

## Instantaneous normal modes of Na in supercooled liquid and glassy states

Ten-Ming Wu

*Institute of Physics, National Chiao-Tung University, HsinChu, Taiwan 300, Republic of China*

Shiow-Fon Tsay

*Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan, 80424 Republic of China*

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The instantaneous-normal-mode (INM) densities of states (DOS) of Na in the supercooled-liquid and glassy states under constant pressure have been calculated via molecular-dynamics simulation, with a rapid quenching rate for the glassy states. In the glassy states, at frequencies less than  $\omega_m$ , the frequency corresponding to the lowest-lying traveling waves permitted by the simulated system, the real-frequency INM DOS, strongly deviates from the liquidlike behavior, which is linearly dependent in frequency, but still has a great enhancement as compared with the phonon DOS of the Debye model for crystals. At  $T=5$  K, peaks in the distribution of the INM participation ratio are observed at frequencies around  $\omega_m$  and  $\sqrt{2}\omega_m$ , the latter corresponding to the second lowest-lying traveling waves. [S0163-1829(98)05325-9]

At low temperatures, many phonon-related properties, such as specific heat, thermal conductivity, and Raman spectra of amorphous materials behave quite anomalously from their crystalline counterparts. These anomalous behaviors are, at present, interpreted as resulting from some excess disorder-induced vibrational modes at low frequencies, as compared with the Debye model.<sup>1,2</sup> Usually, in terms of molecular-dynamics (MD) techniques, the density of states (DOS) of harmonic vibrational modes in the glassy states are calculated with the steepest-descent approach, in which the vibrational modes are restricted to potential local minima. Therefore, in such an approach, only the stable modes exist and are referred to as quenched normal modes (QNM's).<sup>3</sup> For the soft-sphere glasses, the DOS of QNM's at low frequencies has been shown to behave intermediately between that of the Debye model and the linear frequency dependence.<sup>4,5</sup>

In recent years, there has been a great interest in studying the vibrational DOS in disordered (liquids and glasses) systems in terms of the instantaneous-normal-mode (INM) approach.<sup>6,7</sup> In general, the INM DOS consists of two lobes, corresponding to the stable (real frequency) and the unstable (imaginary frequency) modes, and has a linear dependence in the low-frequency range for both lobes, with the thermodynamic state of the system being in the liquid or supercooled-liquid phases. Bembenek and Laird have used the INM approach to study the soft-sphere systems.<sup>8</sup> The low-frequency INM DOS of the real-frequency lobe they presented showed an almost linear frequency dependence from the temperature above the melting point down to almost zero temperature. In principle, as temperature decreases, the DOS of INM's should approach that of QNM's. Thus, in the glassy states, the behavior of the stable INM DOS at low frequencies should deviate from the linear dependence. Recently, we have reported the INM DOS of Na liquid.<sup>9</sup> In the present paper, in order to explore the feature of the INM DOS at temperatures lower than the glass transition temperature, we report the INM DOS of Na in the supercooled-liquid and

glassy states, by reducing the temperature of the system down to 5 K with a rapid quenching rate in computer simulation.

A system of 375 Na atoms, subject to periodic boundary conditions and interacting via an interatomic pseudopotential as described in Ref. 9, was simulated by means of MD techniques with the velocity-Verlet algorithm. First, the system was prepared in an equilibrated thermodynamic state at  $T=378$  K (just above the melting temperature) by running about 20 000 time steps (each time step=5 fs). From this equilibrated state, ten different configurations were extracted as the initial seed configurations for quenching. With each initial liquid configuration, we used the damped-force method<sup>10</sup> to quench the system to the desired temperature with a rapid cooling rate of  $6 \times 10^{13}$  K/s, followed by another equilibration run of 10 000 time steps. The pressure of the system during quenching was found to be very sensitive to the mean atomic volume. In this work, the pressure was kept constant at 1 bar with a fluctuation about 15%. For the supercooled liquid states, which will be described later, 200 configurations were extracted with an interval of 100 time steps. For the glassy states, 20 configurations were extracted in the same manner as for the supercooled-liquid state, except for repeating the same procedure with each of the ten different initial seed configurations. Care was taken to exclude those crystallized configurations during each procedure.

