Influence of the Potential Energy Landscape on the Equilibration and Specific Heat of Glass Forming Liquids

Clare C. Yu and Hervé M. Carruzzo

Department of Physics and Astronomy, University of California, Irvine, Irvine, California 92697

(Dated: January 11, 2022)

We show that a glass transition, signaled by a peak in the specific heat vs. temperature, can occur because a glassy system that shows no signs of aging progresses so slowly through the energy landscape that the time needed to obtain an accurate estimate of the thermodynamic averages exceeds the observation time. We find that below the glass transition temperature of a three dimensional binary mixture of soft spheres, the specific heat increases with measurement time spans orders of magnitude longer than previously recognized equilibration times.

As a glass forming liquid is cooled or compressed, a glass transition occurs when the system falls out of equilibrium, i.e., when the time scale for reaching equilibrium exceeds the observation time. Like many complex systems, such as proteins and neural networks, the dynamics of such a system is strongly influenced by the potential energy landscape where each point corresponds to a particular configuration and energy of the system. The energy landscape can be used to describe the three ways in which a system can fall out of equilibrium. First a system can become trapped in a metastable minimum where it stays for the duration of the observation time. Second a system can be in an energetically unlikely part of phase space and proceed slowly to a region of the energy landscape where its configurations obey a Boltzmann distribution. As such a nonequilibrium system evolves toward more probable regions of phase space, it exhibits aging which means its properties systematically change with time and do not obey stationarity. The aging time, after which aging stops, is equal to the α relaxation time which is the characteristic time for the system to forget its initial configuration.

The third way is not widely appreciated and is the subject of this paper. Namely, even after a glassy system no longer ages and has reached basins with appropriate energies, the system proceeds so slowly through the energy landscape that it takes a long time to accumulate the large number of statistically independent measurements needed to accurately determine a thermodynamic average. We find from molecular dynamics simulations that a glass forming liquid can undergo a glass transition, as signaled by a peak in the specific heat $C_V$ versus temperature, that is due to insufficient averaging by a system that shows no signs of aging. The distribution of energies that a system samples in a basin of the energy landscape is a subset of the full distribution of energies available to the system. Since this subset has a smaller variance than the full distribution, the resulting specific heat, which is proportional to the variance of the energy, will be smaller when calculated from short time spans than from long time spans. These smaller values account for the values below the peak in $C_V$ on the low temperature side. Going to longer time spans eliminates the peak, though at temperatures below the peak temperature $T_p$, these longer time spans can be orders of magnitude longer than previously recognized equilibration times.

We have performed a molecular dynamics simulation on a three dimensional glass forming liquid consisting of a 50:50 mixture of two types of soft spheres, labelled A and B, which differ only in their sizes. The interaction between two particles a distance $r$ apart is given by $V_{\alpha\beta}(r) = \epsilon\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} + X_{\alpha\beta}(r)\right]$ where the interaction length $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$, and the ratio of the ratio of the diameters $\sigma_B/\sigma_A = 1.4$ (α, β = A, B). The cutoff function $X_{\alpha\beta}(r) = r/\sigma_{\alpha\beta} - \lambda$ with $\lambda = 13/12^{13}$. The interaction is cutoff at the minimum of the potential $V_{\alpha\beta}(r)$.

Energy and length are measured in units of $\epsilon$ and $\sigma_A$, respectively. Temperature is in units of $\epsilon/k_B$, and time is in units of $\sigma_A\sqrt{m/\epsilon}$ where $m$, the mass of the particles, is set to unity. The equations of motion were integrated using the leapfrog method with a time step of 0.005. During each run the density $\rho_0 = N/L^3$ was kept constant. $N = N_A + N_B$ is the total number of particles. The system occupies a cube with volume $L^3$ and periodic boundary conditions. According to the ideal mode coupling theory, the relaxation time diverges at a temperature $T_C$. For our system $T_C = 0.3033$.

