ELSEVIER

Physica B 316–317 (2002) 606–609

PHYSICA B

www.elsevier.com/locate/physb

Local geometric structures of instantaneous resonant modes in Ga liquids

Ten-Ming Wu[a,*], Wen-Jong Ma[b], S.L. Chang[a], Shiow-Fon Tsay[c]

[a] *Institute of Physics, National Chiao-Tung University, HsinChu, Taiwan, ROC*
[b] *Institute of Mathematics, Academia Sinica, Nankang, Taiwan, ROC*
[c] *Department of Physics, National Sun Yat-sen University, Kaoshiung, Taiwan, ROC*

Abstract

Recently, we have numerically found the instantaneous resonant modes (IRMs) in high-temperature Ga liquids. The occurrence of these IRMs is attributed to the cooperation of the exotic repulsive core of the Ga pseudopotential and the local volume expansion. In this paper, the local structures around the quasilocalized centers of these IRMs are analyzed. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 61.25.Mv; 61.25.−f; 63.50.+x

Keywords: Instantaneous resonant modes; Quasilocalization; Ga liquid

Great efforts have been made in the past to search for the low-frequency, quasilocalized vibrational excitations, termed as the resonant modes, in condensed matter. These modes are believed to play an important role in many anomalous thermal properties of amorphous solids [1] and the presence of the boson peak in some glass-forming supercooled liquids [2]. Computer simulation has been a powerful tool to do this job. In terms of the instantaneous normal mode (INM) analysis [3,4], and a measure for quasilocalization, some of us have presented the evidence for the existence of resonant modes [5] and their characteristics [6] in simple dense fluids with short-range interactions. The resonant modes found in fluids are thus referred to as the instantaneous resonant modes (IRMs). With the same techniques, we have recently shown numerical evidence of the IRMs in high-temperature Ga liquids [7], in which the particle interactions are long range. The occurrence of the IRMs in Ga liquids is essentially determined by two factors: (A) a curvature dip in the repulsive core of the Ga pseudopotential, and (B) local volume expansion due to density fluctuation. In this paper, by analyzing local structures, we give a physical scenario on how the IRMs occur in Ga liquids.

The INMs of a system are obtained from diagonalizing the Hessian matrix of each instantaneous configuration. For a 3D system of particles interacting via the pairwise potential $\phi(r)$, the Hessian matrices are composed of the 3-dimensional matrices $K_{ij} = -\mathbf{t}(\vec{r}_{ij})$ for every pair of two particles i and j, which are functions of their relative position vectors, and $K_{ii} = -\sum_{i\neq l} K_{il}$. The curvature tensor $\mathbf{t}(\vec{r})$ can be decomposed into the longitudinal component $\mathbf{t}_{\mathrm{L}}(\vec{r}) = \phi''(r)\hat{r}\hat{r}$ and

*Corresponding author. Fax: +886-03-5720728.
E-mail address: tmw@cc.nctu.edu.tw (T.-M. Wu).

0921-4526/02/$ - see front matter
PII: S0921-4526(02)00586-0

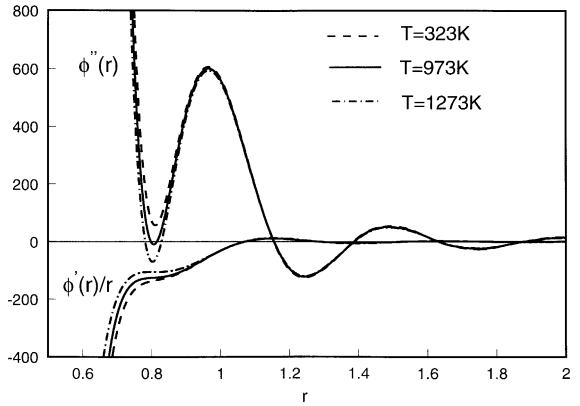

Fig. 1. The longitudinal (ϕ'') and transverse (ϕ'/r) curvatures of the Ga pseudopotential at three temperatures. The unit of energy is about 47 K and that of length (σ) is about 4.05 Å.

the transverse one $\mathbf{t}_T(\vec{r}) = \phi'(r)/r\ (\mathbf{I}_3 - \hat{r}\hat{r})$, where $\hat{r}$ is the unit vector along $\vec{r}$, and $\mathbf{I}_3$ is the 3-dimensional unit matrix [3]. The longitudinal and transverse components are, respectively, associated with the vibrational and rotational motions between two particles. Fig. 1 shows the temperature dependence of the longitudinal and transverse curvatures of a first-principle calculated Ga pseudopotential [8], with which the experimental structure factors of Ga liquids are reproduced with accuracy, including the shoulder on the high-q side of the first peak at temperatures just above the melting point. It is clear that the function of the longitudinal curvature has a sharp dip near 0.8σ in the repulsive core. The significance of this curvature dip stands for a dramatical drop in the vibrational force constant as the separation of a Ga pair is close to the dip.