The values of internal energy  $E$  as a function  $T$  are shown in Fig. 1, in which the circles are the results of MD simulation, calculated as in Ref. 11, and the smoothed curve was obtained from  $E=c_0+c_1T+c_2T^2$  using the standard least-squares regression method. Compared to this smoothed curve, the fluctuation of the simulated results is overall small (less than 0.1%). Through the function of  $E(T)$ , the liquid-to-glass transition for the present MD simulation was found to occur around  $T=130$  K, which is close to the transition temperature reported early for the rapidly quenched and the pressure-induced Na glasses.<sup>12</sup> To determine the occurrence of the liquid-to-glass transition more clearly, the self-

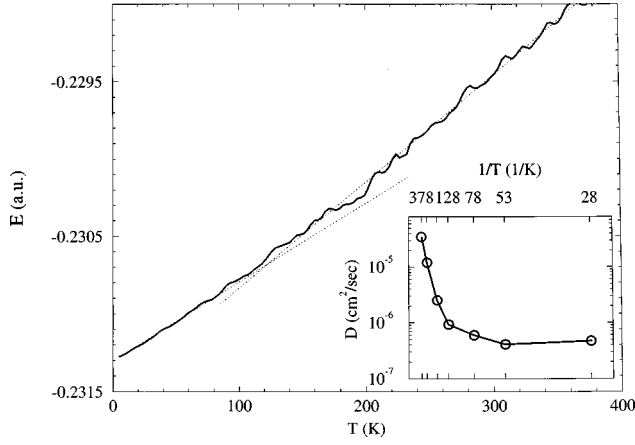


FIG. 1. The value of  $E(T)$ , determined as described in the text, for the presently considered rapidly quenched Na metal. The energy scale is in units of a.u.  $\equiv 4.357 \times 10^{-18}$  J. In the inset, the temperature dependence of self-diffusion coefficient as obtained from the mean-square displacement calculated by MD simulation.

diffusion coefficient was calculated by performing another run of 20 000 time steps from the configurations recorded at each temperature in the present MD simulation; the results for several temperatures are given in the inset of Fig. 1. This lends support to the regions given in Fig. 1 for the glassy and supercooled-liquid states for the rapidly quenched Na metal in the present consideration. We have done the analysis for the time dependence of atomic mean-square displacements and the pair-distribution functions, and the results give the same conclusion on the two regions.

The details of the procedure for calculating the INM DOS  $D(\omega)$  from the MD generated configurations is given in Ref. 9. The calculated  $D(\omega)$  spectra for Na in two supercooled-liquid and three glassy states, with temperatures ranging from 278 to 5 K, are presented in Fig. 2. As the system is still in the supercooled-liquid state, the INM DOS of the real-frequency lobe,  $D_s(\omega)$ , is still linear in frequency in the low-frequency range, and no structures appear in the high-frequency range. In the glassy states, as temperature decreases, the behavior of  $D_s(\omega)$  gradually deviates from the