We cool the system from a high temperature ($T=1.5$) by lowering the temperature in steps of $\Delta T = 0.05$. At each temperature we equilibrate for $10^4$ time steps and then measure the quantities of interest for $10^4$ additional steps. The results are then averaged over different runs. At the glass transition the system falls out of equilibrium and becomes trapped in a basin of the energy landscape. In order to avoid this, we have used parallel tempering together with molecular dynamics. We implement parallel tempering (PT) by running molecular dynamics simulations in parallel at chosen temperatures using a temperature constraint algorithm to keep the temperature of each simulation constant. At 100 time step intervals we attempt to switch the configurations of two neighboring temperatures using a Metropolis test which
ensures that the energies of the configurations sampled at any given temperature have a Boltzmann distribution. Let $\beta_1$ and $\beta_2$ be two neighboring inverse temperatures, and let $U_1$ and $U_2$ be the corresponding potential energies of the configurations at these temperatures. If $\Delta = (\beta_1 - \beta_2)(U_2 - U_1)$, then the switch is accepted with probability unity if $\Delta \leq \exp(-\Delta)$ if $\Delta > 0$. The acceptance ratio is between 30% and 75%. Near $T_p$, the acceptance ratio was above 60%. After a swap is accepted, the velocities of the particles in each configuration are rescaled to suit their new temperature. Switching configurations allows a given simulation to do a random walk in temperature space in which it visits both low temperatures and high temperatures. This helps to prevent it from becoming trapped in a valley of the energy landscape at low temperatures. Typically we equilibrate for 2 million time steps and then do measurements for an additional 4 to 10 million molecular dynamics (md) steps. We average over different runs which have different initial positions and velocities of the particles at each temperature.

We calculate the specific heat $C_V$ per particle at constant volume in two ways. The first uses the fluctuations in the potential energy $U$ per particle: $C_V = (3k_B/2) + Nk_B\beta^2 (\langle U^2 \rangle - \langle U \rangle^2)$ where the first term is the kinetic energy. The second way uses $C_V = d < U > /dT \approx (\langle U(T_{i+1}) \rangle - \langle U(T_i) \rangle)/T_{i+1} - T_i$. The results are shown in Figure 1. Notice that there is a sharp asymmetric peak centered at $T_p = 0.305 \pm 0.003$. The low temperature side of the peak drops steeply. The curves for 216 and 512 particles coincide, indicating that there is no size dependence. The discrete points are calculated from the energy fluctuations. The solid line is calculated from the derivative of the energy. The fact that the two coincide indicates that the system was equilibrated in all the basins of the energy landscape that were visited. For comparison we also show the result of cooling through the transition ($\phi$). The peak in $C_V$ found by cooling coincides with the peak found in parallel tempering.

We do not believe that the parallel tempering peak in the specific heat is due to the system becoming trapped in a metastable minimum in the energy landscape for the following reason. The configurations corresponding to the bottom of the basins of the energy landscape are called inherent structures [1]. We sampled the configurations that were visited during the parallel tempering runs and found the corresponding inherent structure energy $\langle e_{1S} \rangle$ per particle by minimizing the potential energy locally using the method of conjugate gradients [2]. In the inset of Figure 1 we plot the average inherent structure energies versus the temperature of the configuration that was originally saved. As the temperature decreases below 0.5, $\langle e_{1S} \rangle$ decreases rather steeply [3]. The temperature of the inflection point of this decrease coincides with the temperature $T_p$ of the peak in the specific heat. We also show $\langle e_{1S} \rangle$ for a system of 512 particles that was cooled from $T = 1.5$. At low temperatures $\langle e_{1S} \rangle$ is rather independent of temperature for the cooled system, indicating that the system is trapped in an energy basin. Such a flattening off at low temperatures is not observed when parallel tempering is used, indicating that the system is able to visit deeper energy basins as the temperature decreases.

However, this does not mean that the peak in the specific heat is an equilibrium feature. We will now show that the peak is the result of not sampling enough of phase space below $T_p$. None of the runs we have done at $T < T_p$ have reached the time which is necessary in order to achieve an accurate thermodynamic average. To show this, we took a configuration of 512 particles generated by parallel tempering at $T = 0.289855$, equilibrated for $5 \times 10^7$ time steps, and then ran for an additional $10^8$ time steps during which we recorded the energy at every time step. Then we did block averaging in which we divided
our 100 million time steps into equal segments, each of length $\Delta t_b$, and calculated the specific heat from energy fluctuations for each segment $[13]$. The block averaged specific heat versus time for 2 different time spans $\Delta t_b$ is shown in the inset of Figure 2. Notice that for any given time span, there is no sign of systematic aging. However, the specific heat averaged over time increases with $\Delta t_b$.

