Instantaneous resonant modes in high-temperature gallium liquids

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We have studied the low-frequency, quasilocalized vibrational excitations in Ga liquids in terms of instantaneous-normal-mode analysis. We present strong numerical evidence for the existence of the instantaneous resonant modes (IRM's) in high-temperature Ga liquids. It is the exotic repulsive-core interaction between Ga particles that gives rise to the IRM's, which are associated with special local structures created by density fluctuation. In general, the IRM density of states is found to increase with temperature.

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Searching for the low-frequency, quasilocalized vibrational excitations, usually termed resonant modes, in disordered materials has been a long-standing problem, because they are believed to play important roles in many anomalous thermal properties of amorphous solids[1] and the boson peak of some glass-forming supercooled liquids.[2] Since the pioneering work of Biswas *et al.*,[3] most of the numerical studies have been done on analyzing the normal modes (NM's) of the computer-generated disordered systems in the inherent configurations, which correspond to the local minima of the potential-energy landscape.[4] However, the conclusions are somewhat controversial. Feldman, Allen, and Bickham[5] recently argued that in a mostly fourfold coordinated model of *a*-Si, the resonant modes were the artifacts of the finite size of the simulated systems and would not exist in the infinite-size limit. On the other hand, the usage of the participation ratio[6] as a quantity to identify the localization of the resonant modes is questionable. Mazzacurati *et al.*[7] have shown that even in the very large systems of Lennard-Jones (LJ) glasses, the inherent NM's in the low-frequency region are not localized in nature, in spite of the appearance of the small-value participation ratios in this region.

One technical difficulty in the calculation of the inherent NM spectra is the sparseness in the low-frequency part, which should follow the Debye law and have a lower-end cutoff beyond which no NM's can exist for a finite-size system. Resulting from the mixing of a localized motion with the extended NM's of similar frequencies due to some anharmonic interactions, a resonant mode has the hybridized character of spatial localization and extension. Therefore, the averaged participation ratio may not be an effective measure to identify the resonant modes as it is for the high-frequency localized modes. Recently, the instantaneous-normal-mode (INM) analysis[8,9] on the dynamics of normal and supercooled liquids has had great attention. The INM's are obtained from diagonalizing the Hessian matrix of each instantaneous configuration. Without restricting to the local minima of the potential-energy landscape, the INM spectra, obtained after configuration average, have the real-frequency and the imaginary-frequency lobes. Because of the presence of the imaginary-frequency lobe, the low-frequency part of the real-frequency lobe does not need to obey the Debye law any more, but has a linear dependence in frequency, which implies that even for the finite-size systems, the INM spectra contain more low-frequency relaxation modes than the inherent NM spectra have. In order to distinguish the resonant modes from the extended modes at the same frequencies, Wu and Ma[10] recently proposed a measure, the reduced participation ratio, for quasilocalization. With this measure, the quasilocalized, low-frequency INM's, named the instantaneous resonant modes (IRM's), were effectively separated out in a truncated LJ (TLJ) fluid, but were never found in the LJ dense fluids.

Through a series of model studies, Wu, Ma, and Chang[11] have shown that in the simple dense fluids the IRM's can be created due to local density fluctuation, as long as the interaction range of the pair potential is a little shorter than the mean nearest-neighbor separation, and the local structure of each quasilocalized IRM has a barely isolated central particle, with a Voronoi volume[12] larger than the average. If the short-range interaction is purely repulsive, the IRM's only occur in the imaginary-frequency lobe; however, a tiny attractive well in the pair potential will make the IRM's spread into the real-frequency lobe.

