Longitudinal collective modes in simple liquid binary alloys: A computer simulation study

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The dynamic collective properties of the liquid Li$_{0.7}$-Mg$_{0.3}$ alloy are studied by molecular-dynamics simulation. The dynamic structure factors and longitudinal current correlations at wave vectors between the hydrodynamic and kinetic regime ($0.2<k<4$ Å$^{-1}$) are analyzed. In order to discuss the influence of the mass difference between particles on the longitudinal modes, the same alloy, except that the mass of the heavy atoms was increased by a factor of 10, was simulated. The resulting properties are compared with those of the ordinary Li$_{0.7}$-Mg$_{0.3}$ alloy. It is shown that at wave vectors prior to the hydrodynamic region both fast and slow longitudinal modes of kinetic character propagate through light and heavy particles, respectively. In the hydrodynamic limit fast and slow modes merge into a single acoustic mode. It is corroborated that fast propagating modes in disparate mass liquid mixtures have a kinetic character. The number-number and concentration-concentration time correlation functions were also determined. The former shows a behavior analogous to that of the corresponding function in one-component liquids. The second reflects the existence of propagating concentration modes.

I. INTRODUCTION

Molecular-dynamics (MD) simulation is a powerful tool to investigate the dynamic collective properties of liquids. MD is particularly useful to analyze these properties at intermediate wave vectors and frequencies, i.e., the same $k$-$\omega$ region that may be explored in neutron-scattering experiments. Recently, MD simulation has been extensively applied to the study of both the structure and the dynamic properties of liquid metals whereas liquid alloys have received less attention, especially in the case of dynamic collective properties. Since the pioneer MD simulation of Na-K liquid alloy the majority of studies have been centered on the alloy Li$_0$Pb. In a MD simulation of this system Bosse et al. observed the existence of high-frequency peaks in the partial Li-Li dynamic structure factors at rather large wave vectors. These peaks were associated with longitudinal modes that propagate through light particles with a velocity much higher than that of the ordinary sound (the so-called “fast sound”). In recent years this topic has been the subject of controversy. High-frequency modes were detected by neutron-scattering experiments in Li$_0$Pb and Li$_0$TI alloys as well as in binary rare-gas fluid mixtures by both neutron scattering and MD simulation. In addition, the existence of high-frequency modes beyond the hydrodynamic regime in disparate mass binary mixtures was predicted by kinetic theory. Recent MD calculations have suggested that fast modes propagating through the light particles have a nonhydrodynamic (kinetic) character and they are accompanied by slow modes involving the heavy particles.

One of the objectives of the present study is to analyze the dynamic collective properties of liquid Li-Mg at wave vectors and frequencies between the hydrodynamic and kinetic regions. This system may be considered as representative of simple “ideal” alloys since it does show neither the ionic character of Li-Pb (Ref. 11) nor the tendency to phase separation of Li-Na. In particular, we have simulated the Li$_{0.7}$Mg$_{0.3}$ alloy. To our knowledge there is no experimental information or MD results on the dynamic collective properties of this alloy. The study will be based on the MD results obtained with an interatomic potential that reproduces the main structural features of Li-Mg alloys. Another objective is to investigate the relationship between the differences in the atomic masses of the species in the mixture and the existence of fast and slow propagating longitudinal modes as well as the character of these modes. For this purpose we have also simulated the Li$_{0.7}$Mg$_{0.3}$ alloy, which is identical to Li$_{0.7}$Mg$_{0.3}$ except that the mass of the Mg atoms was increased by a factor of 10 (they will be termed Mg*). Then, the mass ratio in this system ($m_{\text{Mg}^*}/m_{\text{Li}}\approx 35$) is similar to that in the Li-Pb alloy ($m_{\text{Pb}}/m_{\text{Li}}\approx 30$).

