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QUENCH ECHOES IN LENNARD-JONES AND RUBIDIUM FROZEN FLUIDS--TEMPERATURE DEPENDENCE OF THE ANHARMONIC BEHAVIOR

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Abstract. - We have found a new echo phenomenon that appears in molecular dynamics simulations of a solid. The echo appears in the behavior of the temperature after the system recovers from two abrupt quenches. This effect can be explained in terms of classical normal mode analysis of the system. We have applied these echo techniques to the study of close packed glasses with Lennard-Jones and rubidium interatomic potentials. We have been able to study the degree of anharmonic behavior in the system as a function of temperature as the sample is heated from the glass to the liquid state. We have also studied this behavior when the attractive and repulsive terms in the Lennard-Jones potential are varied.

In a recent paper,¹ a new echo phenomenon was reported that can be observed in molecular dynamics simulations of amorphous and crystalline solids. The echo occurs when the temperature (which is simply proportional to the total kinetic energy of the system), is quickly lowered two times in succession with an interval, t_1 , between quenches. At a time t_1 after the second quench, if the system is allowed to run freely, the temperature suddenly drops and then rises again. In Fig. 1, we show the echo behavior of the temperature after the second quench when an interval $t_1 = 45\Delta t$ separates the two quenches. Here Δt is the time step used in the integration of Newton's equation in the molecular dynamics simulation.² Note the large dip in temperature at a time t_1 after the second quench. This quench echo can be explained in terms of classical normal mode analysis. In a completely harmonic solid each mode will vibrate independently. The decay of a mode will be caused by anharmonic interactions between the modes. The modes which have just the right frequency, $\omega = \frac{n\pi}{t_1}$ where n is an integer, will escape the second quench without losing any of their kinetic energy. All the other modes (those with the "wrong" frequency) will lose some energy during the second quench. Assuming a completely harmonic system it is possible to write down exactly the behavior of the temperature as a function of time. After the first quench each mode contributes an amount to the kinetic energy and therefore to the temperature depending on its amplitude at the time of the quench. All modes start off after the first quench with the same phase. Hence

$$T(t) = \sum_i A_i^2 \sin^2 \omega_i t \tag{1}$$

where A_i is proportional to the amplitude of mode i at $t = 0$. After a second quench the new amplitude will be $A_i \cos \omega_i t_1$ so that, measuring time from the moment of the last quench:

$$T(t) = \sum_i A_i^2 \cos^2 \omega_i t_1 \sin^2 \omega_i t \tag{2}$$

If there are many modes in the system, distributed over a smooth density of states, this

expression leads to a well-defined echo at $t = t_1$. Each additional quench will introduce another factor $\cos^2 \omega_i t_2$ where t_2 is the interval between the last two quenches

$$T(t) = \sum_i A_i^2 \cos^2 \omega_i t_1 \cos^2 \omega_i t_2 \sin^2 \omega_i t \tag{3}$$

where time is again measured from the last quench. This will create echoes at t_1 (which we shall refer to as the "stimulated echo"), t_2 and smaller ones at $|t_2 \pm t_1|$. The degree to which a particular solid is anharmonic can be measured by observing whether the echo behavior obeys these equations exactly.

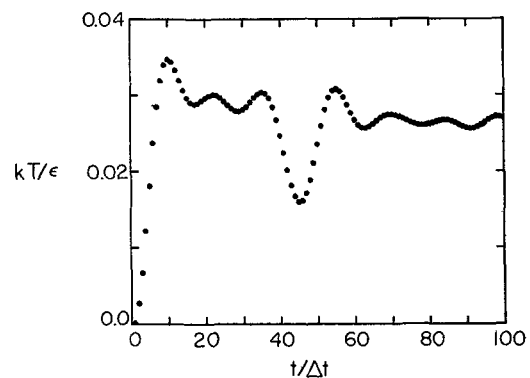


Fig. 1.--Temperature versus time after two-quenches with an interval $t_1 = 45\Delta t$ between them. Note the echo at $45\Delta t$.