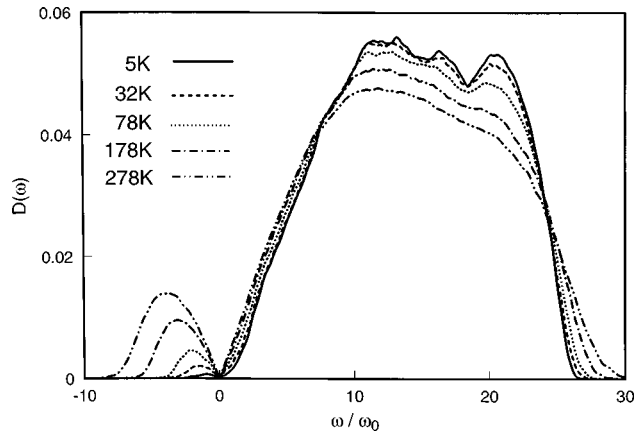


FIG. 2. The configuration-averaged INM DOS of Na in two supercooled-liquid and three glassy states. As usual, the real-frequency lobe is plotted along the positive frequency axis and the imaginary-frequency lobe is plotted along the negative frequency axis. The frequency unit  $\omega_0$  is  $1.173 \text{ ps}^{-1}$ .

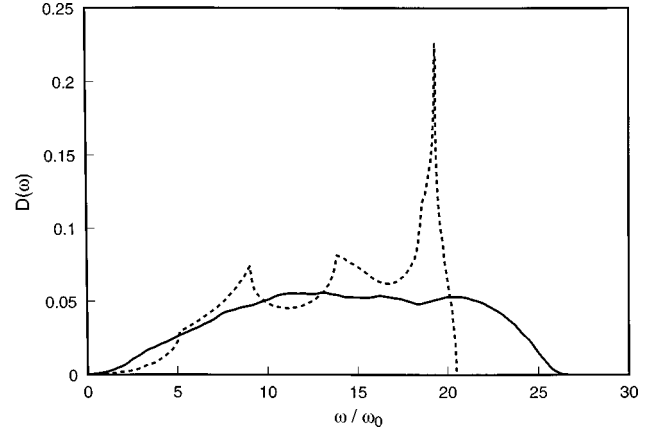


FIG. 3. The calculated real-frequency INM DOS of Na glass at  $T=5$  K (solid line) compared with the phonon DOS of Na crystal (dashed line), which is taken from Ref. 13. Both areas under the curves are normalized to be one.

linear dependence for  $\omega < 3.5\omega_0$ , and some weak structures appear for  $\omega > 10\omega_0$ , where  $\omega_0 = 1.173 \text{ ps}^{-1}$ .  $D_s(\omega)$  calculated at  $T=5$  K is compared in Fig. 3 with the phonon DOS of Na crystal.<sup>13</sup> Figure 3 clearly shows that the low-frequency  $D_s(\omega)$  in the glassy states is enhanced as compared with the phonon DOS of the Debye model. In the presently simulated Na glasses, the short-range order, which essentially determines the vibrational properties, is not strong enough to produce the features of the Van Hove singularities observed in the crystalline phonon DOS. On the other hand, for the imaginary-frequency lobe, the change of the unstable INM DOS,  $D_u(\omega)$ , with temperature does not show any discontinuity, and the ratio of the unstable-mode fraction decreases from 6.5% to less than 0.2%, as the temperature of the system decreases from 278 to 5 K.

The spatial extension of an INM is measured by its participation ratio<sup>3</sup>

$$p_\alpha = \left( N \sum_{j=1}^N (\mathbf{e}_j^\alpha \cdot \mathbf{e}_j^\alpha)^2 \right)^{-1}, \quad (1)$$

where  $\mathbf{e}_j^\alpha$  is the projection of the normalized eigenvector of the INM labeled  $\alpha$  on atom  $j$ . For an INM extended in space,  $p_\alpha$  is independent of the system size. For a localized INM,  $p_\alpha$  is inversely scaled with  $N$ , the total particle number. After an ensemble average is made over all instantaneous configurations, the averaged participation ratio of INM's with frequency  $\omega$  is defined as<sup>9,14,15</sup>

$$p(\omega) = \frac{\langle \sum_{\alpha=1}^{3N} p_\alpha \delta(\omega - \omega_\alpha) \rangle}{D(\omega)}. \quad (2)$$