II. COMPUTER SIMULATION DETAILS

MD simulations of the Li$_{0.7}$Mg$_{0.3}$ alloy at $T=887$ K and $\rho=4.071\times 10^{-2}$ Å$^{-3}$ were carried out. The system was made up of 570 particles enclosed in a cubic box with ordinary periodic boundary conditions. Effective interatomic pair potentials obtained according to the neutral pseudoatom method were used. These potentials, which are free of adjustable parameters, describe accurately the structure of liquid Li, Li-Na, and Li-Mg, and were successfully applied to the MD study of the dynamic collective properties of liquid Li (Ref. 16) and Li-Na. The partial intermediate scattering functions $[F^j(k,t); j = 1, 2; 1 = \text{Li}, 2 = \text{Mg}^*]$ as well as the partial longitudinal current correlation functions $[C^{ij}_L(k,t)]$ were calculated during the MD simulation runs according to the usual definitions. These properties were determined for 26 wave vectors ranging from $k=0.26$ Å$^{-1}$ to $k=3.97$ Å$^{-1}$, compatible with the periodic boundary conditions. The frequency-dependent spectra $[S^j(k,\omega), C^{ij}_L(k,\omega)]$ were obtained by Fourier transforming the corresponding time-dependent correlation functions. We have also analyzed the number density-concentration correlation functions, defined as.
FIG. 1. Partial intermediate scattering functions for the Li$_{0.7}$Mg$_{0.3}$ (lines) and Li$_{0.7}$Mg$_{0.3*}$ (dots) alloys.

\[
F_{\text{NN}}(k,t) = x_1 F^{11}(k,t) + x_2 F^{22}(k,t) + 2(x_1 x_2)^{1/2} F^{12}(k,t),
\]

\[
F_{\text{NC}}(k,t) = x_1 x_2 [F^{11}(k,t) - F^{22}(k,t) + (x_2 - x_1) \times (x_1 x_2)^{-1/2} F^{12}(k,t)],
\]

\[
F_{\text{CC}}(k,t) = x_1 x_2 [(x_2 - x_1) F^{11}(k,t) + x_1 F^{22}(k,t) - 2(x_1 x_2)^{1/2} F^{12}(k,t)],
\]

where $x_1$ and $x_2$ are the molar fractions of species 1 and 2, respectively. Analogous definitions were used for the other correlation functions and corresponding spectra. It should be noted that the NN correlations represent the averaged behavior of the system and in the limiting case of a mixture of two identical species they are identical to the correlation functions directly calculated for the pure liquid.

We also performed MD simulations of the same system at the same temperature and atomic density but assuming that the atomic mass of the heavier atoms ($M_{\text{Mg}} = 2 \times M_{\text{Li}}$) is ten times larger than that of magnesium ($m_{\text{Li}} = 10 m_{\text{Mg}}$). The interaction potentials, MD procedure, and calculated properties were the same as for Li$_{0.7}$Mg$_{0.3*}$. However, the $k$-dependent properties for Li$_{0.7}$Mg$_{0.3*}$ were only obtained up to $k = 1.48 \, \text{Å}^{-1}$ and special attention was paid to the results at low wave vectors. So, an additional MD simulation using 6000 particles allowed us to determine the collective properties down to $k = 0.12 \, \text{Å}^{-1}$. We checked that properties for very similar wave vectors in the low-$k$ region obtained from MD simulations with either 570 or 6000 particles were in good agreement.

FIG. 2. Number-number intermediate scattering functions (a) and dynamic structure factors (b) for the Li$_{0.7}$Mg$_{0.3}$ alloy.

III. DYNAMIC STRUCTURE FACTORS

A. Li$_{0.7}$Mg$_{0.3}$ system

Figure 1 shows the partial intermediate scattering functions [$F^{ij}(k,t)$] obtained for two representative wave vectors in the low-$k$ region. $F^{12}(k,t)$ is negative and the three functions go monotonically to zero, showing slower decays as $k$ decreases. The long-time behavior of the $F^{ij}(k,t)$ functions should be reflected in the Rayleigh peaks at $\omega = 0$ of the corresponding dynamic structure factors [$S^{ij}(k,\omega)$]. In the hydrodynamic limit, the Rayleigh peak of the dynamic structure factor [$S(k,\omega)$] for pure liquids represents a nonpropagating thermal mode. In these systems the collective mass currents are zero and the decay of the $F(k,t)$’s at low $k$’s are quite fast [see, for example, the $F(k,t)$’s for liquid Li (Ref. 16)]. However, the Rayleigh peak in binary liquids is related to both heat conduction and diffusion as well as to coupling effects. This should be the origin of the large discrepancies between $F^{ij}(k,t)$ and $F(k,t)$ at low $k$’s. The slow decays of the former should then be mainly associated with diffusion effects.

