行政院國家科學委員會專題研究計畫成果報告

瞬間正則運動模與非晶型物質之相變 (II)
Instantaneous Normal Modes and Dynamics of Glass Transition (II)

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一、中文摘要

利用瞬間正則分析及一新定義的測度，簡化的參與比例，我們證實共振模存在於截斷 Lennard-Jones 流體內。在此流體內分子間作用力僅只有 Lennard-Jones 位能的斥力部份。我們稱這些共振模爲瞬間共振模。藉檢驗這些瞬間共振模的位能井，我們得到的結論是瞬間共振模都發生在有很強偏離簡偕振動的單一位能井。

關鍵詞：瞬間共振模,截斷 Lennard-Jones 流體，簡化的參與比例

Abstract

In terms of the instantaneous-normal-mode (INM) analysis, and a newly defined measure for quasilocalized modes, we present the evidence for the resonant modes in a model fluid, in which the pair interaction is merely the repulsive portion of the Lennard-Jones potential. We name such a quasilocalied INM as an instantaneous resonant mode (IRM). By examining the potential energy profile beyond the INM approximation, we conclude that the IRMs occur in single-well potentials with strong enough anharmonicity.

Keywords: Instantaneous resonant modes, Truncated Lennard-Jones (TLJ) fluid, Reduced participation ratio.

二、緣由與目的

Although both liquids and glasses lack periodic structure, their dynamics behave quite different. Due to its fluidity, the shear viscosity of a liquid is extraordinarily small and the characteristic molecular relaxation times are extraordinarily short, as compared with its glassy counterparts. For glasses, many phonon-related anomalous properties, such as the so-called "boson peak" in Raman scattering, have been explained in terms of the quasilocalized resonant modes, and the existence of the resonant modes in glasses has been confirmed by experiments and computer simulation. However, for some glasses-forming liquids, the boson peaks are still observable in the supercooled-liquid regime, and for some materials the signals even survive in the liquid phase. A general question arises as to whether the resonant modes usually defined in the glassy states will still persist in the liquid states. If the answer is yes, what is the characteristic of a resonant mode in the liquid phase?

The concept of the resonant modes can be understood from the phonon theory of crystals with impurities. If the impurities in a crystal are heavy enough and/or coupled weakly enough to the host crystal, the low frequency qusilocalized vibrational modes in the acoustic phonon band will be created. In such a qusilocalized mode, the vibrational motion is sharply localized to the impurity and its nearby particles, and the decaying of the host crystal oscillation amplitudes away from the impurity center is much weaker than the exponential decay. Due to some anharmonic interaction, the resonant mode is a result of the hybirdization of a localized vibrational motion with the acoustic phonons of similar frequencies. In glasses, the resonant modes are predicted by the soft potential model to occur in the single-well potentials with strong anharmonicity. In addition to the resonant modes with one localized center, through the investigation of their eigenvectors, some resonant modes were found to be localized around two or more will separated centers, with interaction between them. To distinguish from the one-centered resonant modes, the multi-centered resonant modes are referred as the interacting resonant modes.

Recently, there has been a great interest in studying the dynamics of disordered systems (liquids and glasses) in terms of the INM analysis. The motivation of the INM analysis is to extend the standard harmonic normal-mode analysis to the disordered systems at finite temperatures. Without restricting to configurations at the local potential minima as in the steepest-descent approach, the INM approach is applied to all possible instantaneous configurations, at which the potential energy surface may have both positive and negative curvatures; therefore, the INM density spectrum has the real-frequency and the imaginary-frequency lobes, respectively. So far, in various kinds of liuqid systems, including the sofe-sphere system, the LJ liquids, metallic liquids, molecular liquids, or ionic liquids, the localized INMs are all found in the high-frequency ends of both lobes. The spatial distribution of a high-frequency localized INM is more like an exponential decay. On the other hand, the low-freuqency quasilocalized INMs are only found in the glassy systems.

In this report, using the technique of INM analysis, we present evidence for the existence of the low-frequency quasilocalized INMs in the TLJ fluid. We name these INMs as the instantaneous resonant modes (IRMs).

三、結果與討論

The reason for the occurrence of IRMs in our model is that the interplay between the interaction range and the average nearest-neighbor distance leads to the presence of barely isolated centers. Because the interactions between particles in our model are purely repulsive, the IRMs we found only exist in the imaginary-frequency lobe.