For Na liquid, the distribution of  $p(\omega)$  has been presented in Ref. 9. From the study of the size dependence on  $p(\omega)$ , it is found that the INM's with  $p(\omega)$  less than 3%, which only occur in the high-frequency ends of both the real-frequency and the imaginary-frequency lobes, are localized modes; the INM's with  $p(\omega)$  larger than 40%, which occur in the small-frequency regions of both lobes, are extended modes. Between the localized-mode and the extended-mode regions in frequency, there is a transition region in which the characteristic of the INM changes from extended to localized in

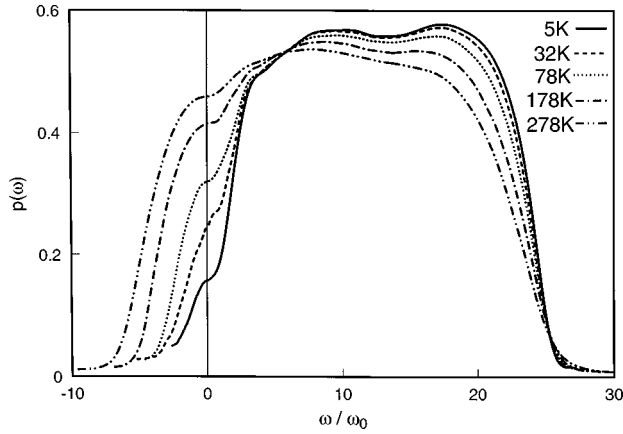


FIG. 4. The averaged participation ratio of Na in the thermodynamic states as for the DOS in Fig. 2.

space. The spatial extensions of the localized INM's and the INM's in the transition region have been shown in Ref. 14. The excited particles involved in a localized INM have been proved to reside almost all within the first nearest-neighbor shell of the particle with the largest projection component; an INM in the transition region has more than one excited centers, with the spatial extension of each center from the central particle to the second or high-order shell.

The averaged INM participation ratio  $p(\omega)$  of Na in the thermodynamic states as for the DOS in Fig. 2 are given in Fig. 4. The curves in Fig. 4 are obtained by smoothing the original MD simulation data, with the detail as described in Ref. 9. However, we should make a note of caution here that the degenerate zero-frequency modes, which correspond to translation of the system's center of mass, have been removed. In the supercooled-liquid states, by assuming that the limit percentages of  $p(\omega)$  for the localized and extended INM's are the same as those of the liquid states, the averaged number of particles involved in a localized INM is about ten or less. Also, as temperature decreases, the transition region in the imaginary-frequency lobe moves toward smaller frequencies. In the glassy states, from the stable modes with real frequencies less than  $3\omega_0$  to all of the unstable modes,  $p(\omega)$  drops rapidly with decreasing temperature, and the fluctuation of the original simulation data grows (the simulation data for  $T=5$  K are shown in Fig. 5). The lower limit of  $p(\omega)$  in the imaginary-frequency lobe, which corresponds to the smallest averaged number of the excited particles in a localized unstable INM, increases with decreasing temperature.

In order to study the size dependence of small-frequency  $D(\omega)$  and  $p(\omega)$  in the glassy states, we did a MD simulation for two larger sizes,  $N=750$  and  $1200$ , of Na glasses at  $T=5$  K with the same cooling rate as for  $N=375$ , from which for  $N=1200$  a total of 105 configurations were extracted from seven different liquid seed configurations.

The calculated  $D(\omega)$  and  $p(\omega)$  for the three different sizes are presented in Fig. 5. We found that for each of these three different-size Na glasses the  $D_s(\omega)$  with frequencies less than  $\omega_m$ , as indicated in Fig. 5, are strongly deviated from linear frequency dependence, and correspondingly  $p(\omega)$  has a peak around  $\omega_m$ . The peak in  $p(\omega)$  was also observed by Schorber and Oligschleger for the QMN's in the