In this paper, we report evidence for the existence of the IRM's in a realistic system, Ga liquid at temperatures much higher than the melting point ($T_m = 303$ K), in which the interaction between two Ga ions is long range. However, the occurrence of the IRM's in the high-temperature Ga liquids is attributed to the well-known curvature change in the repulsive core of the Ga pseudopotential. The curvature change is explained either as arising from the interplay of two characteristic distances: the effective diameter of the repulsive core and the wavelength of Friedel oscillation,[13] or by the partial-covalence effects.[14]

In terms of a first-principle calculated pseudopotential, one of us has reproduced with accuracy the structure factors of Ga liquids from $T = 323$ K to 1273 K,[15] including the shoulder on the high-q side of the first principal peak at temperatures just above the melting point. The comparison of the calculated Ga pseudopotential to that of Na liquid[16] or to the LJ potential is presented in Fig. 1, which clearly shows that the repulsive core of the Ga pseudopotential below 10ϵ is similar as the LJ potential, but becomes softer above 10ϵ. Shown in the inset of Fig. 1 are the functions of the longitudinal (ϕ'') and transverse (ϕ'/r) curvatures of the Ga

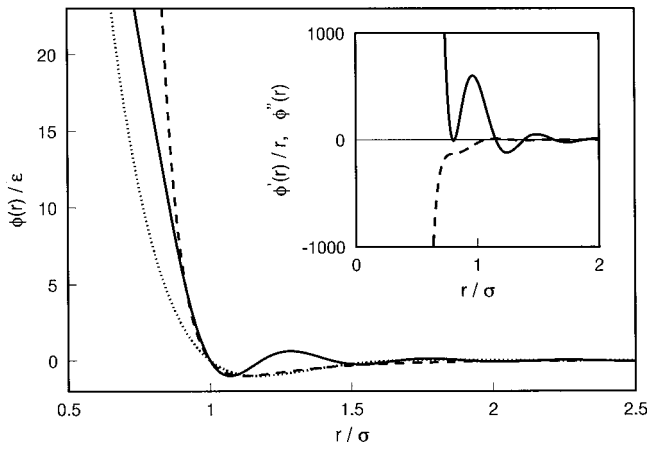

FIG. 1. The scaled pseudopotentials of Ga at $T=973$ K (solid lines) and Na at $T=378$ K (dotted line) and the LJ potential (dashed line). For each potential curve, energy is scaled with ϵ, the depth of its main attractive well, and distance with σ, the shortest distance where the potential is zero. For the Ga and Na pseudopotentials, ϵ are about 47 K and 456 K, and σ are about 4.05 Å and 3.42 Å, respectively. The second derivative (solid line) and the first derivative over r (dashed line) of the scaled Ga pseudopotential are given in the inset.

pseudopotential. The longitudinal component has a sharp dip in the repulsive core, with the value of the dip to be almost zero at $T=973$ K and a little higher at $T=323$ K. Thus, those Ga pairs with separations close to this curvature dip are weakly coupled in vibrational motions, since the longitudinal components of the $\mathbf{t}(r)$ tensor[17] in the Hessian matrix almost vanish, and only the small transverse components survive.

By means of the pseudopotential, we have simulated by molecular dynamics (MD), with the details given in Ref. 15, the Ga systems of 500 and 1000 particles on equilibrium states at constant pressure (about 1 bar) and $T=323$ K, 973 K, and 1273 K, respectively. The INM densities of states (DOS) $D(\omega)$ of Ga liquids are presented in Fig. 2(a), which exhibits the general behavior of the INM spectra of simple liquids. The averaged NM participation ratio $P_N(\omega)$ of a N-particle system is the configuration average of R_N^α/N for all NMs with ω frequencies, where R_N^α, the number of particles participating in the NM α, is usually defined as

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

with $\mathbf{e}_j^\alpha$ the projection component of the normalized eigenvector on particle j. For a simple fluid, such as the supercooled LJ liquid[18] or Na liquid,[16] in which all low-frequency INM's in both lobes are extended modes, the $P_N(\omega)$ near zero frequency has a constant value and is independent of the system size for a quite broad range in temperature. Contrary to the cases of those atomic fluids, the value of $P_N(\omega \approx 0)$ of Ga liquid, shown in Fig. 2(b), decreases substantially as temperature increases from 323 K to 1273 K. Also, demonstrated in the inset of Fig. 2(b), at the small-real-frequency region, the higher the temperature, the stronger the dependence of $P_N(\omega)$ on the system size. All of these results imply that in