In the present paper we will show the temperature dependence of the quench echoes in the glass and liquid phases of two 500 particle systems interacting via different interatomic potential: a Lennard-Jones 6-12 potential and an interatomic potential which corresponds to that found in liquid rubidium.³ The reduced temperature, given by $T^* = k_B T/\epsilon$ where ϵ is the depth of the interatomic potential well, was varied. These two systems have been studied previously^{4, 5, 6} and were found to have very

different properties in the liquid state. The liquid rubidium sample showed well-defined modes out to large wavevectors (wavelengths as small as 1.25 times the interparticle spacing⁵) whereas the Lennard-Jones liquid showed that this phonon behavior disappears much more rapidly with wavevector (wavelengths only as small as 5 times the interparticle distance⁵). By studying the behavior of the quench echoes in these two systems we have found evidence of a similar difference between the behavior of these two systems in the glass phase at temperatures much below the melting temperature. The decay in time of the normal modes in the Lennard-Jones system is much faster than that of the modes in the rubidium sample at the same value of the reduced temperature. The echo behavior contains no information about the spatial distribution of a mode but only about its time dependence.

There are several ways to demonstrate the presence of anharmonic behavior in a system using quench echoes. As can be seen from Eq. 3, it does not matter for the subsequent behavior of a harmonic system whether the interval t_1 comes before or after the interval t_2 in the quench sequence that creates the echoes at t_1 , t_2 and $|t_2 \pm t_1|$. By quenching the same system first with the intervals in one order and then again with the intervals reversed, one can monitor the amount of anharmonic behavior in a system by seeing how different the response of the system is to the two different quench sequences.

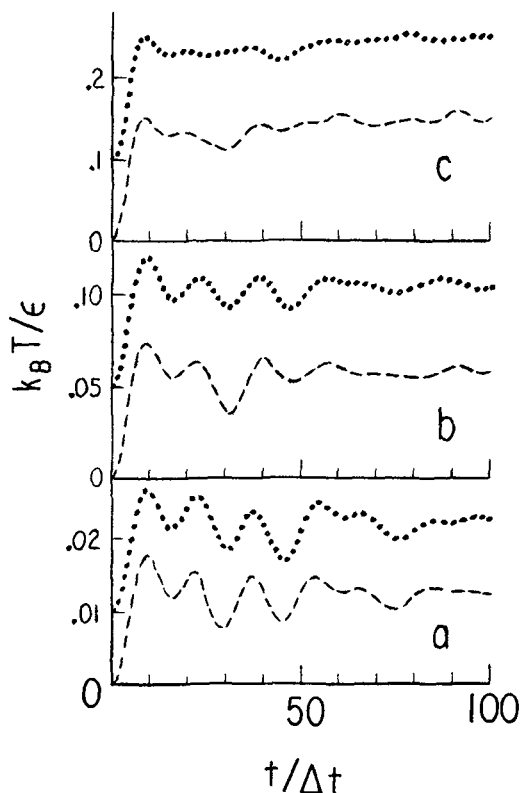


Fig. 2.--The temperature versus time for the Lennard-Jones system quenched three times with $t_1 = 45\Delta t$ and $t_2 = 30\Delta t$ (dashed line) and with $t_1 = 30\Delta t$ and $t_2 = 45\Delta t$ (dotted line). The two curves are displaced vertically. The initial temperatures are (a) $T^* = 0.11$, (b) $T^* = 0.46$ and (c) $T^* = 1.2$.

In Fig. 2 we show the results of this behavior for intervals of $30\Delta t$ and $45\Delta t$ for the Lennard-Jones system at 3 temperatures. In each case the curves are displaced vertically from each other for comparison and the lower curve in each set is for $t_1 = 45\Delta t$ and $t_2 = 30\Delta t$ and the upper curve is for $t_1 = 30\Delta t$ and $t_2 = 45\Delta t$. At very low starting temperatures, we can observe no difference between the two curves. However at a starting temperature of $T^* = 0.11$ (Fig. 2a), we already see that the depth of the two echoes is different in the two curves indicating a sizable amount of anharmonicity. Even at this low temperature ($\sim 1/8$ of the melting temperature of the f.c.c. crystal) the behavior of the solid shows that approximately 20% of the energy of a mode is dissipated per period. At higher temperatures we see that the anharmonic behavior becomes progressively more pronounced until, in the liquid at $T^* = 1.2$ we have difficulty seeing any echo behavior at all.

