Reply to "Comment on 'Frequency dependence and equilibration of the specific heat of glass-forming liquids' "

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We reply to Flenner and Szamel's Comment on our recent paper [Phys. Rev. E **69**, 051201 (2004)]. We point out that while their method works well above the mode coupling temperature, at temperatures below the mode coupling temperature, times much longer than the α relaxation time are still needed to accurately determine the specific heat.

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In our recent paper [1] we found that the mininum sampling time needed to accurately determine the specific heat in a supercooled liquid using energy fluctuations is on the order of $10^3\alpha$ relaxation times, which is much longer than the sampling time used in most simulations. Such long times are inconvenient. In the accompanying Comment [2], Flenner and Szamel propose a way to find the equilibrium value of the specific heat in a glass forming liquid from simulations that run for 15 α relaxation times. However they only demonstrated their correction technique at temperatures above the mode coupling temperature T_C. According to the ideal mode coupling theory [3], the relaxation time obtained from a time correlation function like the intermediate scattering function diverges at T_C. However, ideal mode coupling theory is applicable only at temperatures somewhat above T_C where the system easily equilibrates. T_C is not a transition temperature, but merely a characteristic crossover temperature above which Gaussian statistics can be attained relatively quickly without an enormous number of measurements. Below T_C, much longer series of measurements are needed to achieve Gaussian statistics. Since it is below T_C where a technique is most needed that takes significantly less time than the minimum sampling time, we have tested their approach at a temperature just below T_C. We find that below T_C, times much longer than15 α relaxation times are needed to accurately determine the specific heat. We now present the details of our results.

The system, described in our paper [1], is a three-dimensional binary mixture of soft spheres with $T_C=0.303$ [4]. Defining the α relaxation time τ_α as the time when the full intermediate scattering function has decayed to $1/e$ of its initial value, we find $\tau_\alpha=(1.0\pm0.1)\times10^6$ time steps at $T=0.289\,855<T_C$ [4]. At this temperature we found that the block specific heat $C_{\Delta t_b}$ continued to increase up to a block size of $\Delta t_b=200\tau_\alpha$. This is shown by the solid circles in Fig. 1. Notice that $C_{\Delta t_b}\sim\ln(\Delta t_b)$ for $\Delta t_b<100\tau_\alpha$.

Now we apply Flenner and Szamel's approach to our data. We can calculate the integrated energy correlation time τ_U using [5,6]

$$\tau_U=\int_0^\infty dt\frac{\langle U(t)U(0)\rangle-\langle U\rangle^2}{\langle U^2\rangle-\langle U\rangle^2}, \tag{1}$$

where $U(t)$ is the potential energy per particle at time t. We find that $\tau_U=3.2\times10^6$ time steps. The number n of statistically independent measurements in a block of Δt_b measurements is given by $n=\Delta t_b/[2\tau_U/\delta t+1]$, where δt is the time interval between measurements. Assuming that there is a Gaussian distribution of n independent measurements leads to the following formula for correcting the block specific heat to find the true expectation of the specific heat C:

$$C_\infty^P=C_{\Delta t_b}\left(\frac{n}{n-1}\right), \tag{2}$$

where C_∞^P is the predicted equilibrium specific heat. The corrected specific heat C_∞^P is shown as open squares in Fig. 1. It

