行政院國家科學委員會補助專題研究計畫成果報告

※※※※※※※※※※※※※※※※※※※※※※※※※
※　　　　　　　　　　　　　　　　　　　　　　　※

※　　　　短程力液體內瞬間共振模之探討　　　　※

※　　　　　　　　　　　　　　　　　　　　　　　※
※※※※※※※※※※※※※※※※※※※※※※※※※

計畫類別：個別型計畫
計畫編號：NSC　89－2112－M－009－042
執行期間： 89 **年** 8 **月** 1 **日　至**　90 **年** 7 **月** 31 **日**

計畫主持人：吳天鳴　教授

本成果報告包括以下應繳交之附件：
- □赴國外出差或研習心得報告一份
- □赴大陸地區出差或研習心得報告一份
- □X 出席國際學術會議心得報告及發表之論文各一份
- □國際合作研究計畫國外研究報告書一份

執行單位：國立交通大學物理研究所

中　華　民　國　　90 **年** 10 **月** 27 **日**

行政院國家科學委員會專題研究計畫成果報告

國科會專題研究計畫成果報告撰寫格式說明

Preparation of NSC Project Reports

計畫編號：NSC 89-2112-M-009-042
執行期限：89 年 8 月 1 日 至 90 年 7 月 31

主持人：吳天鳴 教授 國立交通大學物理研究所
計畫參與人員：張世良博士研究生 國立交通大學物理研究所

一、中文摘要

我們已研討液體內瞬間共振模和粒子間作用力長短的關係

關鍵詞: 瞬間共振模，短程作用力，相互最臨近配對

Abstract

We have studied the dependence of the instantaneous resonant mode DOS with the interaction ranges between particles. The cusps found in the INM DOS in the low-density fluids are interpreted with the mutual nearest-neighbor pairs.

Keywords: Instantaneous resonant modes,
Short-ranged interaction,
Mutual-Nearest-Neighbor Pair.

二、緣由與目的

In recent years, the analysis of liquid dynamics in terms of instantaneous normal modes (INMs) has attracted much attention [1,2]. The frequencies of the INMs are the square roots of the Hessian matrices, the curvature tensors of the potential energy surface. Usually, the INMs of a liquid are obtained from the diagonalization of the Hessian matrix of each configuration generated by computer simulations, and after an ensemble average, the density of states (DOS) of the INMs is obtained.

Recently, we have presented the numerical evidence for the instantaneous resonant modes (IRMs), which are the low-frequency, quasilocalized INMs, in truncated Lennard-Jones (TLJ) fluids [3] and high-temperature Ga liquid [4], and their character [5]. In this project, we have studied the IRMs in fluids with short-ranged interactions, which are models of many realistic physical systems, like Colloidal dispersions [6].

The model potential we studied is the Lennard-Jones (LJ) 2n-n potential, $ö(r)=4å[(ó/r)^{2n} - (ó/r)^{n}]$, which has an attractive well with a fixed depth å but variable interaction range with the scale of the particle size ó. As n=6, the model potential becomes to be the ordinary LJ potential. The interaction range becomes shorter as n increases. The phase diagram, structural factors, and dynamical properties of the LJ 2n-n systems have been well studied in Ref. [7].

A resonant mode is resulted from the hybridization of a localized vibrational motion with the extended ones due to some anharmonic interactions. Thus, resonant modes have the character intermediate between the localized and the extended modes. In terms of the INM eigenvectors, we defined a measure, called the reduced participation ratio (RPR) [3], for distinguishing between the quasilocalized and extended INMs with similar frequencies, whose RPR values are at the extreme limits of 0 and 1, respectively. With this measure, the IRMs were found in the TLJ fluids, but never found in the LJ dense fluids. It has been shown [5] that in simple dense fluids with short-ranged pair interactions, each IRM, created by local density fluctuation, has a local structure with a barely-isolated central particle, which Voronoi-cell volume is larger than the average. If the short-ranged interaction is purely repulsive, the IRMs only occur in the imaginary-frequency lobe; however, a tiny attractive well in the pair potential will make the IRMs penetrate into the real-frequency lobe.