Usually, the measure of localization of an INM in an N-particle system is the participation ratio $p=R/N$, where R is the number of particles involved in this INM. For a localized INM, p will scale inversely with N. For an extended INM, p is of order unity. For those high-frequency localized INMs, the participation ratio is a good measure of localization, since the major contribution in R comes from the localization center. However, due to the hybirdization with the extended phonon modes, both the localized and the extended parts of a resonant mode contribute to R. Thus, the participation ratio may not be an effective measure of localization for all resonant modes, except for those with strong localization. In this report, we propose an alternative definition for the measure of localization, according to the quasilocalized character if a resonant mode.

We define the reduced number of involved particles, Q, of each INMs, which is similar as R given in Ref. [1], except that the term due to the largest projection component is excluded, and the reduced participation ratio $s=R/Q$. Thus, s is a quantity between 0 and 1. For the extreme case, such as a resonant mode in a crystal with heavy impurities, in which one particle has a sharply peaked project on component among other particles, R is of order unity but Q will be larger in a few orders than R. Therefore, a will be very close two zero. On the contrary, for an extended INM, both R and Q are of the same order in magnitude. Therefore, s will be close to unity. With this new measure, we expect to find the IRMs in our model fluid.

To test our ideas, we perform molecular-dynamics simulation with the periodic boundary condition on a system of particles, interacting via the LJ potential, but lifted by the depth of the potential well and then truncated at the minimum. We refer this fluid as the truncated LJ fluid. To underscore the effect of missing attractive force, we also simulated the original LJ fluid at the same reduced density (=0.88) and temperature (=0.84). The redial distribution functions of these two fluids are almost identical, as a result that the repulsive part of the potential dominates the equilibrium structure. Also, the two fluids have similar diffusion constants and pressures. For the INM density of states (DOS), the real-frequency spectra of thess two fluids have almost identical tails; however, the fraction of the imaginary-frequency INMs increase from 0.189 to 0.277 by truncating out the attracting portion in the pair potential.

The distribution functions of R for the TLJ fluid of 375 and 750 particles are shown in Ref. [1]. Apparently, in the imaginary-frequency lobe, the R distribution has a sharp dip in the region of frequencies less than 5w, with the depth near 2.5w. The ratio curve of these two distributions also has a dip in the corresponding region, and the value of the ratio curve is about 1.65. This implies that in the TLJ fluid not all of the INMs with small imaginary frequencies are extended modes, but quite a portion of them quasilocalized. No corresponding dip, except those due to fluctuations, is found in the ratio curve of the original LJ fluids with these two different sizes. This suggests that those small-frequency quasilocalized INM occurred in the TLJ fluid is resulted from the truncation of the pair potential. To distinguish the quasilocalized INMs with the same frequencies, we introduce the reduced participation ratio s as another variable in the function of the normalized INM DOS. The 3-D plots of the TLJ and the original LJ fluids are shown in Ref. [1].

The typical characteristic of the resonant, the extended and the interacting-resonant INMs are illustrated in Ref. [1]. In the IRM, the central particle interacts very weakly with its nearby particles and forms a barely isolated center. The potential energy profile is strongly anharmonic, and the overall profile is almost a singe well, except for some small variation near the origin. For the interacting IRM, another excited center is created in the third shell of the central particle, and the anharmonicity in the energy profile is not so strong as in the case of the IRM. In the extended INM, by contrast, the central particle interacts much strongly with its near neighbors, and the anharmonicity in the energy profile is even weaker.

In the summary, in terms of INM analysis and the reduced participation ratio, we have clearly show that existence of the resonant modes in a model fluid of short-range pair interaction, which is only the repulsive portion of the LJ potential. Since the INM approach is a short-time description of the liquid dynamics, we name these resonant modes as the IRMs. By examining the potential energy profile of the IRMs, our investigation show that the IRMs occur in single-well potential with strong anharmonicity. This physical picture is analogous to the resonant modes predicted by the soft-potential model for low-temperature glasses. However, the relaxation times of the IRMs are expected to be much shorter than those of resonant modes in glasses. Due to the repulsive pair interaction in our model, the IRMs we found are only in the imaginary-frequency lobe. The real-frequency IRMs are expected, if the short-range interaction has an attractive well. Our results suggest that an overall investigation on the resonant modes in a system from the glassy to the liquid states is necessary for comprehending the boson peak. Further works on the IRMs in mode realistic liquids are underway.

四、參考文獻

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