The $F_{\text{NC}}(k,t)$ and $F_{\text{CC}}(k,t)$ correlation functions at low $k$’s show persistent long-time decays analogous to those of the $F^{ij}(k,t)$’s. Nevertheless, the $F_{\text{NN}}(k,t)$’s are one order of magnitude lower than the $F^{ij}(k,t)$’s and decrease much faster with time [see Figs. 1 and 2(a)]. This should be attributed to large cancellations between the three partial functions since $F^{12}(k,t)$ is of similar magnitude but opposite sign than $F^{11}(k,t)$ and $F^{22}(k,t)$. The behavior of $F_{\text{NN}}(k,t)$ is similar to that of $F(k,t)$ for pure liquids. $F_{\text{NN}}(k,t)$ at $k$
$=0.26 \text{Å}^{-1}$ shows marked oscillations which become more
damped at smaller $k$'s being practically reduced to a single peak
at $k=0.74 \text{Å}^{-1}$ [Fig. 2(a)]. This is in agreement with
the oscillating $F_{NN}^1(k,t)$ functions found for the K-Cs alloy
at low $k$'s. As unlike the partial $F_{ij}^1(k,t)$'s, $F_{NN}^1(k,t)$ goes to
zero at rather short times and $S_{NN}^1(k,\omega)$ could be reliably
calculated. The $S_{NN}^1(k,\omega)$'s at the lowest $k$'s explored in this
study show a clear Rayleigh-Brillouin structure similar to
that of $S(k,\omega)$ for pure liquids near the hydrodynamic
regime. As $k$ increases, the $S_{NN}^1(k,\omega)$ Brillouin peak be-
comes more poorly resolved and for wave vectors between
$k\approx 0.4 \text{Å}^{-1}$ and $k\approx 1.5 \text{Å}^{-1}$ only remnant shoulders are
noticed [Fig. 2(b)]. No significant peaks or shoulders can be
observed for $k$ higher than $\approx 1.5 \text{Å}^{-1}$ (Fig. 3).

$S_{NN}^1(k,\omega)$ at $k=0.26 \text{Å}^{-1}$ show a marked Brillouin peak
at $\omega_b=8.1 \text{ps}^{-1}$ [Fig. 2(b)] that may be associated with
propagating acoustic modes through the mixture. The ve-
clocity of propagation of these modes can be calculated
according to the relation $c_s=\omega_b/k$. Thus, the estimated value of
the adiabatic sound velocity in Li$_{0.7}$Mg$_{0.3}$ is $c_s^{\text{LiMg}}=3.1$
$\times 10^3 \text{m s}^{-1}$. To our knowledge this velocity has not been
experimentally determined. We can compare our result with
that from an earlier MD simulation of liquid Li at similar
conditions ($T=843 \text{K}$ and $\rho=4.162 \times 10^2 \text{Å}^{-3}$) and also
using an effective potential obtained by the neutral pseudo-
tom method. The $c_s$ value obtained in one such MD study,$^16$
$c_s^{\text{Li}}=4.3 \times 10^3 \text{m s}^{-1}$, is in good agreement with the experi-
mental value. If one assumes that in the hydrodynamic
limit the mixture is equivalent to a pure liquid made up of
particles with an average atomic mass $m_{\text{LiMg}}=0.7m_{\text{Li}}$
$+0.3m_{\text{Mg}}$ and using a simple mass scaling law,$^23$ one obtains:
$c_s^{\text{Mg}}c_t^{\text{Li}}(m_{\text{LiMg}}/m_{\text{Li}})^{1/2}=3.2 \times 10^3 \text{m s}^{-1}$. This value
is very close to that estimated from $\omega_b$ in $S_{NN}^1(k,\omega)$ at $k$
$=0.26 \text{Å}^{-1}$.

