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Evidence for instantaneous resonant modes in dense fluids with repulsive Lennard-Jones force

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In terms of instantaneous-normal-mode (INM) analysis and a newly defined measure for quasilocalization, 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 quasilocalized 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. © *1999 American Institute of Physics.*
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I. INTRODUCTION

Although both liquids and glasses lack periodic structure, their dynamics behave quite differently. 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,[1] and the existence of the resonant modes in glasses has been confirmed by experiments[2] and computer simulation.[3,4] However, for some glass-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.[5,6] 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.[7,8] If the impurities in a crystal are heavy enough and/or coupled weakly enough to the host crystal, the low-frequency quasilocalized vibrational modes in the acoustic phonon band will be created. In such a quasilocalized 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 hybridization of a localized vibrational motion with the acoustic phonons of similar frequencies. In glasses, the resonant modes are predicted by the soft potential model[9,10] 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 well-separated centers, with interaction between them. To distinguish from the one-centered resonant modes, the multicentered resonant modes are referred as the interacting resonant modes.[4,11]

Recently, there has been a great interest in studying the dynamics of disordered systems (liquids and glasses) in terms of the instantaneous-normal-mode (INM) analysis.[12,13] 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,[4] the INM approach is applied to all possible instantaneous configurations, at which the potential energy surface may have both the 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 liquid systems, including the soft-sphere system,[14] the Lennard-Jones (LJ) liquids,[12,13] metallic liquids,[15,16] molecular liquids,[17] or ionic liquids,[18] 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.[16] On the other hand, the low-frequency quasilocalized INMs are only found in the glassy systems.[14,19]

In this paper, using the technique of INM analysis, we present evidence for the existence of the low-frequency quasilocalized INMs in a model fluid, in which the particle pair interaction is only the repulsive portion of the LJ potential. Since in the INM analysis the configurations are the snap shots of the instantaneous particle position, we name the low-frequency quasilocalized INMs we found as the instantaneous resonant modes (IRMs). The reason for the oc-

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currence 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 interaction between particles in our model are purely repulsive, the IRMs we found only exist in the imaginary-frequency lobe. In Sec. II, we introduce a new measure for the IRMs. The evidence for the IRMs in our model fluid is presented in Sec. III. Our conclusion is given in Sec. IV.

II. REDUCED PARTICIPATION RATIO AND SIMULATION

Usually, the measure of localization of an INM labeled α in an N-particle system is the participation ratio[4,14–18] $p_\alpha \equiv R_N^\alpha/N$, with R_N^α to be the number of particles involved in this INM and defined as

$$R_N^\alpha=\left(\sum_{j=1}^{N}|\mathbf{e}_j^\alpha|^4\right)^{-1}, \tag{1}$$

where $\mathbf{e}_j^\alpha$ is the projection component of the INM eigenvector on atom j. For a localized INM, p_α will scale inversely with N. For an extended INM, p_α 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_N comes from the localization center. However, due to the hybridization with the extended phonon modes, both the localized and the extended parts of a resonant mode contribute to R_N. Thus, the participation ratio may not be an effective measure of localization for all resonant modes, except for those with strong localization. In this paper, we propose an alternative definition for the measure of localization, according to the quasilocalized character of a resonant mode.

We define the reduced number of involved particles, Q_N^α, of each INM, which is similar as R_N^α given in Eq. (1), except that the term due to the largest projection component $\mathbf{e}_1^\alpha$ is excluded, and the reduced participation ratio $s_\alpha \equiv R_N^\alpha/Q_N^\alpha$. The relation between R_N^α and Q_N^α is $R_N^{\alpha-1}=|\mathbf{e}_1^\alpha|^4+Q_N^{\alpha-1}$. Thus, s_α is a quantity between 0 and 1. For the extreme case, such as a resonant mode in a crystal with impurities, in which one particle has a sharply peaked projection component among other particles, R_N^α is of order unity but Q_N^α will be larger in a few orders than R_N^α. Therefore, s_α will be very close to zero. On the contrary, for an extended INM, both R_N^α and Q_N^α are of the same order in magnitude. Therefore, s_α will be close to unity. With this new measure s_α, we expect to find the IRMs in our model fluid.

