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Dynamics of liquid and strongly supercooled alkali metals by instantaneous normal-mode analysis

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The spectrum of instantaneous normal modes has been evaluated by molecular dynamics simulation for cesium in liquid and glassy states. The velocity autocorrelation function derived from the real-frequency part of the spectrum compares favorably with that calculated directly from simulation data, especially for the glassy state. We have pushed this comparison to the first memory-function level. It appears that the normal-mode analysis gives the correct short-time behavior, where correlated binary collisions play an important role. Such agreement extends toward intermediate times in the glassy state, where solidlike features are manifested by strong oscillations.

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In recent years, the interpretation of the dynamical properties of disordered systems (liquids and glasses) in terms of instantaneous normal modes (INM's) has attracted considerable attention [1–3]. Although such an approach can only provide quantitative descriptions of the short-time behavior of the correlation of any dynamical variable, some attempts have been made towards the characterization of the overall time behavior from knowledge of the INM spectrum [2,3]. The portion of the spectrum corresponding to "unstable" modes, that is, those with imaginary frequencies, is known to lead to divergences of the correlation functions, and has been related to some thermostatic properties, e.g., the average potential energy and the constant-volume heat capacity [2(e)], or even to some long-time property such as the self-diffusion coefficient [1]. On the other hand, relevant information regarding the microscopic dynamics at short times, and especially that regarding collective motions, is contained in the spectrum of "stable" (real-frequency) modes.

This communication reports the results of a molecular dynamics (MD) investigation of alkali metals in liquid and glassy states, a choice stemming from experimental evidence showing that even after melting they can support collective excitations at wavelengths as short as the average separation between neighboring atoms [4,5]. The choosing of such a system was also motivated by the existence of clear scaling behavior for both static and dynamical properties [6], which enables one to extend the conclusions to all the other alkali metals.

A system of 250 Cs atoms in a cubic box of length $L = 31.1$ Å (corresponding to a density $= 1.83\ \mathrm{g\,cm^{-3}}$) at a temperature $T = 308$ K (close to the melting temperature) interacting via the potentials described in [7] was simulated by means of MD techniques. The spectrum of INM's was calculated from the eigenvalues of the Hessian matrix for a particular configuration during the MD run, repeating the procedure for 100 configurations and eventually performing an average. As is customarily done, the part of the frequency spectrum corresponding to negative eigenvalues leading to imaginary frequencies (unstable modes) is drawn on the negative frequency axis as shown in Fig. 1. As a first comment, a comparison with results regarding Lennard-Jones (LJ) systems [2(a),2(b)] serves to illustrate the sensitivity of the spectra to the model potential. In particular, the lobe of imaginary frequencies is strongly reduced for the alkali metals, indicating that the number of unstable modes is sensibly lower, and also the distribution of real frequencies becomes more symmetric, showing a more reduced high frequency tail. A relatively small fraction of unstable modes was also found in studies on some other more complicated cases such as liquid water by Cho *et al.* [1].

The Einstein frequency $\omega_E = 4.38\ \mathrm{ps}^{-1}$ is close to that where the distribution attains its maximum, and almost equal to half the maximum frequency represented in the spectrum. A similar comparison for the LJ system (where $\omega_E = 7.7\ \mathrm{ps}^{-1}$) shows that this characteristic frequency is still close to the frequency of the maximum of the dis-

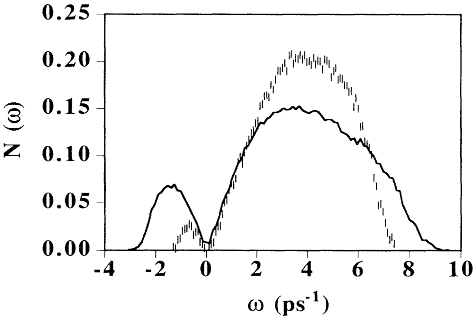

FIG. 1. Spectrum of the instantaneous normal modes $N(\omega)$ for Cs liquid near the melting point (solid line) and in the glassy state at $T = 20$ K (vertical bars). Both functions are normalized to unit area. On the negative x axis are represented the imaginary frequencies. The contribution of the translational modes at $\omega = 0$ has been subtracted.

tribution but located at very low frequency with respect to the maximum extent of the spectrum. This can be attributed to the more harmonic character of the oscillations undergone by the Cs atoms. This behavior is even more emphasized, as also shown in the figure, if the system is brought into a glassy state by a rapid quench down to ≈ 20 K, which brings the final configuration close to a local minimum of the potential energy. As seen by comparison of the spectra for liquid and glass, the number of unstable modes strongly decreases upon vitrification, also leading to an increase in the frequency of the maximum and to a further reduction in the amplitude of the high frequency tail. In other words, a more symmetric spectrum of INM's with respect to its maximum develops after glassification. Similar features, observed even in the LJ system explored by Seeley and Keyes [2(a)], have been interpreted as a consequence of the fact that the atoms undergo a more harmonic motion when they are found close to a potential minimum.