The calculation of the three partial dynamic structure fac-
tors $S_{ij}^1(k,\omega)$ can provide interesting information on the
microscopic mechanisms of propagating longitudinal modes.
So, for example, it was suggested that the peaks displayed by
$S_{ij}^1(k,\omega)$ in Li$_2$Pb can be associated with propagating fast
modes supported by the light particles alone.$^2$ However, the
low-$k$ $S_{ij}^1(k,\omega)$ factors for Li$_{0.7}$Mg$_{0.3}$ can hardly be obtained
due to the slow decays of the $F_{ij}^1(k,t)$’s. Since the influence
on $F_{NN}^1(k,t)$ [and therefore on $S_{NN}^1(k,\omega)$] of the long-time
part of the $F_{ij}^1(k,t)$’s is very weak we tried to remove it.
According to viscoelastic theory, which was successfully
applied to Li-Na alloy,$^17$ the long-time decay of $F_{ij}^1(k,t)$ may
be approximately represented by an exponential function.
Thus, we defined

$$F_{ij}^1(k,t) = F_{ij}^1(k,t) - A_{ij} \exp(-\alpha_{ij}t),$$  \hspace{1cm} (2)

where $A_{ij}$ and $\alpha_{ij}$ are $k$-dependent constants that were deter-
mined by fitting $A_{ij} \exp(-\alpha_{ij}t)$ to the long-time part of
$F_{ij}^1(k,t)$ for a given $k$. We checked that the values of the
resulting constants were quite close to those directly calcu-
lated according to the viscoelastic approximation. As ex-
pected, the new $F_{ij}^2(k,t)$ function keeps both the oscillatory
and the fast-decaying components of $F_{ij}^1(k,t)$ whereas the
slow-decaying component is practically absent. These
$F_{ij}^2(k,t)$ functions were Fourier transformed to obtain the

![FIG. 3. Corrected partial dynamic structure factors $S_{ij}^1(k,\omega)$
and $S_{ij}^2(k,\omega)$ (as defined in the text) and number-number dynamic
structure factors $S_{NN}^1(k,\omega)$ for the Li$_{0.7}$Mg$_{0.3}$ alloy.](image)
B. Li$_{0.7}$Mg$_{0.3}$ system

The main trends of the partial $F^{ij}(k,t)$ functions for Li$_{0.7}$Mg$_{0.3}$ are similar to those for Li$_{0.7}$Mg$_{0.3}$ (Fig. 1). The most significant discrepancy is that $F^{ij}(k,t)$ for the former system shows more persistent time decays than for the second, especially in the case of $F^{22}(k,t)$, which is consistent with the bigger mass of Mg*. Nevertheless, the $F^{11}(k,t)$ functions for Li$_{0.7}$Mg$_{0.3}$* are markedly different from those for Li$_{4}$Pb. For Li$_{4}$Pb they show small initial values and quite fast oscillatory decays while their $S^{11}(k,\omega)$ spectra present noticeable Brillouin peaks that reveals the existence of high-frequency modes.$^{2,9}$ On the contrary, the $F^{11}(k,t)$ functions for Li$_{0.7}$Mg$_{0.3}$* show initial values one order of magnitude higher and much more slower decays than for Li$_{4}$Pb. Then, possible oscillations in $F^{11}(k,t)$ and corresponding $S^{11}(k,\omega)$ peaks remain unseen. These findings prove that the large discrepancies between the $F^{ij}(k,t)$’s for both Li$_{0.3}$Mg$_{0.7}$ and Li$_{0.7}$Mg$_{0.3}$ with regard to those for Li$_{4}$Pb cannot be attributed only to the differences between the atomic masses of species in the mixtures.