The specific heat, averaged over time spans of a given size and over different runs, versus time span size $\Delta t_b$ at several temperatures is shown in Figure 2 by the solid lines. To obtain time spans that are longer than any given run, we concatenated the energies from the runs done at a given temperature to make one huge run, and then did block averaging on the huge run. The results are shown as open symbols in Figure 2. There is good agreement between the solid lines and symbols. Notice that the specific heat initially increases with time span but then levels off when the time span is long enough to exceed the time needed to achieve the thermodynamic value of the specific heat. This time increases with decreasing temperature. Thus at $T = 0.289855 < T_p$, the specific heat continues to increase with time span up to $\Delta t_b = 10^8$ time steps which is 100 times longer than the $\alpha$ relaxation time $\tau$. Equilibrated values of $C_V$ near $T_p$ are plotted in Figure 2 and lie above the peak in $C_V$ found with parallel tempering. Thus the specific heat peak found with parallel tempering is the result of not sampling enough of phase space at $T < T_p$ to obtain the true thermodynamic value of the specific heat $C_V^{true}$. The exploration of the energy distribution below $T_p$ is slow even with parallel tempering because the probability of sampling large increases in $U$ are exponentially small.

Note that $C_V^{true}$ is proportional to the variance $\sigma_U^2$ of the distribution $P(U)$, i.e., $C_V^{true} = N\sigma_U^2/(k_BT^2)$. If $\sigma_U^2$ is finite and if $n$ sample values of $U$ are statistically independent and identically distributed, then basic statistics dictates that the measured $C_V$, which is proportional to the sample variance $S_n^2$ of $U$, has an expectation value of $\langle C_V \rangle = C_V^{true}(1 - 1/n)$ $[13]$. Since the potential energies in a time series can be correlated, the number $n$ of statistically independent energies is given by $n = \Delta t_b/\tau_U$ where $\tau_U$ is the energy correlation time. Fitting the data that is within 5 to 10% of $C_V^{true}$ in Figure 2 to $\langle C_V \rangle = C_V^{true}(1 - 1/n)$ yields $\tau_U \approx 3 \times 10^6$, $1 \times 10^6$, and $5 \times 10^3$ time steps at $T = 0.2898551$, 0.308642, and 0.342466, respectively. These values are comparable to the $\alpha$ relaxation times $\tau$ of $1 \times 10^6$, $6 \times 10^4$, and $2 \times 10^4$ time steps, respectively (see below). They imply that the energies are correlated and that $n$ is substantially smaller than the total number of energies.

Note that at shorter time spans and lower temperatures Figure 2 shows that $C_V \sim \ln(\Delta t_b)$. This occurs because the system does not uniformly sample $P(U)$ during these shorter time spans. As the system travels through the energy landscape, it samples the energies of each basin that it visits. As shown in Figure 2, we find that the distribution of energies sampled from the basins visited during a shorter time span has a smaller variance than the total distribution $P(U)$. Furthermore, the centers of the smaller distributions do not necessarily coincide with the center of the total distribution. Rather the smaller distributions are centered at the inherent structure energy plus the energy of vibrations around $e_{IS}[4]$. In support of this, we show in the inset of Figure 2 that the block averaged energy versus time approximately coincides with $(e_{IS}(t) + 3k_BT/2)$ vs. time. As more basins are visited, the sample average $\langle U \rangle$ moves towards the average of the full distribution and the variance grows. This corresponds to $C_V$ increasing with time span.

We now cite evidence that systems at temperatures just below $T_p$ have equilibrated in the sense of showing no signs of aging. First the inset of Fig. 2 shows the lack of aging in the specific heat versus time for a given value of $\Delta t_b$. Second is the absence of aging in the $\alpha$ relaxation time $\tau$. We have calculated $\tau$ using the full intermediate scattering function $F_B(k,t) = (1/N_B)(\rho\rho_0(t)\rho_0(0))$ for the B particles where $N_B$ is the number of B particles and $\rho\rho_0(t) = \sum_{i=1}^{N_B} \exp(-ik\cdot\vec{r}_i(t))$. We choose $k = k_{max}$, the wavevector of the maximum in the partial static structure factor $S_{BB}(k)$ for the B particles, because $F_B(k,t)$ relaxes slowest at $k_{max}[15]$. The relaxation time $\tau$ is defined by $F(k,\tau)/F(k,t = 0) = 1/e$. We have averaged