In Fig. 3, we show the behavior of the rubidium sample after a similar series of quenches. The lowest temperature studied was $T^* = 0.15$. Although this temperature is above that for Fig. 2a where $T^* = 0.11$, it is clear that there is considerably less anharmonic behavior than in the Lennard-Jones system since the two curves show much smaller deviations from each other. As the temperature is raised we consistently see that the rubidium system is much more harmonic than the Lennard-Jones one at a comparable temperature.

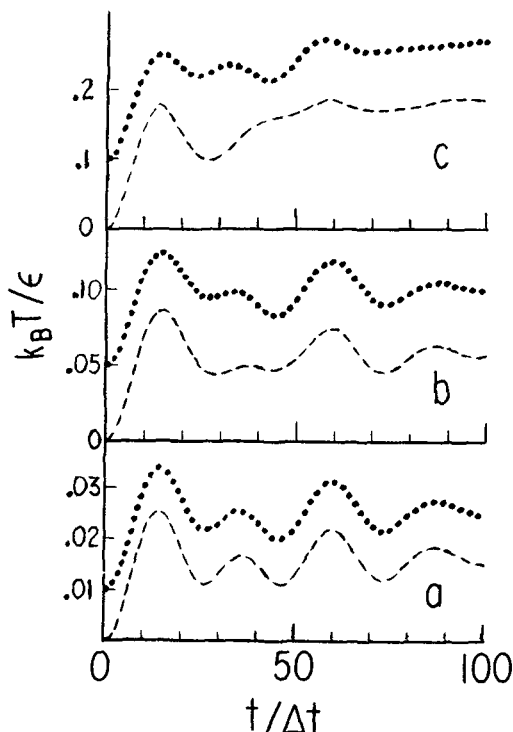


Fig. 3.--The results of a similar quench sequence as in Fig. 2 when applied to the rubidium sample. The initial temperatures are (a) $T^* = 0.15$, (b) $T^* = 0.5$ and (c) $T^* = 1.1$.

In Fig. 4 we show the decay as a function of time interval, t_2 , of the stimulated echo for the

Lennard-Jones sample at $T^* = 0.11$ and the rubidium sample at $T^* = 0.15$. We can determine from the slope of the decay of the echo the extent of anharmonic mode coupling. We see that the echo in rubidium decays much more slowly than in the Lennard-Jones sample. This is consistent with what was found from the data in Figs. 2 and 3.

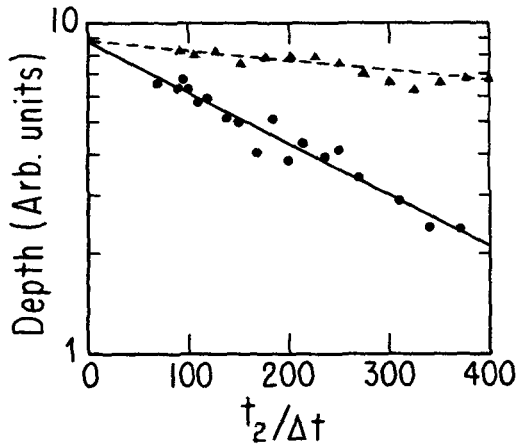


Fig. 4.--The decay of the stimulated echo as a function of t_2 for the rubidium sample at $T^* = 0.15$ (triangles) and for the Lennard-Jones sample at $T = 0.11$ (circles). In each case $t_1 = 30\Delta t$.

The conclusion from this analysis of the quench echoes is that the Lennard-Jones glass is much more anharmonic than the rubidium. This anharmonicity becomes more and more pronounced as the temperature is raised towards the liquid phase. These results suggest that in the liquid the sound modes of the Lennard-Jones fluid would be much more quickly damped than in rubidium in part due to the greater anharmonicity in the former system. This is what is partially responsible for the fact that sound modes are not observed at large wavevectors in Lennard-Jones fluids.