As with Li$_{0.7}$Mg$_{0.3}$, the slow long-time decays of the three $F^{ij}(k,t)$ partials for Li$_{0.7}$Mg$_{0.3}$* are largely cancelled when $F^{NN}(k,t)$ is calculated. At small $k$’s, $F^{NN}(k,t)$ show oscillations (smoother than for Li$_{0.7}$Mg$_{0.3}$) which become a shoulder (less pronounced than for Li$_{0.7}$Mg$_{0.3}$) at intermediate $k$’s [Figs. 6(a) and 2(a)]. This behavior is clearly reflected in the corresponding $S^{NN}(k,\omega)$ spectra. As seen in Figs. 6(b) and 2(b), the $S^{NN}(k,\omega)$ Brillouin peak for Li$_{0.7}$Mg$_{0.3}$ at $k = 0.26 \, \text{Å}^{-1}$ is less pronounced and shifted towards lower frequencies than that for Li$_{0.7}$Mg$_{0.3}$ while the shoulder at $k = 0.74 \, \text{Å}^{-1}$ for the former system is less visible than for the second. We also calculated the $S^{11}(k,\omega)$ and $S^{22}(k,\omega)$ functions at low $k$’s for Li$_{0.7}$Mg$_{0.3}$* by using Eq. (2). Unlike for Li$_{0.7}$Mg$_{0.3}$, the frequency of the $S^{11}(k,\omega)$ and $S^{22}(k,\omega)$ peaks are still different at the lowest wave vectors explored in this work. Although the frequencies corresponding to light and heavy particles become closer as $k$ decreases they remain different down to wave vectors much lower than in the case of Li$_{0.7}$Mg$_{0.3}$ (Fig. 7). This should be associated with the larger difference of masses of the two species in Li$_{0.7}$Mg$_{0.3}$. Results in Fig. 7 also corroborate that the peaks and shoulders in the $S^{NN}(k,\omega)$ functions must be mainly associated with the majority Li particles. As in the case of Li$_{0.7}$Mg$_{0.3}$, the sound velocity in Li$_{0.7}$Mg$_{0.3}$* has been estimated by two routes. On the one hand, according to the scaling law,$^{24}$

$$c_{s}^{\text{LiMg}*} \approx c_{s}^{\text{Li}}(m_{\text{Li}} / m_{\text{LiMg}*})^{1/2} = 1.3 \times 10^{3} \, \text{m} \, \text{s}^{-1}.$$  

On the other hand, through the frequency of the Brillouin peak of $S^{NN}(k,\omega)$ at $k = 0.26 \, \text{Å}^{-1}$, $\omega_{NN} \approx 3.6 \, \text{ps}^{-1}$. Thus, $c_{s}^{\text{LiMg}*} \approx 1.4 \times 10^{3} \, \text{m} \, \text{s}^{-1}$, which is consistent with the value obtained through the scaling law.

IV. LONGITUDINAL CURRENTS

A. Li$_{0.7}$Mg$_{0.3}$ system

Other properties usually employed to analyze the longitudinal collective modes in liquids are the longitudinal current

![Partial intermediate scattering functions](image1)

![Partial intermediate scattering functions](image2)
correlation functions \( C_L(k,t) \). The corresponding spectra \( C_L(k,\omega) \) is related to the dynamic structure factor by \(^{15,17}\)

\[
C_L(k,\omega) = \omega^2 S(k,\omega). \tag{3}
\]

According to this relation the Rayleigh component in \( S(k,\omega) \) does not show up in \( C_L(k,\omega) \) whereas the high-frequency part of \( S(k,\omega) \) is enhanced. Besides \( C_L(k,\omega) \) has a visible peak at any \( k \). At very low \( k \)’s the frequency of this peak is the same as that of the Brillouin peak in \( S(k,\omega) \) whereas at higher \( k \)’s the frequency of the Brillouin peak, if visible, is somewhat lower.\(^24\) The partial \( C_L^{ij}(k,t) \) functions were determined during the simulations while the \( C_L^{NN}(k,t) \) functions and corresponding spectra \([C_L^{ij}(k,\omega), C_L^{NN}(k,\omega)]\) were calculated later. The contributions of both \( C_L^{NN}(k,\omega) \) and \( C_L^{ij}(k,\omega) \) to \( C_L^{NN}(k,\omega) \) are rather small for all \( k \)’s. This shows that \( C_L^{NN}(k,\omega) \) is largely dominated by correlations of the majority light particles (Fig. 8). \( C_L^{NN}(k,\omega) \) for \( k=0.26 \text{ Å}^{-1} \) shows a maximum at a frequency \((\omega_L^{NN} = 10.2 \text{ ps}^{-1})\) similar but slightly higher than that of the \( S^{NN}(k,\omega) \) Brillouin peak. Hence, as with pure liquids, the sound velocity defined through \( C_L^{NN}(k,\omega) \) is somewhat greater than that through \( S^{NN}(k,\omega) \). The longitudinal dispersion relations \( \omega_L^{NN}(k) \), \( \omega_L^{11}(k) \), and \( \omega_L^{22}(k) \) corresponding to \( C_L^{NN}(k,\omega) \), \( C_L^{11}(k,\omega) \), and \( C_L^{22}(k,\omega) \), respectively, are depicted in Fig. 9. \( \omega_L^{NN}(k) \) shows the same features as \( \omega_L^{11}(k) \) for pure Li at similar temperature and density.\(^16\) So, both \( \omega_L^{NN}(k) \) and \( \omega_L^{22}(k) \) have an initial linear increase followed by a maximum at \( k=1.3 \text{ Å}^{-1} \) and a deep minimum at \( k=2.4 \text{ Å}^{-1} \) that corresponds to the de Gennes narrowing.