Another reason to study the INMs in systems with short-ranged interactions is that the physical meanings of the imaginary –frequency INMs are still unclear. What we know about them is that the projected potential energy profile for an imaginary-frequency INM is on the top of a barrier. In this project, we decomposed the INM DOS into those from the mutual-nearest-neighbor (MNN) pairs, suggested by Stratt [8], which are the two particles as nearest neighbor for each other, and those not. As the range of the pair interaction becomes short, the collective effects on the INMs are reduced. So, we expect that the decomposition of the DOS will provide useful information to understand the physical meaning of the imaginary-frequency INMs.

三、結果與討論

We have carried out a series of molecular dynamics simulations for the LJ 2n-n systems. The details of the simulations are referred to Ref. [9]. The INM DOS of the LJ 6-12 fluids at several densities are shown in Fig. 1.

In terms of the RPR, the DOS of the INMs with the

RPRs less than 0.1 in those LJ 6-12 fluids are shown in Fig. 2, and the DOS of the INMs with RPRs less than 1, 0.5 and 0.1 in the LJ 6-12 fluid at reduced density ñ*=0.3
are shown in the inset of Fig. 2.

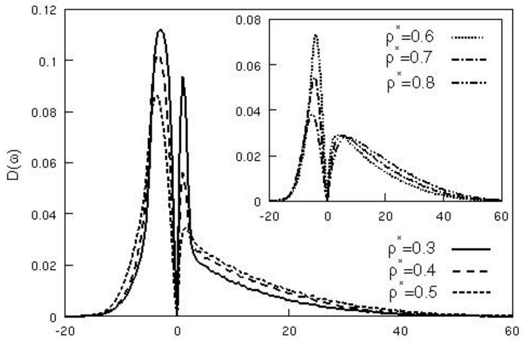

Fig. 1 The INM DOS of the LJ 6-12 fluids at T*=1.4. ù$_0$=(å/mó^2)$^{1/2}$, where m is the
mass of the particles.

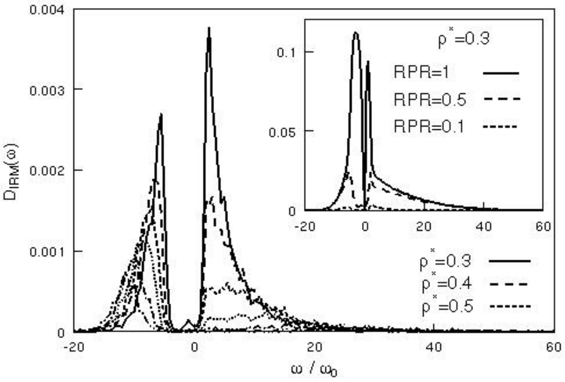

Fig. 2 The IRM (RPR less than 0.1) DOS of the LJ 6-12 fluids at various densities. The inset shows the INM DOS of the fluid at low density for RPRs less than 1, 0.5 or 0.1.

Apparently, the higher the density of the fluid is, the smaller the DOS of the IRMs is. At ñ*=0.8, the IRM DOS of the real-frequency lobe is rather rare.

The INM DOS of the LJ 12-24 and 18-36 fluids at low and densities are given in Fig. 3.
At low density (ñ*=0.3), the shape of the DOS of the real-frequency lobe consists of two parts: a very high value in DOS at low frequencies and an extremely long following tail with rather low value. At the case of the LJ 18-36 fluid, some cusps, which are very like the Van Hove singularity in the phonon DOS of crystalline [10], appears; as density increases, the cusps are smeared out. The IRM DOS of these two fluids with short rangeed interactions are also shown in Fig. 3.
Comparing the real–frequency IRM DOS of these three kinds of fluids at the same density, we conclude that as the range of the particle interactions is reduced the IRM DOS increases.

In order to understanding the cusps found in the LJ 18-36 fluid at low density, with the first-order perturbation theory as described in Ref. [9], we have calculated the normal-mode DOS of the MNN pairs, which consists of two branches for the rotational and vibrational motions of a pair. The DOS of the MNN pairs also create cusps almost at the positions of those in the INM DOS. Thus, it is very conceivable that the cusps in the INM DOS are originated from the MNN pairs in the fluid.