With the pseudopotential, we have carried out molecular dynamics (MD) simulations of the Ga liquid systems at constant pressure (about 1 bar) and several different temperatures [7,8]. The INM densities of states (DOS) of Ga liquids were calculated and are presented in Fig. 2(A). In terms of the INM eigenvectors, we have defined a measure, called the reduced participation ration (RPR) [5], for distinguishing between the quasilocalized and extended modes with similar frequencies, whose RPR values are at the extreme limits of 0 and 1, respectively. We, thus, refer the IRMs as

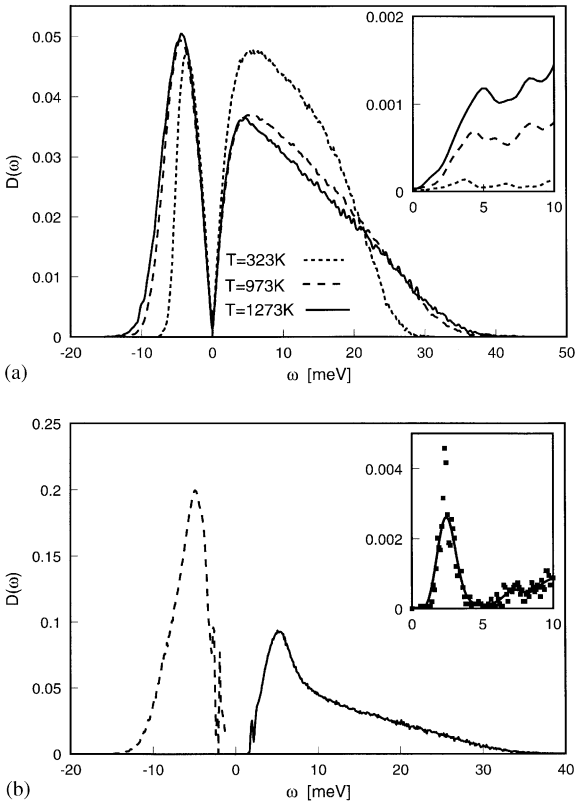

Fig. 2. Different kinds of INM DOS of Ga liquids: (a) the INM DOS due to the full Hessian matrices and the corresponding IRM DOS (in the inset) at three temperatures [7], (b) the INM DOS due to the longitudinal component (the real-frequency lobe) or the transverse one (the imaginary-frequency lobe) of the Hessian at $T = 973$ K. The IRM DOS due to the longitudinal component is shown in the inset, in which the symbols are obtained from MD simulation and the solid line is their smoothed result.

those low-frequency INMs with the RPRs <0.5 [5]. The IRM DOS of Ga liquid, which increases with temperature, is shown in the inset of Fig. 2(A). Truncating out the long-range Friedel oscillations in the Ga pseudopotential makes the structures of the IRM DOS more apparent and their positions in frequency slightly shift toward zero [7]. In Fig. 2(B), the two well-separated lobes corresponding to the real and imaginary frequencies are, respectively, the INM DOS calculated with the longitudinal component only and the transverse only of the Hessian matrices of a Ga liquid. However, only the longitudinal

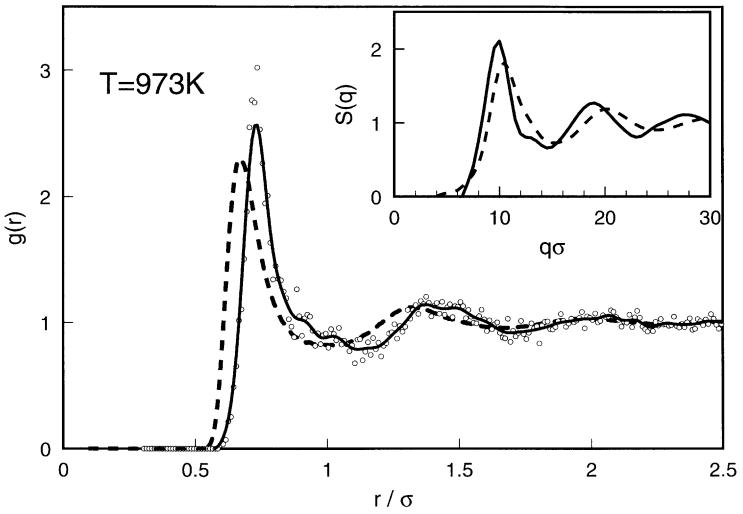

Fig. 3. The radial distribution functions $g(r)$ (the dashed line) and $g_{\mathrm{irm}}(r)$ (the circles) of Ga liquid at $T = 973\,\mathrm{K}$. The solid lines are obtained from smoothing the circles. The structure factors, shown in the inset, are calculated from $g(r)$ and $g_{\mathrm{irm}}(r)$, respectively.