Consistently with the \( S^{NN}(k,\omega) \) findings, the three partial \( C_L^{ij}(k,\omega) \) functions for \( k=0.26 \text{ Å}^{-1} \) have a maximum at the same frequency as \( C_L^{NN}(k,\omega) \) (Fig. 8). This corroborates the hydrodynamic like behavior of light and heavy particles at this \( k \). For higher wave vectors, the frequencies of the \( C_L^{11}(k,\omega) \) maxima increases with \( k \) whereas the frequencies of \( C_L^{ij}(k,\omega) \) maxima are significantly lower and remain almost independent of \( k \) beyond \( k=0.6 \text{ Å}^{-1} (\omega_L^{NN} \approx 20 \text{ ps}^{-1}) \). It should be pointed out that the \( \omega_L^{NN}(k) \) values are almost identical up to \( k \approx 1.5 \text{ Å}^{-1} \) and also very similar to the \( \omega_L^{ij}(k) \) values for pure Li. The marked differences between the frequencies for Li and Mg atoms suggest that their motions are largely uncorrelated at intermediate wavelengths still far from the kinetic region. The \( \omega_L^{11}(k) \) function displays a noticeable minimum at \( k=2.44 \text{ Å}^{-1} \) that should be associated with the de Gennes narrowing. We want to emphasize that for this wave vector \( \omega_L^{11}(k) \) is quite close to \( \omega_L^{NN}(k) \), while \( \omega_L^{NN}(k) \) coincides with \( \omega_L^{22}(k) \) despite the fact that Li atoms are in the majority in the mixture. These findings show that dynamic collective properties are strongly influenced by the marked spatial correlations at wavelengths corresponding to the maxima of the partial static structure factors.

It is also interesting to investigate the possible existence of propagating concentration modes in simple liquid mixtures. Jacucci and McDonald\(^1\) did not find evidence of any propagating concentration fluctuation in their former study of the Na-K alloy whereas Jacucci et al.\(^25\) found side peaks in \( S^{CC}(k,\omega) \) for Li–Pb at the same frequencies as in \( S^{NN}(k,\omega) \). The absence of noticeable concentration modes in Na-K may be attributed to the dominance of the diffusive contributions to the intermediate scattering functions and dynamic struc-
The longitudinal currents, we have analyzed the contributions have little influence on the longitudinal currents, we have analyzed the contributions.

For the sake of clarity the dispersion relations corresponding to the $C_{L}^{CC}(k,\omega)$ peaks are illustrated in Fig. 9. It should be pointed out that number-number longitudinal current spectra for the Li$_{0.7}$Mg$_{0.3}$ alloy. For the sake of clarity the $C_{L}^{NC}(k,\omega)$ and $C_{L}^{CC}(k,\omega)$ functions have been multiplied by suitable factors as indicated in the figure.

The dispersion relations corresponding to the $C_{L}^{CC}(k,\omega)$ peaks are illustrated in Fig. 9. It should be pointed out that for $k$ higher than $k=0.8$ Å$^{-1}$ the high-frequency maxima become smooth shoulders and only the low-frequency peaks could be plotted in Fig. 9. Beyond $k=2$ Å$^{-1}$, the CC modes are very damped and $C_{L}^{CC}(k,\omega)$ shows a broad maximum (Fig. 10) at frequencies intermediate between those of $C_{L}^{11}(k,\omega)$ and $C_{L}^{22}(k,\omega)$. The positions of these $C_{L}^{CC}(k,\omega)$ peaks are not well defined, which leads to rather large uncertainties of the results for this $k$-region displayed in Fig. 9. Moreover, the frequencies of the fast concentration modes tend to a finite value as $k$ goes to zero, which is a characteristic trend of kinetic modes. This corroborates that peaks in $C_{L}^{CC}(k,\omega)$ for intermediate $k$s, at the same frequencies as those in $C_{L}^{11}(k,\omega)$ and $C_{L}^{22}(k,\omega)$, have no acoustic character but should be considered fast kinetic propagating modes. The low-frequency concentration modes at the same frequen-
cies as in $C_{L}^{22}(k,\omega)$ cannot be observed in the hydrodynamic region, which suggests that these slow propagating modes also have a kinetic character.