![Figure 2: Block averaged specific heat versus time span $\Delta t_b$ for 512 particles at $T = 0.289855$, 0.308642, and 0.3424658. Solid lines are the result of block averaging each run and then averaging over the number of runs shown. Open symbols are the result of stringing runs together and then block averaging. Inset: Block averaged specific heat versus time for 512 particles at $T = 0.289855$. The lower curve corresponds to $\Delta t_b = 10^6$ md steps, and the upper to $\Delta t_b = 4 \times 10^6$ md steps. The time is the time (in md steps) in the middle of each block. The data at $T = 0.289855$ is averaged over 23 runs. Parameters for both figures are the same as in Figure 1.](image-url)
The lack of aging is to be expected since the aging time is the same as the equilibrium value. The aging time is equal to $\tau$ which is much less than $t_W$. We have confirmed that the aging time is the same as the equilibrium value of $\tau$ by starting from 11 different equilibrium configurations at $T = 1.5$, quenching to $T = 0.289855$, and measuring $\tau$ after waiting times of $t_W = 0$, $5 \times 10^4$, $5 \times 10^5$, $10^6$, $5 \times 10^6$, and $2.5 \times 10^7$ md steps. For $t_W < 10^6$ md steps, $\tau$ increases with $t_W$ which indicates aging. However, for $t_W \geq 10^6$ md steps, there is no aging and $\tau$ equals its equilibrium value of $10^6$ md steps.

Third we have looked for signs of aging in the inherent structure energy versus time in our single temperature molecular dynamics runs of $10^8$ time steps at $T = 0.289855 < T_p$. During the run, configurations were recorded every so often. Averaging over 40 runs, we find no evidence that the inherent structure energy decreases systematically with time, though the noise in the data prevents us from seeing changes smaller than 1%.

We have also examined the root mean square displacement \( \langle \Delta r^2(t) \rangle^{1/2} \) where \( \langle \Delta r^2(t) \rangle = \langle 1/N \sum_{i=1}^{N} (r_i(t) - r_i(0))^2 \rangle \). We found that \( \langle \Delta r^2(t) \rangle^{1/2} \gtrsim 10\sigma_A \) in each run examined after $10^8$ time steps at $T = 0.289855$. This is comparable to the box size $L = 9.48\sigma_A$ for a system of 512 particles. So the system does not appear to be getting stuck in a metastable minimum of the energy landscape.

Our work is a cautionary tale for those who perform numerical simulations on slowly relaxing systems. It indicates that to obtain accurate thermodynamic averages, one must not only check that the system shows no signs of aging, but one must also check that the quantity to be measured has sampled enough of phase space to obtain a large number of statistically independent values. This sampling time can be orders of magnitude longer than previously recognized time scales such as the aging time and the $\alpha$ relaxation time.

We thank Francesco Sciortino, Bulbul Chakraborty, Jon Wellner and Sue Coppersmith for helpful discussions. This work was supported in part by CULAR funds provided by the University of California for the conduct of discretionary research by Los Alamos National Laboratory and by DOE grant DE-FG03-00ER45843.

1Present address: Internap, Atlanta, GA 30309.

\begin{thebibliography}{99}
\bibitem{1} M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem 100, 13200 (1996), and references therein.
\bibitem{2} M. Goldstein, J. Chem. Phys. 51, 3728 (1969).
\bibitem{3} S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature 393, 554 (1998).
\bibitem{4} W. Kob and J. L. Barrat, Phys. Rev. Lett. 78, 4581 (1997); Eur. Phys. J. B 13, 319 (2000).
\bibitem{5} T. A. Weber and F. H. Stillinger, Phys. Rev. B 31, 1954 (1985).
\bibitem{6} W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994).
\bibitem{7} D. C. Rapaport, \textit{The art of molecular dynamics simulation} (Cambridge University Press, New York, 1995).
\bibitem{8} W. G"otze and L. Sj"ogren, Rep. Prog. Phys. 55, 241 (1992).
\bibitem{9} H. M. Carruzzo and C. C. Yu, to be published in Phys. Rev. E (2002).
\bibitem{10} W. Kob, C. Brangian, T. Stuhn, and R. Yamamoto, in \textit{Computer Simulation Studies in Condensed Matter Physics XIII}, edited by D. P. Landau, S. P. Lewis, and H. B. Schuttler (Springer-Verlag, Berlin, 2001), p. 153.
\bibitem{11} F. H. Stillinger and T. A. Weber, Physical Review A 25, 978 (1982); Science 225, 983 (1984).
\bibitem{12} W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, \textit{Numerical Recipes in C: The Art of Scientific Computing (2nd ed.)} (Cambridge University Press, Cambridge, UK, 1992), p. 420.
\bibitem{13} A. M. Ferrenberg, D. P. Landau, and K. Binder, J. Stat. Phys. 63, 867 (1991).
\bibitem{14} T. B. Schroder, S. Sastry, J. G. Dyre, and S. C. Glotzer, J. Chem. Phys. 112, 9834 (2000).
\bibitem{15} A. Rinaldi, F. Sciortino, and P. Tartaglia, Phys. Rev. E 63, 061210 (2001).
\end{thebibliography}