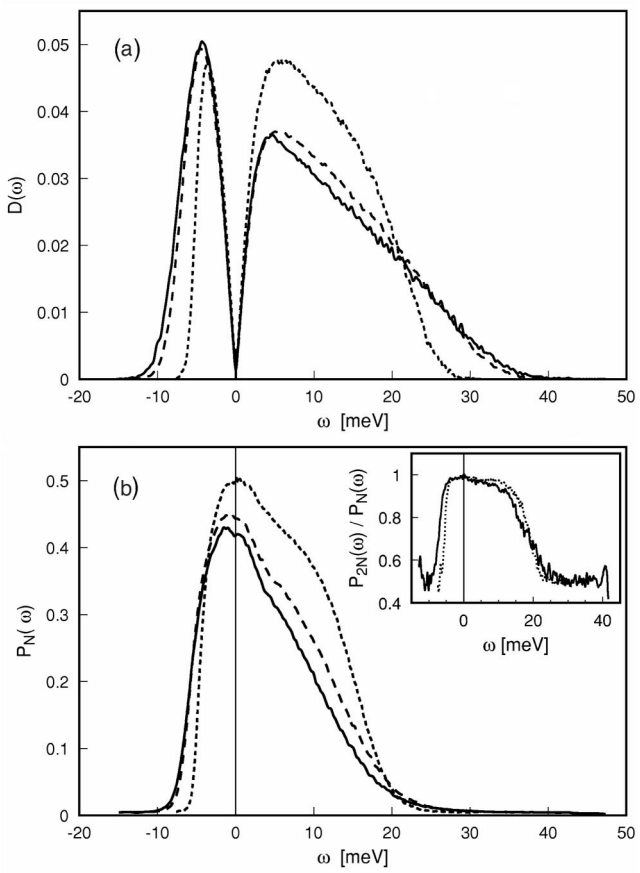

FIG. 2. The densities of states (a) and the averaged participation ratios (b) of INM's in Ga liquids at $T=1273$ K (solid line), 973 K (dashed line), and 323 K (short-dashed line). Shown in the inset of (b) are the ratio curves $P_{2N}(\omega)/P_N(\omega)$ $(N=500)$ at $T=973$ K (solid line) and 323 K (dotted line).

the high-temperature Ga liquid a significant portion of the low-frequency INM's in the real lobe are not extended modes, and the percentage increases with temperature.

The reduced participation ratio s_α is defined as the ratio R_N^α/Q_N^α, where Q_N^α is similar to R_N^α given in Eq. (1), except that the contribution of the largest projection component $\mathbf{e}_1^\alpha$ is excluded from the summation. As the value of s_α increases from 0 to 1, the corresponding INM changes from a quasilocalized one, which has a peaked projection component among a small amplitude surrounding, to an extended one, in which all projection components are comparable in magnitude.[10] Through comparing the INM's of the TLJ and the LJ dense fluids at the same density and temperature, the IRM's can be identified as those low-frequency INM's with $s_\alpha < 0.5$.

In terms of s_α, we have successfully separated out the IRM's from the low-frequency INM's of Ga liquids. The characteristics of an IRM in Ga liquid is presented in Fig. 3 by plotting $|\mathbf{e}_j^\alpha|$ as a function of the distance from the particle with the largest projection component and its potential-energy profile along the eigenvector direction. In this example, there is indeed a peaked projection component as we described above for a quasilocalized mode, and the potential-energy profile is almost harmonic near the bottom and domi-