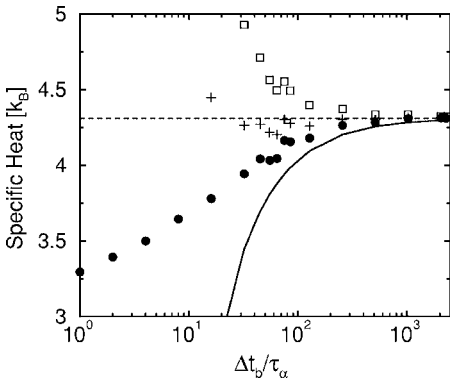

FIG. 1. Block averaged specific heat $C_{\Delta t_b}$ (•) at $T=0.289\,855<T_C$ vs rescaled block size $\Delta t_b/\tau_\alpha$ on a log-linear plot. The solid circles are from Ref. [1] and are the result of stringing 23 runs together with each run having 100 million energies. The corrected block averaged specific heat C_∞^P, shown as open squares (□), was calculated with $\tau_U=3.2\times10^6$ time steps. The predicted block average specific heat $C_{\Delta t_b}^P=C_\infty(1-1/n)$ is shown as a solid line. The dashed line shows the asymptotic value ($\Delta t_b\to\infty$) of $C_{\Delta t_b}$ which we take to be C_∞. The plus signs (+) denote the specific heat corrected using $\tau_s=1.2\times10^6$ time steps that was calculated using the statistical inefficiency.

appears that one still needs about 200 τ_α to get an accurate value of the specific heat. Inverting Eq. (2) leads to the predicted block averaged specific heat $C^P_{\Delta t_b}=C_\infty(1-1/n) \sim C_\infty(1-1/\Delta t_b)$. This is shown as a solid line in Fig. 1. Notice the large deviation of $C^P_{\Delta t_b}$ at small time spans from the observed logarithmic dependence of $C_{\Delta t_b}$, implying that the energy distribution sampled at these time spans is non-Gaussian.

Another way to find τ_U is to note that if $\tau_U \gg \delta t$, then $2\tau_U=s$ where s is the statistical inefficiency [6,7]. The statistical inefficiency is the limiting ratio of the observed variance of an average to the limit expected on the assumption of uncorrelated Gaussian statistics. As we describe in our paper [1,7],

$$s = \lim_{\Delta t_b \to \infty} \frac{\Delta t_b \sigma^2(\bar{U}_b)}{\sigma^2(U)}, \tag{3}$$

where the variance of the energies is $\sigma^2(U) =(\Delta t_{\mathrm{run}})^{-1}\Sigma_{t=1}^{\Delta t_{\mathrm{run}}}[U(t)-\bar{U}_{\mathrm{run}}]^2$, the variance of the average block energies is $\sigma^2(\bar{U}_b)=n_b^{-1}\Sigma_{b=1}^{n_b}(\bar{U}_b-\bar{U}_{\mathrm{run}})^2$, the average block energy is $\bar{U}_b=(\Delta t_b)^{-1}\Sigma_{t=1}^{\Delta t_b}U(t)$, the average run energy is $\bar{U}_{\mathrm{run}}=(\Delta t_{\mathrm{run}})^{-1}\Sigma_{t=1}^{\Delta t_{\mathrm{run}}}U(t)$, the number of blocks in a run is $n_b=\Delta t_{\mathrm{run}}/\Delta t_b$, and Δt_{run} is the time span of a run. To find s, we calculate the ratio $\Delta t_b\sigma^2(\bar{U}_b)/\sigma^2(U)$ for each run for various time spans Δt_b. Then for each time span we average the ratio over all the runs at a given temperature. By plotting the ratio vs Δt_b^{-1} on a log-log plot, we can extrapolate $(\Delta t_b)^{-1}$ to 0 to estimate s. At $T=0.289\,855$, we find $s\approx 2.4\times 10^6$, which implies $\tau_s=s/2=1.2\times 10^6$. We have used this value of τ_s to calculate n and the corrected specific heat. The result for C^P_∞ is shown as plus signs in Fig. 1. This appears to give values close to C_∞ in a shorter amount of time, though one would still need about time spans of about 75 τ_α to obtain C_∞. Using τ_s to calculate the predicted values of $C^P_{\Delta t_b}$ gives values very close to those predicted using τ_U, i.e., almost the same as those represented by the solid line in Fig. 1.

In conclusion, below the mode coupling temperature the method of Flenner and Szamel will require runs much longer than their claim of 15 α relaxation times. This required time will increase dramatically as the temperature decreases and times orders of magnitude longer than τ_α will still be required at low enough temperatures.

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