adapts the Debyelike model for dipole relaxation to hopping between localized states.\[30\] In this case the external force is an electrical field that modifies asymmetrically the energies of the two-level system, and consequently the height of the barrier seen from each state, so that the transition rates of Eq. (9) depend on the electric field.\[30\]

We apply to the two-level system the usual scanning calorimetry method, that is, we increase the temperature of the quenched system and measure the heat release. The increase of temperature affects the transition rates, producing changes in occupation and energy, which can be calculated by integration of the master equation.

Our starting point is a two-level system with the fictive temperature \( T_f = 130 \) K obtained by quenching the system from a high temperature to a low temperature \( T_g \). If we apply a constant heating rate \( b = dT/dt \), the evolution of the concentration as a function of temperature is determined from Eq. (13):
Fig. 4. (a) Energy of the two-level system versus temperature at two heating rates, starting from a quenched state with a fictive temperature of 130 K. The numbered arrows indicate the stages of evolution of energy as discussed in the text. (b) Heat capacity versus ambient temperature for the two-level system at two heating rates. The curves indicate the equilibrium quantities of Fig. 3.

\[ \frac{df_1}{dT} = -\frac{1}{b \tau(T)} (f_1 - f_{1e}) \tag{16} \]

Note that we have removed the time dependence in Eq. (16), because the differential scanning calorimetry results are reported as a function of temperature. The experimental time scale is described in Eq. (16) through the parameter \( b \). Equation (16) can be readily integrated numerically. The results are shown in Fig. 4 at two different heating rates to illustrate that the kinetic behavior of a glass depends strongly on the observation time scale. The total energy \( \varepsilon f_1 \) and the heat capacity that is obtained by multiplying Eq. (16) by \( \varepsilon \) are shown.

When the system is heated according to \( T(t) = T_e + bt \), at some time the temperature-dependent relaxation time \( \tau(T) \) becomes smaller than the accessible observation time, but \( T(t) \) is still below \( T_g \). Hence, the system begins to relax by depopulating the higher energy level, and we observe that \( \langle E(t) \rangle \) decreases, at least over some time interval, giving rise to the negative heat capacity in Fig. 4(b). The reason is that the two-level system glass at 100 K, with \( T_g = 130 \text{ K} \), has a higher concentration in the upper state than it should at equilibrium. Thus, once the heat bath activates the transitions, the dominant transitions are from the high to low energy state \((1\rightarrow0)\), with the consequent decrease of energy despite the increase of temperature. Eventually, \( \langle E(t) \rangle \) begins to increase again when \( T(t) \) becomes sufficiently high.

Another way to look at this is to observe in Fig. 4(a) that while the temperature increases the energy relaxes to the equilibrium curve. We discuss this dependence with reference to the circled numbers in Fig. 4(a). In the first stage \( \{1\} \) there is no change of energy at all because the transition rates are very small at these low temperatures. Then \( \{2\} \) as mentioned before the energy decreases, and it does so following the shortest path to the equilibrium curve in a relaxation process. Note that this feature is much stronger for the slow heating rate, in which the system has longer time to relax to equilibrium while its temperature increases. The intersection with the equilibrium curve \( \{3\} \) is at zero slope according to Eq. (16), and this intersection is the point where the heat capacity becomes positive. When at \( \{3\} \) the energy surpasses the equilibrium curve it bends rapidly \( \{4\} \) toward the equilibrium line, producing the positive spike of the heat capacity. Thereafter \( \{5\} \) the energy values begin to converge to the equilibrium curve. At high temperature \( \{6\} \) the relaxation rate becomes comparable to or faster than the heating rate, and \( \langle E(t) \rangle \) follows the "equilibrium" energy corresponding to the temperature \( T(t) \).

Differential scanning calorimetry curves qualitatively similar to those in Fig. 4(b) are widely observed experimentally. As remarked, the measured heat capacitance shows the transition between the equilibrium values \( C_{\text{glass}} \), to that of the liquid, \( C_{\text{liquid}} \). Both these specific heats are equilibrium thermodynamic quantities, as \( C_{\text{glass}} \) is well defined as an ordinary specific heat. (Glasses and crystalline forms of the same substance have essentially the same heat capacity, which in each case is vibrational in origin.) As we have discussed, the measured \( C \) in the transition region is not the equilibrium specific heat. The transition region contains important information on kinetic quantities, such as the activation energy of the internal transitions that govern the transformation from solid to liquid. These kinetic parameters can be extracted from differential scanning calorimetry results with the aid of phenomenological models.