B. Li$_{0.7}$Mg$_{0.3}$ system

The $C_{L}^{NN}(k,\omega)$’s for Li$_{0.7}$Mg$_{0.3}$ have single maxima at frequencies decreasing with $k$ that are very close to those of the corresponding $C_{L}^{11}(k,\omega)$ (Fig. 11). We want to emphasize the existence of a second maximum (or a shoulder) for wave vectors lower than $k \approx 0.3 \text{ Å}^{-1}$ that becomes more marked as $k$ decreases [Fig. 11(c)]. Although its frequency is lower than that of the “ordinary” peak and very close to that of $C_{L}^{22}(k,\omega)$, the second peak in $C_{L}^{NN}(k,\omega)$ should be mainly attributed to $C_{L}^{CC}(k,\omega)$ [see Fig. 11(b)]. Moreover, the frequency of this peak (or shoulder) agrees with that in $S_{L}^{11}(k,\omega)$ (Fig. 3). The high-frequency peak is hardly visible in $S_{L}^{11}(k,\omega)$ but, according to Eq. (3), it is noticeably enhanced in $C_{L}^{11}(k,\omega)$. These findings suggest that during the transition to the hydrodynamic regime $C_{L}^{11}(k,\omega)$ for mixtures of disparate mass particles is the superposition of two functions with peaks at different frequencies.

The resulting $C_{L}^{NN}(k,\omega)$, $C_{L}^{NC}(k,\omega)$, and $C_{L}^{CC}(k,\omega)$ at two representative wave vectors are depicted in Fig. 12. At very low $k$’s $C_{L}^{CC}(k,\omega)$ shows a high-frequency peak whereas the second peak at lower frequency in $C_{L}^{NN}(k,\omega)$ and $C_{L}^{NC}(k,\omega)$ is not visible in this function. However, for $k$ higher than $\approx 0.7 \text{ Å}^{-1}$ two maxima may be observed in $C_{L}^{CC}(k,\omega)$. As with Li$_{0.7}$Mg$_{0.3}$ the two frequencies of $C_{L}^{CC}(k,\omega)$ for a given $k$ are very close to those of $C_{L}^{11}(k,\omega)$ and $C_{L}^{22}(k,\omega)$, respectively (Fig. 13). Moreover, the high-frequency concentration modes go to a finite value as $k$ goes to zero whereas the low-frequency concentration modes can only be noticed at $k$’s quite far from the genuine hydrodynamic region. This confirms that the peaks of the $C_{L}^{CC}(k,\omega)$ functions should be associated with either slow or fast propagating kinetic modes. The NC cross correlations are also important in Li$_{0.7}$Mg$_{0.3}$ (Fig. 12).

The dispersion relations $v_{L}^{11}(k)$ and $v_{L}^{22}(k)$ are compared with $v_{L}^{NN}(k)$ and $v_{L}^{CC}(k)$ in Fig. 13. For the sake of clarity the low frequencies in $C_{L}^{11}(k,\omega)$ for $k$ lower than $\approx 0.3 \text{ Å}^{-1}$ are not displayed in this figure. The frequencies corresponding to Mg* in Li$_{0.7}$Mg$_{0.3}$ are markedly lower than those for Mg in Li$_{0.7}$Mg$_{0.3}$, as corresponds to the larger difference between their atomic masses (Figs. 9 and 13). The comparison of the results for identical Li particles in different systems is
The main features of the oscillations of Fernández-Pereira with \( k \), which corroborate the kinetic character attributed to the environment down to rather low wave vectors. More-

\[ \omega_{NN}(k) \] for \( Li_{0.7}Mg_{0.3}^* \) and \( Li_{0.7}Mg_{0.3} \) has also been plotted in Fig. 13 and also very close to \( \omega_{L}^{11}(k) \) for pure Li. This shows that frequencies corresponding to the light particles are independent of the environment down to rather low wave vectors. Moreover, \( \omega_{L}^{11}(k) \) and \( \omega_{NN}^{11}(k) \) for \( Li_{0.7}Mg_{0.3}^* \) do not go to zero with \( k \), which corroborate the kinetic character attributed to these modes. These findings are consistent with the conclusions of Fernández-Pereira et al., which associated the high-frequency longitudinal modes in \( Li_{4}Pb \) (already predicted by kinetic theory) with short-lived out-of-phase motions of light atoms.