To test our ideas, we perform molecular-dynamics simulations with the periodic boundary condition on a system of particles having each a mass m, interacting via the potential $V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]+A(r/\sigma)+B$, with a cutoff r_c, beyond which $V(r)=0$. The coefficients A and B are chosen so as to ensure continuity for both the potential and the force at r_c. We choose $r_c=2^{1/6}\sigma$, the minimum of the original LJ potential, $A=0$ and $B=\epsilon$; thus, the potential is equivalent to a lifted LJ potential without attractive tail. We refer this fluid as the truncated LJ (TLJ) fluid. After the simulated system was in equilibrium, we collected data of 400 and 200 configurations with an interval of 400 time steps [each time step$=0.002$ in unit of $\tau\equiv(m\sigma^2/\epsilon)^{1/2}$] for systems of 375 and 750 particles, respectively, for the TLJ fluid at the density $\rho\sigma^3=0.88$ and temperature $k_BT/\epsilon=0.836$. To underscore the effect of missing attractive force, at the same density and temperature we also collected data for the original LJ fluid with $r_c=3.5\sigma$.

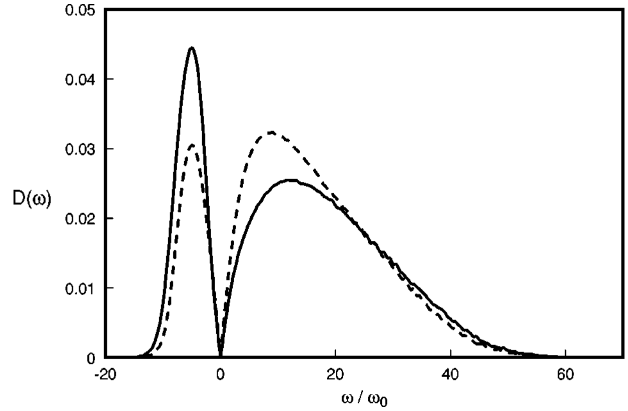


FIG. 1. Densities of states of INMs in the original LJ (dashed line) and the TLJ (solid line) fluids. As usual, the real frequencies are plotted along the positive frequency axis and the imaginary frequencies are plotted along the negative frequency axis. Frequencies are scaled by $\omega_0\equiv(\epsilon/m\sigma^2)^{1/2}$.

III. INSTANTANEOUS RESONANT MODES

The radial distribution functions of these two fluids with different cutoffs are almost identical, as a result that the repulsive part of the potential dominates the equilibrium structure.[20] Also, the two fluids have similar diffusion constants and pressures.[21] The INM densities of states $D(\omega)$ of these two fluids are shown in Fig. 1. In the real-frequency lobe, these two spectra have almost identical tails. However, the fraction of the imaginary-frequency INMs increases from 0.187 to 0.277 by truncating out the attractive portion in the pair potential.

After a configuration average for R_N^α of INMs within a small frequency width, we define $R_N(\omega)$ as the averaged number of particles involved in INMs within the frequency width.[18] Figure 2 shows the distributions of $R_N(\omega)$ for the TLJ fluid of 375 and 750 particles. The ratio of these two distributions, after smoothed as described in Ref. 15, is given in the inset. Apparently, in the imaginary-frequency lobe, the $R_N(\omega)$ distribution has a sharp dip in the region of frequencies less than $5\omega_0$ $(\omega_0=\tau^{-1})$, with the depth near $2.5\omega_0$. The ratio curve also has a dip in the corresponding frequency region, and the value of $R_{750}(\omega)/R_{375}(\omega)$ near the depth 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 are quasilocalized. The ratio curve $R_{750}(\omega)/R_{375}(\omega)$ of the original LJ fluid is shown with the dashed curve in the inset of Fig. 2 for comparison. No corresponding dip is found, except those due to fluctuations. This suggests that those small-frequency quasilocalized INMs occurred in the TLJ fluid is resulted from the truncation of the pair potential.