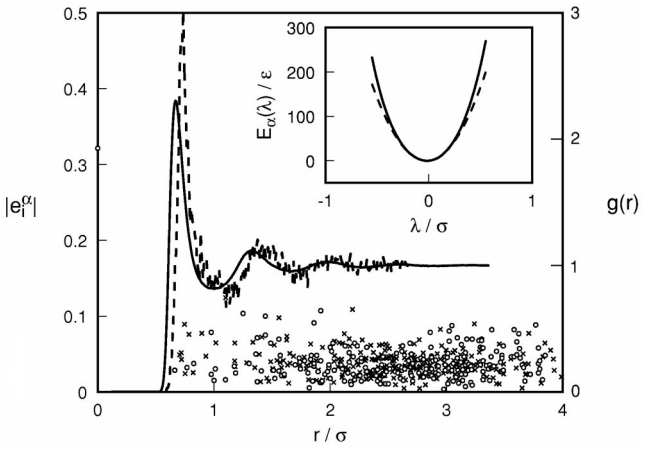

FIG. 3. The characteristics of an IRM with $\omega=4.25$ meV and $s_\alpha=0.24$ in Ga liquid at $T=973$ K. The open circles and the crosses represent particles with $\mathbf{e}_j^\alpha \cdot \mathbf{e}_1^\alpha$ greater and less than zero, respectively. The solid and the dashed lines are, respectively, for $g(r)$ and $g_{irm}(r)$. The left-hand and right-hand vertical scales are for $|\mathbf{e}_j^\alpha|$ and $g(r)$, respectively. In the inset, the potential-energy profile along the eigenvector direction of this IRM is given by the solid line and the INM approximation,[10] in which the potential-energy profile is expanded up to the second order of the displacement, by the dashed line.

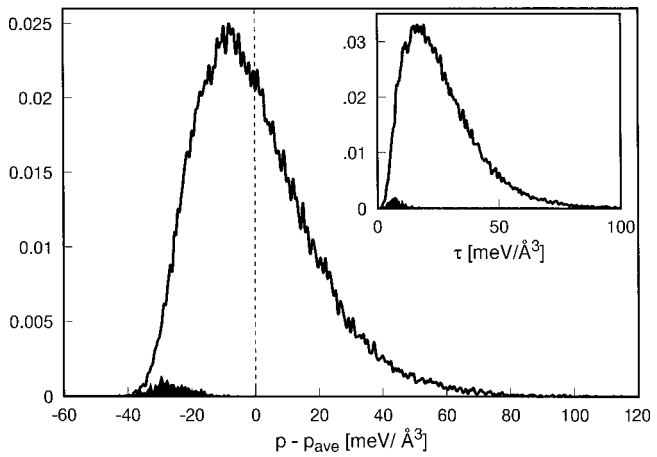

FIG. 5. The distributions of the local pressure and the shear stress (in the inset) for Ga liquid at $T=973$ K. The shaded areas are for the central particles of the quasilocalized IRM's with real frequencies less than 10 meV.

nated by a quartic anharmonicity at energies above 50ϵ from the bottom. Quantitatively, the IRM DOS $D_{irm}(\omega)$, shown in Fig. 4, apparently increases with temperature, and the relative DOS, the ratio $D_{irm}(\omega)/D(\omega)$, at $\omega\approx 4.77$ meV increases about ten times from $T=323$ K to $T=1273$ K. It seems that $D_{irm}(\omega)$ has some structures. In a model liquid, in which the Ga pseudopotential is truncated out at $\sigma=1$, the IRM's still exist and the structure of $D_{irm}(\omega)$ becomes more apparent, but their positions slightly shift toward zero frequency. Also, by neglecting the transverse components in the Hessian matrix, we found that it is the longitudinal components that are responsible for the occurrence of the IRM's. Thus, we claim that it is the curvature change in the repulsive core, not the long-range Friedel oscillation, that causes the IRM's in Ga liquids.

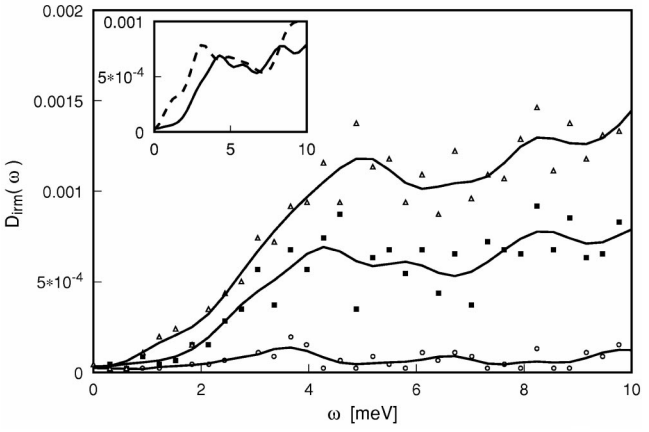

FIG. 4. The DOS of IRM's in Ga liquids at $T=1273$ K (open triangles), 973 K (filled squares), and 323 K (open circles), respectively. The symbols are obtained directly from MD simulations and the solid lines are their smoothed results. The inset shows the comparison of the IRM DOS of the realistic Ga liquid (the solid line) to that of a model liquid (the dashed line), in which the pair interaction is only the repulsive part of the Ga pseudopotential, at the same density and temperature.