components give rise to the IRMs, whose DOS is shown in the inset of Fig. 2(B). Thus, it is very clear that the curvature dip in the longitudinal component is responsible for the occurrence of the IRMs.

Fig. 3 shows the comparison of the radial distribution functions $g(r)$ and $g_{\mathrm{irm}}(r)$, which are, respectively, averaged for all particles and the central particles of the IRMs only. Relative to $g(r)$, $g_{\mathrm{irm}}(r)$ has an outward shift in the first shell and slight in the second shell, which are accompanied with small ripples next to the maximum of each shell. The corresponding signatures in structure factor (in the inset of Fig. 3) are found to be an overall shift toward small q and the presence of a hump in between the first and second maxima. These naive features in local structures originated from the local volume expansion due to density fluctuation. This can be understood from the geometric analyses on the local structures of the particles in Ga liquids. As shown in Fig. 4, the Voronoi cell volumes of the central particles of IRMs at $T = 973\,\mathrm{K}$ are mostly distributed above the averaged cell volume of the liquid. Also, according to the coordination-number distributions shown in the inset of Fig. 4, the central particles of the IRMs at $T = 973\,\mathrm{K}$ possess less coordination numbers than those of non-central

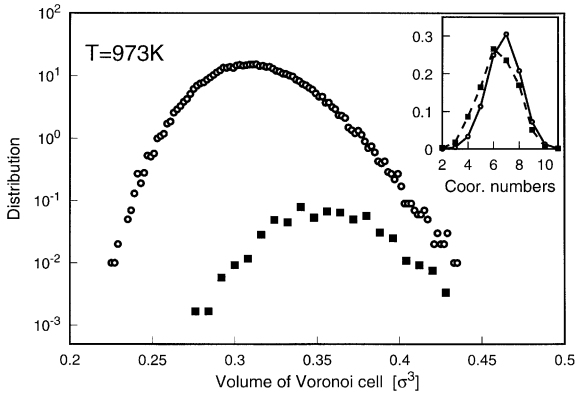

Fig. 4. The distribution of Voronoi cell volume, plotted in logarithmic scale, and that of coordination numbers (in the inset) with the cutoff at 0.8σ of Ga liquid at $T = 973\,\mathrm{K}$. The open circles and the filled squares are, respectively, for all particles and the central particles of the IRMs only.

particles. However, the difference in coordination numbers between these two groups of particles reduces as temperature is lowered.

Once the neighbors of a particle are pushed into the curvature-dip region due to local volume expansion, the force constants between this particle and its neighbors become much smaller, and the center of a quasilocalized vibrational mode is generated. This is how the special local structures produce the IRMs in Ga liquids.

We conclude that the quasilocalized IRMs in Ga liquids are resulting from the cooperation of two factors: the curvature dip in the repulsive core, which creates a region of weak coupling in vibrations between particles, and the local volume expansion, which pushes more neighbors of the central particle of an IRM into the weak-coupling region.

Acknowledgements

T.M. Wu would like to acknowledge support from the National Science Council of Taiwan, ROC under Grant No. NSC 90-2112-M009020.

References

[1] J. Jäckle, in: W.A. Phillips (Ed.), Amorphous Solids: Low Temperature Properties, Springer, Berlin, 1981.
[2] A.P. Sokolov, et al., Phys. Rev. Lett. 71 (1993) 2062.
[3] Y. Wan, R.M. Stratt, J. Chem. Phys. 100 (1994) 5123.
[4] T. Keyes, J. Phys. Chem. 101 (1997) 2921.
[5] T.M. Wu, W.J. Ma, J. Chem. Phys. 110 (1999) 447.
[6] T.M. Wu, W.J. Ma, S.L. Chang, J. Chem. Phys. 113 (2000) 274.
[7] T.M. Wu, S.F. Tsay, S.L. Chang, W.J. Ma, Phys. Rev. B 64 (2001) 064204.
[8] S.F. Tsay, S. Wang, Phys. Rev. B 50 (1994) 108.