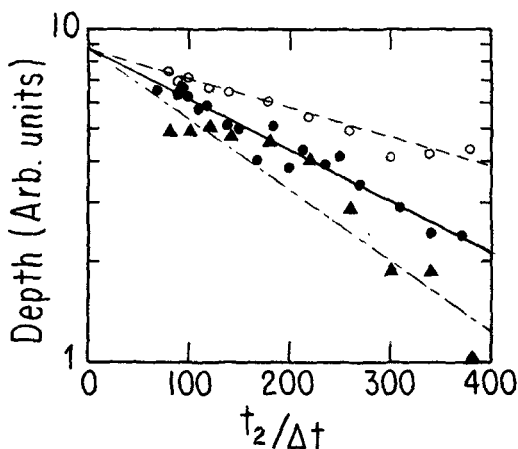


Fig. 5.--The decay of the simulated echo in different potentials as a function of t_2 at $T^* = 0.11$. In all cases $t_1 = 30\Delta t$. The results are for the 10-6 Lennard Jones (open circles); 12-6 Lennard-Jones (closed circles) and 12-8 Lennard-Jones (closed triangles).

In order to understand in more detail the role that the potential plays in the damping of modes we have studied the behavior of the stimulated echo for several different potentials. In each case we start with identical configurations of the atoms so that the effect of the potential on forming the structure is not included. The initial starting temperature of the system is also the same for all the systems studied. The potentials we have used are similar to the Lennard-Jones but with different values for the exponents in order to vary the relative strengths of the repulsive and attractive forces: $V(r) \propto (\frac{\sigma}{r})^n - (\frac{\sigma}{r})^m$. We have studied $n = 12$,

$m = 6$; $n = 10, m = 6$; and $n = 12, m = 8$. The results are shown in Fig. 5. It is clear that the larger the value of $(m + n)$ (i.e., the steeper the potential) the faster is the damping of the echo. The decay of the rubidium echo in Fig. 4 is closest to that of the system with the lowest value of $(n + m)$. The steepness of the potential is apparently what is primarily responsible for the anharmonic coupling of modes. This conclusion is similar to that of Haan *et al.*,⁴ who showed that the sound modes in the liquid were relatively insensitive to the attractive part of the potential.⁷ They concluded that it was the relative steepness of the repulsive core of the Lennard-Jones potential compared to that of rubidium which caused the dramatic effect of the sound modes being highly damped in the former while not in the latter. In the present paper we have extended their results and have shown how the anharmonicity and mode coupling in a glassy system exists even in the solid state and how they grow with temperature. The steepness of the potential is important for the damping of the sound modes in the glass because it causes each atom to feel a strong departure from a purely harmonic potential and thus couples the various normal modes. We presume that the fast decay of the sound modes in the liquid state is in part due to similar effects as observed in the glass.

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1. G. S. Grest, S. R. Nagel and A. Rahman, to be published.
2. For a Lennard-Jones system the interatomic potential is given by $V = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$. The time step of integration used was $\Delta t = 0.01 (\frac{M}{\epsilon})^{1/2}$ where M is the mass of the particle. Similarly for the rubidium potential σ and ϵ are the units of length and energy and the Δt used was $\Delta t = 0.0075(\frac{M}{\epsilon})^{1/2}$.
3. D. L. Price, Phys. Rev. A **4**, 358 (1971).
D. L. Price, K. S. Singwi and M. P. Tosi, Phys. Rev. B **2**, 2983 (1970).
4. S. W. Haan, R. D. Mountain, C. S. Hsu and A. Rahman, to be published.

5. A. Rahman, Phys. Rev. A 9, 1667 (1974).
A. Rahman, Phys. Rev. Lett. 32, 52 (1974).
6. H. Bell, H. Moeller-Wenghoffer, A. Kollmar,
R. Stockmeyer, T. Springer, H. Stiller,
Phys. Rev. A 11, 316 (1975); D. Levesque,
L. Verlet and J. Kurkijarvi, Phys. Rev. A 7,
1690 (1973).
7. In this context the attractive part of the
potential implies the region where
 $\frac{dV(r)}{dr} < 0$. In their study Haan et al.,⁴
truncated their potentials after the first
minimum leaving only the repulsive core of
the total potential. The Lennard-Jones
potentials with the smallest values of $(n + m)$
will have a repulsive core more similar to
rubidium although the attractive part may be
quite different.