Rabani, Gezelter, and Berne Reply: In our recent Letter [1], we used the cage correlation function [2,3] to observe relaxation behavior in defective crystals. We observed a decay that was consistent with stretched-exponential function,

$$C_{\text{cage}}(t) = e^{-(\gamma t)^{\beta}} = \int_0^{\infty} dk\, \rho(k) e^{-kt}, \qquad (4)$$

with $\beta \approx 1/2$ for the three temperatures we studied. Zürcher and Keyes (ZK) [4] describe the relaxation of the cage correlation function using a choice of $\rho(k)$ equivalent to a sum of two delta functions in k (a bi-exponential model). It is evident from Fig. 1 that limiting $\rho(k)$ to their bi-exponential model provides unsatisfactory results at both short and long times. Figure 1 represents a *doubling* of the observation time compared to the original work, and therefore allows us to assess the accuracy of the two models when the correlation has decayed over nearly two full decades.

There is a simple physical explanation why the ZK hypothesis of homogeneous broadening due to phonon motion cannot be correct. Low frequency phonon motion contributes to the short-time decay of the cage correlation function, but in the system sizes that we have studied, the *lowest* frequency phonon mode is around 13 cm^{-1} which corresponds to a vibrational period of 2.6 ps. In our original paper, we had *already* corrected the cage correlation functions for the short-time decay (≈ 5 ps) due to the vibrations, and the function that was plotted is the renormalized $C_{\text{cage}}(t)$ for the period following the initial decay. ZK have chosen a decay constant of 400 ps for the decay of the cage correlation function due to a vibrational mechanism
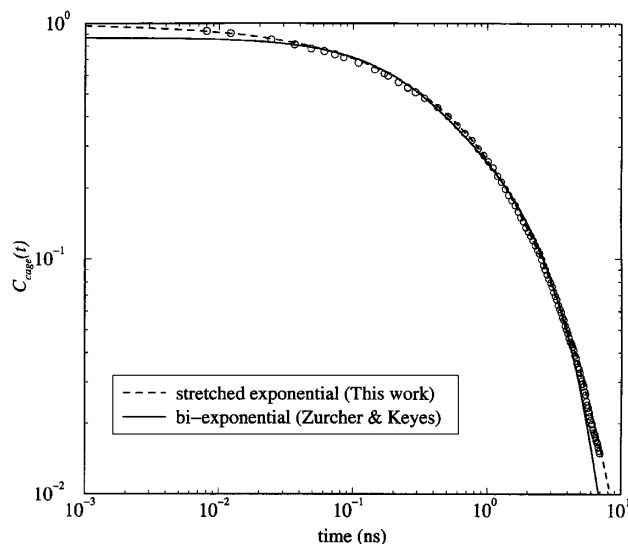

FIG. 1. A log-log plot of the decay of the cage correlation function for a near-crystalline Lennard-Jones system at $T^* = 0.5$. We show the best fits using our stretched exponential model as well as the best-fitting ZK bi-exponential model. Using the temperature-dependent τ_v from the ZK Comment [4] results in even worse agreement with the observed data.

which is more than an order of magnitude slower than the decay due to vibrations that we observed in these systems.

As an additional check on their homogeneous broadening hypothesis, we have looked at the vibrational lifetime of the low frequency modes in a *nearly identical* system (the α-fcc crystal), where the cage correlation function does not show any decay due to diffusive hopping. If the argument about condensed phase homogeneous broadening were valid, one would expect to see decay on the same time scale in the fcc crystal as they postulate in the defective crystals. However, what we observe directly contradicts the explanation given in the ZK Comment [4]: (1) The cage correlation function shows absolutely no decay in the fcc crystal after the initial 5 ps, even when observed to times greater than 100 ns. (2) The lifetime of the lowest frequency vibrational modes in the fcc crystal is found to be only 10 ps. The short lifetimes are to be expected due to the highly anharmonic potential energy surface of the Lennard-Jones system being studied and the temperature range considered. In the defective fcc crystal, one would expect the lifetime of these modes to be even shorter than in the perfect fcc crystal.

ZK's second point centers on a misinterpretation of the stretched exponential function at very short times ($t < 5$ ps). In the original paper, we *explicitly* warned against taking this function literally at short times, but this is exactly what ZK have done in their Comment [4]. It is clear that there is a sensitivity of the diffusion constant to the value of k_{max}, but this sensitivity is more adequately explained by an incomplete knowledge of the behavior of $\rho_q(\omega)$ at very low frequencies [3]. One does not need to postulate vibrational contributions to the decay to explain this sensitivity. The density of states problem is well known from a previous study on molecular liquids [3].

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