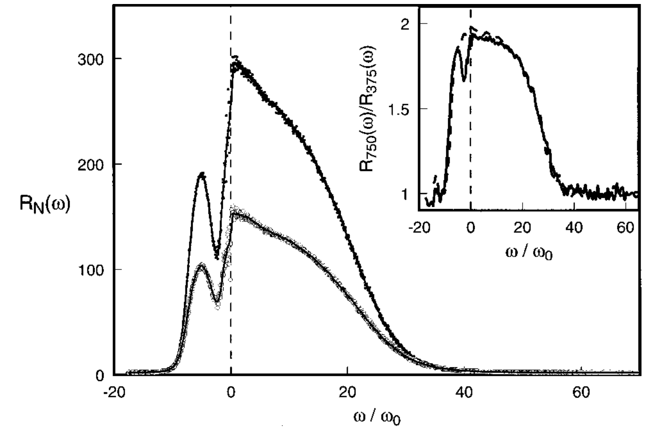


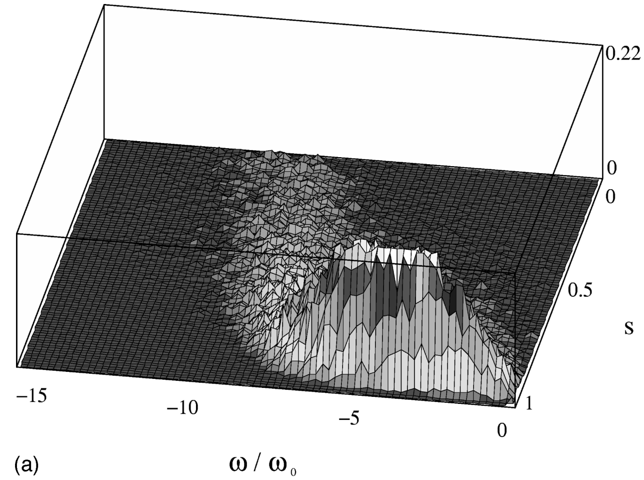
FIG. 2. The averaged number of involved particles of INMs with frequency ω in the TLJ fluid. The dotted points and the open circles are the original simulation results for systems with 750 and 375 particles, respectively. The solid lines, to guide the eye, are obtained by smoothing the simulation data as described in Ref. 15. The function $R_{750}(\omega)/R_{375}(\omega)$ generated by dividing the two smoothed solid lines is given in the insert, in which the solid and dashed lines are for the TLJ and the original LJ fluids, respectively.

To distinguish the quasilocalized INMs from the extended INMs with the same frequencies, we introduce the reduced participation ratio s as another variable in the function of the normalized INM density of states, which is then defined as

$$\tilde{D}(\omega,s)=\left\langle \frac{1}{3N}\sum_{\alpha=1}^{3N}\delta(\omega-\omega_\alpha)\delta(s-s_\alpha)\right\rangle, \tag{2}$$

where an ensemble average has been made over all instantaneous configurations. With this definition, it is easy to prove the relation $\int_0^1\tilde{D}(\omega,s)ds=D(\omega)$. The three-dimensional (3D) plots of $\tilde{D}(\omega,s)$ for the TLJ and the original LJ fluids are given in Fig. 3. The figures show that for imaginary frequencies larger than $5\omega_0$ the general features of $\tilde{D}(\omega,s)$ of these two fluids are similar, and for imaginary frequencies less than $5\omega_0$, most INMs of the original LJ fluid are in the region of s larger than a critical value s_c near 0.5 (our qualitative results is insensitive to the exact value of s_c). Thus, we refer the extended INMs as those with s larger than s_c. However, for the TLJ fluid, within the region of imaginary frequencies less than $3\omega_0$ and s less than 0.1, $\tilde{D}(\omega,s)$ has a prominent distribution with a maximum about 0.16, which indicates that there is a significant amount of quasilocalized INMs, and we refer them as the IRMs. The values of $\tilde{D}(\omega,s)$ between the IRM and the extended-INM regions are less than 0.04. Thus, the INMs within this region are referred as the interacting IRMs, whose characteristic changes from quasilocalized to extended as s increases.

We illustrate the typical characteristics of the resonant, extended and interacting-resonant INMs in Fig. 4 by plotting the magnitudes of $\mathbf{e}_j^\alpha$ as a function of the distance from the largest-projection-component particle, and the potential energy profile $E_\alpha(\lambda)\equiv\Phi(\mathbf{R}_0+\lambda\mathbf{e}^\alpha)-\Phi(\mathbf{R}_0)$ as a function of the displacement λ along the eigenvector $\mathbf{e}^\alpha$, where $\mathbf{R}_0$ is an instantaneous configuration and Φ is the total interacting potential energy. The potential energy profile calculated with