As is well known, the attempt to reconstruct the velocity autocorrelation function (VACF) from the INM spectrum is deemed to fail for at least two intrinsic reasons. First, because the VACF spectrum has a normalized second moment which only coincides with that of the INM if the negative eigenvalues are taken into account. Therefore a VACF derived from the real part of the spectrum is expected to have a faster decay at short times. Secondly, the total area under this VACF is by definition equal to zero since at $\omega = 0$ the INM spectrum is zero. As a matter of fact, the VACF obtained in this way represents the single particle motion in a system in which the diffusion is forced to be zero since the atoms undergo only local oscillations. However, the information contained in such a VACF can be of help in modeling the overall single particle dynamics, as pointed out in [1] and more recently demonstrated by Keyes and co-workers [1], particularly in liquid alkali metals which show clearly solidlike features. The VACF calculated by Fourier transforming the positive lobe of the INM spectrum is compared with that obtained directly by the MD simulation in Fig. 2 for the liquid and glass states. The agreement between the two correlation functions is very good, taking account of the limitations referred to, the INM spectrum being able to reproduce the VACF behavior up to 1 ps in the liquid phase and even better (up to 1.5 ps) in the quenched system. Again, a comparison with similar results for the LJ system reported in Ref. [2(c)] [Figs. 3(a) and 3(b) of that reference] shows that liquid alkali metals seem a more natural benchmark with which to contrast the INM results than the highly anharmonic LJ systems. As a matter of fact, the VACF calculated from the spectrum of stable modes for LJ systems, whether in normal or supercooled liquid states, does not reproduce the position of the first (negative) minimum and in any case deviates from the MD one at shorter times than for Cs. It seems that little effort should be made in the case of alkali metals to modify the calculated VACF and obtain an almost perfect agreement with the true VACF. A possible heuristic route to follow would be the addition of a diffusivelike spectrum to account for the long-time behavior of the VACF. An attempt along this line will not be presented here, since we prefer to discuss a different approach, which gives in principle a deeper insight into the microscopic dynamical processes.

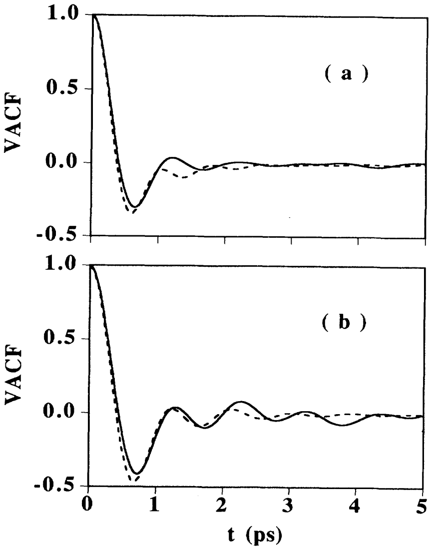

FIG. 2. Normalized velocity autocorrelation function for Cs in (a) liquid phase, (b) glass. The solid line shows the function as directly calculated from the MD run and the dashed line that calculated by Fourier transform of the normal-mode distribution for real frequencies.

Within the Mori-Zwanzig projection operator framework, the correlation function of any dynamical variable is shown to obey a generalized Langevin integrodifferential equation in which the crucial quantity is the memory function $M(t)$ whose time evolution develops in a subspace orthogonal to that of the variables of interest. If one could include all the slow-varying dynamical variables in the set of the relevant ones, then the dynamics at the level of the memory function would occur on a faster time scale and eventually a Markovian approximation could be applied. For the VACF, it is well known that its memory function shows two distinct time regimes, one at short times dominated by the binary collision dynamics and one at long times with a tail which accounts for the important correlations set up in the system [8]. In the past a big effort has been made in modeling this long-time tail, and indeed the mode-mode coupling approach has been successful in reproducing its behavior for a large variety of simple liquids [9–11]. On the other hand, the dynamics at short times is almost inevitably treated on a phenomenological basis. A simple picture in terms of isolated binary collisions is found to be unrealistic at liquid densities because of the lack of separation between the two relevant time scales, namely, the time between two successive collisions and the duration of a collision. A theoretical method to treat correlations between collisions in the very dense phase is therefore still lacking. Then it seems interesting to explore to what extent the dynamics described by the stable part of the INM spectrum can be representative of the above mentioned features of the VACF memory function. From the generalized Langevin equation one obtains the following expression for the Laplace transform of the normalized correlation function $C(t)$:

$$\hat{C}(z) = \frac{1}{z + \hat{M}(z)}, \tag{1}$$

$\hat{M}(z)$ being the Laplace transform of the memory function $M(t)$. From Eq. (1) the spectrum of $M(t)$, i.e., $M(\omega) = (1/\pi)\mathrm{Re}[\hat{M}(z = i\omega)]$, is given by