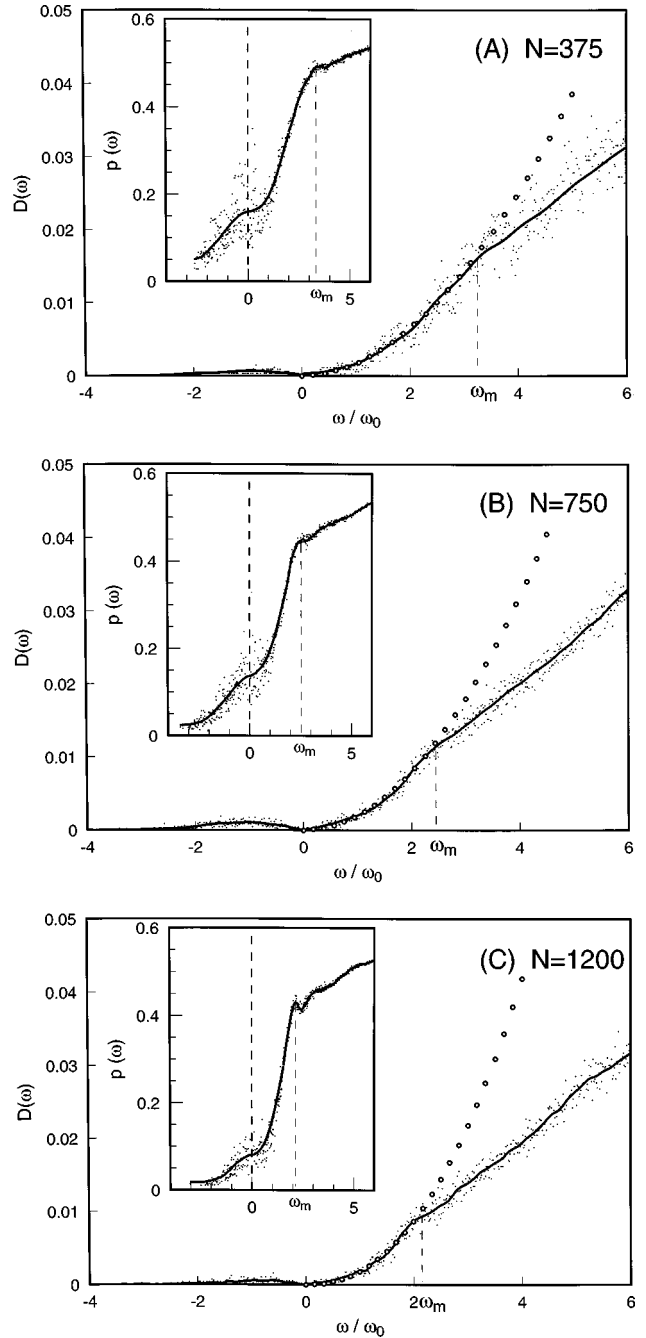


FIG. 5. The size dependence on the small frequency  $D(\omega)$  and  $p(\omega)$ , given in the inset, of Na glass at  $T=5$  K for  $N=375$  (a),  $750$  (b), and  $1200$  (c), respectively. In each part, the dotted points are the original simulation results and the solid curve, to guide the eye, is obtained by smoothing the dotted points with the fast-Fourier transform program as described in Ref. 9. The open circles are calculated with the fit functions  $0.0017(\omega/\omega_0)^{1.94}$  (a),  $0.002(\omega/\omega_0)^2$  (b), and  $0.0018(\omega/\omega_0)^{2.23}$  (c). The indicated  $\omega_m$  are  $3.23\omega_0$  (a),  $2.5\omega_0$  (b), and  $2.14\omega_0$  (c), respectively.