Finally, we express the results in terms of the fictive temperature. According to Eq. (15) we have

\[ f_1 = \frac{1}{1 + e^{\varepsilon/k_B T_f}} \tag{17} \]

If we take the derivative of Eq. (17) with respect to the temperature, we obtain

\[ \frac{dT_f}{dT} = \frac{\varepsilon}{C(T_f)} \frac{df_1}{dT} \tag{18} \]

where \( C \) is defined in Eq. (4). The low and high temperature limits of Eq. (18) can be inferred readily: \( dT_f/dT \) varies from 0 to 1, because in the glass \( T_f \) is constant, while in equilibrium \( T_f = T \). Hence \( dT_f/dT \) is an alternative expression for the heat capacity that removes the equilibrium dependence on temperature and highlights the features of the transition region from glass to viscous liquid.

Our results for the two heating rates of the two-level system are plotted in terms of \( T_f \) in Fig. 5. By comparing Figs. 5 and 1 (which was reported in terms of \( T_f \)), it is seen that the simple two-level model glass displays semi-quantitatively the physical features of real glasses.

Real glasses are not completely described by an ensemble of independent two-level systems. The coupling of the different relaxing units gives rise to nonlinear and nonexponential relaxation that are universally observed in glassy systems. For example, we have remarked that in our model \( T_f \) first decreases because \( T_f \) changes toward equilibrium and then intersects the equilibrium curve at zero temperature gradient [see Fig. 5(a)]. In contrast, in real glasses the evolution...
of $T_f$ during heating “neglects the equilibrium curve,” as remarked in Ref. 38; that is, it first decreases, but then bends upward before arriving at the equilibrium curve so that the intersection shows a positive slope [see, for example, Fig. 1(a)]. This behavior is a manifestation of the memory effect, which is ubiquitous in glasses and whose description requires at least a distribution of relaxation times in the internal relaxing units.\textsuperscript{41} Due to this memory effect, the negative heat capacity feature is less marked in experiments than in the two-level model, for which the positive overshoot is larger.

It is difficult to account for the various and common features of glass relaxation in terms of microscopic models, given the wide variety of structural and chemical characteristics of the materials in which they are observed. This subject is of current research interest.\textsuperscript{6,9} An extension of the two-level system including cooperative relaxation effects which makes the model much closer to the properties of real glasses is given in Ref. 22.

VI. SUMMARY

Although glasses are highly disordered and complex systems where strong dynamic changes take place as the temperature is varied, a simple two-level model displays important experimental characteristics of the glass transition. The internal dynamics of the system is regulated by the transition rates, which depend on the temperature of the thermal bath. When the system starts at a long-lived nonequilibrium state at low temperature, it can lose energy while it is “heated.” The dynamic behavior depends on the interplay between the system’s relaxation time and the experimental time scale of observation. Our simple analysis shows that the master equation is an important tool for describing physical systems that depart strongly from thermodynamic equilibrium.

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\textsuperscript{11}S. A. Brawer, \textit{Relaxation in Viscous Liquids and Glasses} (American Ceramic Society, Columbus, OH, 1985).

![Graph](image-url)
Torsional Oscillator. This torsional oscillator, at the University of Texas in Austin, is one of the few pieces of physics apparatus that I have seen from the firm of Gurley of Troy, New York, best known for surveying instruments. The vertical shaft is pivoted, and the masses on the sliding cross-rod can be slid in and out to vary the moment of inertia of the oscillating system. The spiral spring provides both a zero point, and a linear restoring torque in both angular directions. The torsion constant of the spring is determined by hanging various masses on one end of the string; the other end is wrapped around a pulley of known radius. The period of the system can be measured as a function of the moment of inertia: the square of the period if proportional to the moment of inertia. (Photograph and Notes by Thomas B. Greenslade, Jr., Kenyon College)