$$\mathrm{Re}[\hat{M}(z = i\omega)] = \frac{\mathrm{Re}[\hat{C}(z = i\omega)]}{\{\mathrm{Re}[\hat{C}(z = i\omega)]\}^2 + \{\mathrm{Im}[C(z = i\omega)]\}^2}, \tag{2}$$

where $\mathrm{Re}[\hat{C}(z = i\omega)]$ and $\mathrm{Im}[\hat{C}(z = i\omega)]$ are the cosine and sine transforms of $C(t)$, respectively. The Fourier transform of $M(\omega)$ will provide the required memory function. This procedure has been applied to the VACF calculated from the INM stable spectrum as well as to the one obtained directly from MD simulation. The results for liquid and quenched states are shown in Fig. 3. A first important observation is that the short-time dynamics of the MD memory function is almost perfectly reproduced by the corresponding quantity derived from the INM spectrum, especially for the quenched system. This finding supports the idea that, in common with some other cases explored so far like that of liquid water [1], a good description of the binary contribution can be achieved by the knowledge of the INM spectrum, that is, it contains all the dynamical effects induced in this time regime by correlated collisions. Furthermore, a comparison between results for the quenched and liquid memory functions shows that a solidlike oscillatory behavior becomes more and more evident in the quenched system. In fact the INM memory function in this condition is in agreement with the direct one even at intermediate times (of the order of 1.5 ps). It is worth pointing out that the different plateau levels of the reported memory functions have to be ascribed to the difference between the MD and INM memory function spectra in the low frequency range where $M(\omega \to 0) \propto 1/\mathrm{Re}[\hat{C}(\omega \to 0)]$. An unphysically large peak, which arises in the INM memory function spectrum since $\mathrm{Re}[\hat{C}(\omega \to 0)] \to 0$, can be removed if the first few (three) points of the spectrum are ignored and the remaining part is extrapolated to zero, something which leads to the memory function for the liquid shown by the dash-dot line of Fig. 3(a). The plateau is now in better agreement with the MD finding, at the expense of a poorer representation of the short-time dynamics.

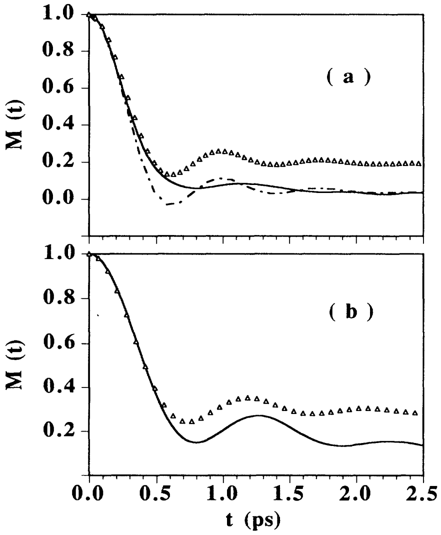

FIG. 3. Normalized memory function of the VACF for Cs in (a) liquid, (b) glass phases. The solid line shows the results from direct calculation, open triangles show those arising from the INM analysis, and the dash-dot line gives the result from INM analysis after an $\omega \to 0$ extrapolation, as described in the text.

As far as the intermediate time regime is concerned, the $M(t)$ memory function derived from the INM's for the liquid seems to overemphasize the oscillatory behavior, as attested by the oscillations for $1 \leq t \leq 2.5$ ps^{-1} which are stronger than those of the MD result. A quantitative understanding of the origin of these oscillations has been achieved from a mode-mode coupling analysis for wave vectors around the first and second peaks of the structure factor, where the intermediate scattering function shows a considerable slowing down [11], and therefore the INM results within this time window clearly underestimate the importance of slow decay processes in the single particle dynamics. However, it has also been pointed out that the success of such an approach is somehow dependent on the particular system under investigation. For liquid lead for example, mode-mode coupling calculations were not able to reproduce the features of the VACF memory function (mainly the deep first minimum) [12]. It has been argued that correlated binary collision effects set up in the short-time regime, not included in the mode-mode coupling approach, can be of overwhelming importance [13]. If, as we believe, the INM analysis gives the right short-time dynamics, a comparison between MD and INM memory functions for liquid lead would be useful to check the validity of this assumption.

In conclusion, we have shown that significant details regarding single particle dynamics are comprised in the stable part of the INM spectrum. In particular, at the level of the first memory function of the VACF, it gives the correct behavior in the short-time regime where correlated binary collision effects are assumed to be important. This holds true in liquid and glassy states, as is demonstrated by the present investigation. At intermediate times the solidlike form of the memory function is likely to give a realistic representation of the true memory function only for the glassy state. A comparison with the VACF data obtained for a LJ system or more complicated liquids [1] shows that liquid alkali metals seem to constitute far more adequate candidates to explore the capabilities of the INM approach, because of the clear experimental counterpart of the oscillatory behavior of these functions in such systems.

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