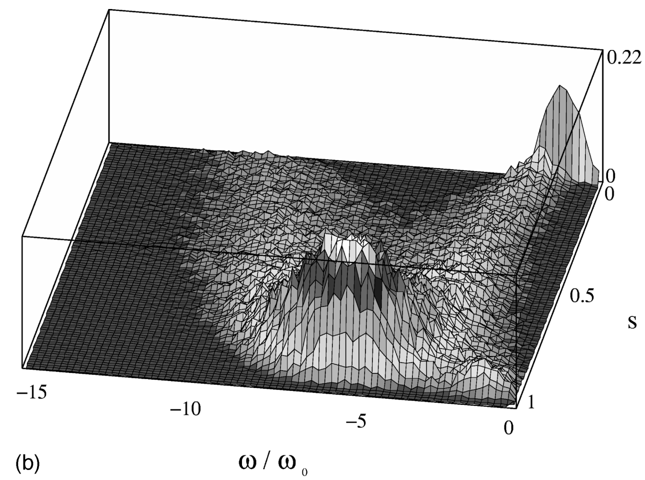


FIG. 3. 3D plots of $\tilde{D}(\omega,s)$ for imaginary-frequency INMs in the original LJ (a) and the TLJ (b) fluids.

the INM approximation, in which $E_\alpha(\lambda)$ is expanded in λ and truncated beyond the second order, is also given in the inset. In the IRM, the central particle interacts very weakly with its nearby particles and forms a barely isolated center. The potential energy profile in large λ is strongly anharmonic, and the overall profile is almost a single 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.

IV. CONCLUSION

In summary, in terms of INM analysis and the reduced participation ratio, we have clearly shown the existence of 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 shows that the IRMs occur in single-

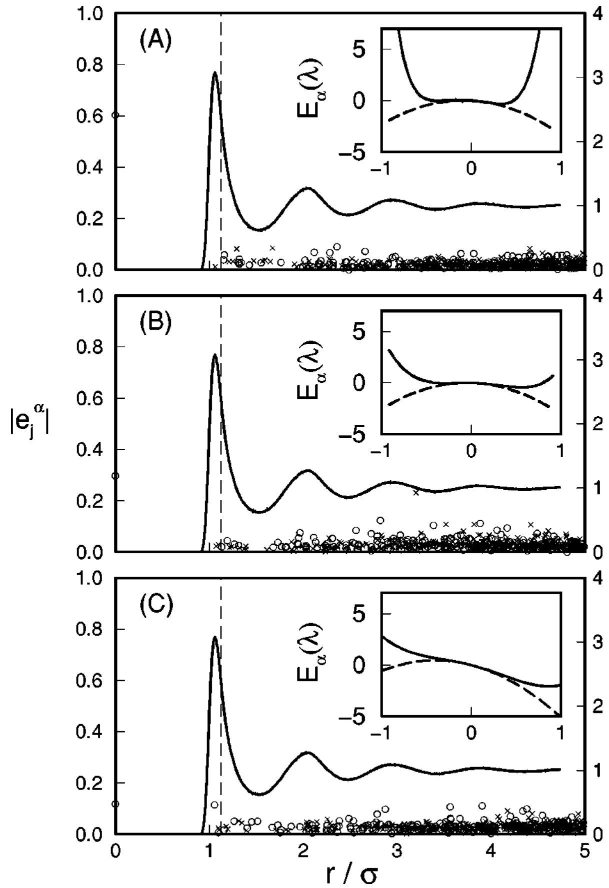


FIG. 4. The projection components $|\mathbf{e}_j^\alpha|$ of three INMs with almost the same imaginary frequencies [$\omega=2.387\omega_0$ (A), $2.383\omega_0$ (B), and 2.388ω (C), respectively] but quite different values of the reduced participation ratio [$s=9.86\times10^{-2}$ (A), 0.43 (B), and 0.94 (C), respectively]. The open circles and the crosses represent particles with $\mathbf{e}_j^\alpha\cdot\mathbf{e}_1^\alpha$ larger and smaller than zero, respectively. In each plot, the left-hand vertical scale is for $|\mathbf{e}_j^\alpha|$ and the right-hand vertical scale is for $g(r)$. The dashed line indicates the cutoff distance in the TLJ potential. In the insert of each part, the solid line is the potential energy profile, $E_\alpha(\lambda)$, of the corresponding INM and the dashed line is the energy profile calculated with the INM approximation as described in the text.

well potentials 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 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 pair 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 more realistic liquids, and its relationship with physical quantities are underway.

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