Some insight into the local structures of the quasilocalized IRM's can be obtained by comparing the radial distribution functions $g(r)$ and $g_{irm}(r)$, which are averaged with respect to all particles and the central particles of the IRM's only, respectively. For Ga liquid at $T=973$ K, the first shell of $g_{irm}(r)$, with an outward shift relative to that of $g(r)$, has a maximum at a distance ($r\cong 0.735\sigma$) closer to the curvature dip in the repulsive core. This outward shift of the first shell[19] results in the much weaker vibrational couplings between the central particle of an IRM and its neighbors, as compared with those between the noncentral particles and their neighbors. Consistently, it has been verified that the central particles of the IRM's have a larger averaged Voronoi volume than the volume averaged for all particles.[11] As temperature decreases, the local volume expansion is expected to occur with more and more difficulty. Therefore, in addition to the mild variation with temperature on the depth of the curvature dip, this volume-expansion picture gives an intuitive explanation as to why as the temperature is lowered, the IRM DOS decreases.

A consequence of the Voronoi cell expansion is a reduction in the local hydrostatic pressure on the cell exerted by other particles in that structure. For a liquid with a central pair interaction, the local pressure on the cell of particle i with volume Ω_i is defined as the negative of the average trace of the atomic-level stress[20]

$$\sigma_i^{\alpha\beta}=\frac{1}{2\Omega_i}\sum_{j\neq i}\frac{\phi'(r_{ij})}{r_{ij}}\, r_{ij}^\alpha\, r_{ij}^\beta, \tag{2}$$

where r_{ij}^α is the α component of the separation vector $\mathbf{r}_{ij}$ between particles i and j. Using the Ga pseudopotential and neglecting its volume dependence, we estimated the aver-

aged local pressure p_{ave} of all particles in Ga liquid at $T = 973$ K to be about 60 meV/ Å^3, which should be balanced by the structure-independent pressures due to the electron-gas and the electron-ion interactions.[21] The distribution of the local pressures is presented in Fig. 5, in which we also show that the local pressure averaged for the central particles of the IRM's is below p_{ave} by about 40%. The Von Mises shear stress τ,[22] constructed from the three principle eigenvalues of the atomic-level stress given in Eq. (2), describes the distortion of the local structure around a particle from the spherical symmetry. The local-structure distortions of the central particles of the IRM's are again in the low-value end of the τ distribution, shown in the inset of Fig. 5. Thus, we have demonstrated that the central particles of the quasilocalized IRM's in high-temperature Ga liquids have local structures with low local pressures and the least distortions from spherical symmetry permissible by the liquid system.

In conclusion, we have numerically demonstrated the existence of the IRM's, which are the low-frequency, quasilocalized INM's, in the high-temperature Ga liquids. We have shown that it is the particular curvature change in the repulsive core of the Ga pseudopotential, rather than the Friedel oscillation, that gives rise to the IRM's. We claim that the IRM's in Ga liquids are not due to the finite-size effect of the simulated systems, but to the special pair interaction between particles. Created by density fluctuation, the expanded Voronoi cell with the least distortion from spherical symmetry is found to be the common feature of the local structures at the quasilocalized centers of the IRM's. Our results suggest that the polyvalent metallic liquids or glasses, which are well known for the exotic shapes in the repulsive core of their pseudopotentials and peculiar local structures, are the possible materials for the occurrence of the resonant modes. The significance of the IRM's on liquid dynamics and the connection between the IRM's and some physical observables are under investigation.

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