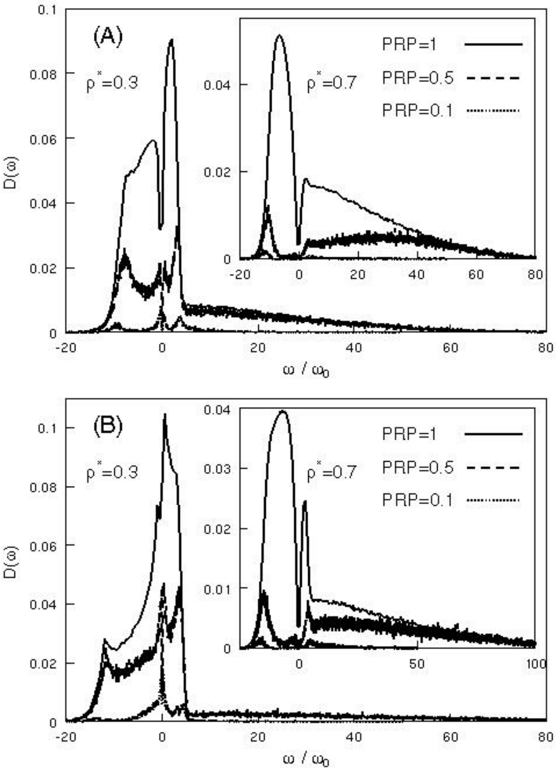

Fig. 3 The INM DOS of the LJ 12-24 fluid at T*=0.7 (A) and 18-36 fluid at T*=1.0 (B) at low and high (in the insets) densities with RPRs less than 1, 0.5 and 0.1, respectively.

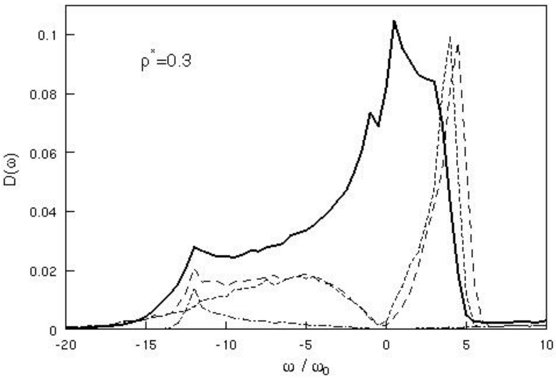

Fig. 4 Comparison of the INM DOS of the LJ 18-36 fluid at low density (solid line) with the normal-mode DOS of the MNN pairs [8] in the fluid (dashed line). The normal-mode DOS is calculated with the first-order perturbation theory as described in Ref. [8]. The dot-dashed and the short-dashed lines are the

contributions of the vibrational and rotational modes of the MNN pairs, respectively.

In conclusion, we have calculated the INM and IRM DOS of the fluids with short-ranged interactions. We conclude that the IRMs may exist in the fluid as the range of the interaction is short enough and disappear as the range increases. Also, the cusps in the INM DOS of the short-ranged fluids at low densities are resulted from the MNN pairs in the fluid.

四、參考文獻

[1] R. M. Stratt, *Acc. Chem. Res.* **28**, 201 (1995) and references therein.
[2] T. Keyes, *J. Phys. Chem.* **101**, 2921 (1997).
[3] T. M. Wu and W. J. Ma, *J. Chem. Phys.* **110**, 447 (1999).
[4] T. M. Wu, S. F. Tsay, S. L. Chang, and W. J. Ma, *Phys Rev. B* **64**, 064204 (2001).
[5] T. M. Wu, W. J. Ma, and S. L. Chang, *J. Chem. Phys.* **113**, 274 (2000).
[6] J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier Science, Amsterdam, 1996)
[7] G. A. Viegenthart, J. F. M. Lodge, and H. N. W. Lekkerkerker, Physica A **263**, 378 (1999).
[8] R. E. Larsen, E. F. David, G. Goodyear, and R. M. Stratt, J. Chem Phys **107**, 524 (1997).
[9] T. M. Wu and S. L. Chang, Phys. Rev. E **59**, 2993 (1999).
[10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College Pub. 1976)