soft-sphere glasses.<sup>5</sup> For  $N=375$ ,  $750$ , and  $1200$ , the values of  $\omega_m$  are estimated to be  $3.23\omega_0$ ,  $2.5\omega_0$  and  $2.14\omega_0$ , respectively. With these data,  $\omega_m$  was found to be inversely proportional to  $N^{1/3}$ , or  $L$ , the length of the simulation box. This result suggests that  $\omega_m$  is determined by the lowest-lying traveling waves with wave vectors in the  $(1,0,0)$  directions and wavelengths of  $L$ . For frequencies less than  $\omega_m$ ,

the  $D_s(\omega)$  were fit with the function  $A(\omega/\omega_0)^\eta$  with  $A$  and  $\eta$  as two fitting parameters.  $\eta$  for the three sizes was found to be around 2; however, the fit value increases about 15% as  $N$  increases from 375 to 1200. For frequencies between  $\omega_m$  and  $6\omega_0$ ,  $D_s(\omega)$  is almost linear in frequency with the same slope for the three different sizes.

Through the ratio of  $p(\omega)$  of  $N=750$  and 1200, we find that at  $T=5$  K almost all of the imaginary-frequency INM's are localized modes with the averaged number of involved particles distributed roughly from 20 to less than 100. The characteristic of the real-frequency INM's changes from localized to extended in space with frequency less than  $1\omega_0$  to larger than  $\omega_m$ , which depends on the system size. For  $N=1200$ , we can clearly see a dip in the function of  $p(\omega)$  between the peak around  $\omega_m$  and the second peak around  $3\omega_0$ , which is about  $\sqrt{2}\omega_m$ . This second peak corresponds to the traveling waves with the wave vectors in the (1,1,0) directions. Although there are some more ripples beyond the second peak, the signal is too weak to allow any significant conclusions.

In conclusion, we have performed the calculation for the INM DOS of Na in the supercooled-liquid and glassy states at constant pressure. Comparing the real-frequency part of the INM DOS  $D_s(\omega)$  with the phonon DOS of Na crystal clearly shows that in the glassy states there is an excess of the vibrational states at low frequencies. Our analysis indicates that in the supercooled-liquid state the behavior of  $D_s(\omega)$  at low frequencies is still linear in  $\omega$  and the distribution function of participation ratio  $p(\omega)$  behaves more like that in the liquid phase.<sup>9</sup> In the glassy states, above  $\omega_m$ , the frequency corresponding to the lowest-lying traveling wave permitted by the simulation box, the behavior of  $D_s(\omega)$  is

still more like those of supercooled liquids. This indicates that in our simulation the configurations in glassy states are almost as disordered as in the supercooled-liquid state. However, below  $\omega_m$ , the behavior of  $D_s(\omega)$  strongly deviates from the linear frequency dependence and becomes more quadratic and size dependent. The cause is that the characteristics of INM's with frequencies less than  $\omega_m$  become quasilocalized. The lower the real frequency is, the more localized an INM is. This can be understood from the fast decay in  $p(\omega)$  at frequencies smaller than  $\omega_m$ . The stronger collective effects in Na systems<sup>16</sup> might be the reason for our results in the behavior of  $D_s(\omega)$  different from those of Bembenek and Laird for the soft-sphere model. On the other hand, in the glassy states, as temperature decreases, the values of  $p(\omega)$  in the imaginary-frequency lobe drop rapidly and the distribution shrinks toward smaller frequencies. However, the lower limit of  $p(\omega)$ , which corresponds to the smallest excited size of a localized unstable INM, increases with decreasing temperature. In the system with larger size, some peaks in the distribution of  $p(\omega)$  in the real-frequency lobe are observed around the frequencies corresponding to the lowest- and the second-lowest-lying traveling waves. These peaks were also observed for the QNM's in the soft-sphere glasses. Therefore, as temperature decreases down to zero, the INM's in a glass are expected to coincide with the QNM's.

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<sup>15</sup> This definition, it may be noted, is equivalent to averaging first the participation ratios of INM's within a frequency bin at  $\omega$  for a configuration, and then following by a configuration average, as long as the number of averaged configurations is large enough. We have checked this in our calculation.

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