**V. CONCLUSIONS**

The results obtained in this MD study show that, in general, the \( F^{ij}(k,t) \) functions for simple binary liquids have greater initial values and slower time decays than the \( F(k,t) \) functions for pure liquids. This should be associated with the dominance of diffusion terms which hide the oscillatory contributions to \( F^{ij}(k,t) \) and corresponding peaks in \( S^{ij}(k,\omega) \). The main features of \( F^{ij}(k,t) \) and \( S^{ij}(k,\omega) \) functions are similar for \( Li_{0.7}Mg_{0.3} \) and \( Li_{0.7}Mg_{0.3}^* \). This confirms that the existence of clearly visible peaks in \( S^{ij}(k,\omega) \) for \( Li_{4}Pb \) cannot be related only to the large ratio between atomic masses but also to other special features of this system, such as the very different size of the Li and Pb particles or the strong deviations from ideal mixing due to the ionic character of this alloy.

The behavior of the \( F^{NN}(k,t) \) functions is analogous to that of \( F(k,t) \) for pure liquids, showing much lower values than the \( F^{ij}(k,t) \)'s and clear oscillations at low \( k \)'s, which are reflected in \( S^{NN}(k,\omega) \) peaks or shoulders. This is the result of large cancellations between the three \( F^{ij}(k,t) \) functions when \( F^{NN}(k,t) \) is calculated. Moreover, the de Gennes narrowing typical of one component liquids may be also observed in liquid mixtures. The marked static correlations between particles at the wavelength characteristic of the structure of the system have a strong influence on the dynamic collective particles. So, in the case of \( Li_{0.7}Mg_{0.3} \) the differences between \( \omega_{NN}^{11} \) and \( \omega_{NN}^{22} \) are noticeably reduced and \( \omega_{NN}^{11} \) becomes almost coincident with \( \omega_{NN}^{22} \) as \( k \) approaches \( 2.44 \) Å\(^{-1}\) (the wave vector corresponding to the maximum of the static structure factors).

A general trend of liquid binary mixtures at wave vectors prior to the hydrodynamic region is the existence of both fast and slow propagating longitudinal modes, which are associated with light and heavy particles, respectively. The high \( \omega^{11} \) and low \( \omega^{22} \) frequencies corresponding to these modes cannot generally be observed in the partial \( S^{ij}(k,\omega) \) functions (except in special systems such as \( Li_{4}Pb \)) but they can be seen if the diffusive contributions are mostly removed by considering the \( C_{ij}^{CC}(k,\omega) \) or the \( S^{ij}(k,\omega) \) functions. The frequencies corresponding to the \( C_{ij}^{CC}(k,\omega) \) peaks are very close to those for the majority light particles. These frequencies are practically independent of the environment down to rather low wave vectors. So, there is a noticeable coincidence between \( \omega_{L}^{11}(k) \) for \( Li_{0.7}Mg_{0.3}^* \) and for \( Li_{0.7}Mg_{0.3} \) as well as with \( \omega_{L}^{11}(k) \) for pure Li. Noticeable maxima have also been found in the concentration \( C_{ij}^{CC}(k,\omega) \) spectra. In most cases these functions show two peaks for a given \( k \) at frequencies close to \( \omega^{11} \) and \( \omega^{22} \), respectively. Our results suggest that both fast and slow propagating modes have a kinematic character, analogous to that of optical modes in ionic solids or molten salts.

In the hydrodynamic limit the high (\( \omega^{11}, \omega^{NN} \)) and low (\( \omega^{22} \)) frequency modes merge into a single acoustic mode. The larger the difference is between the masses of particles in the mixture the lower is the wave number required to reach the hydrodynamic regime. It will be more “difficult” for light particles to oscillate with the same frequency as heavy particles (as they should in the hydrodynamic limit) when there is a large discrepancy between their “natural” frequencies. Although in disparate mass liquid mixtures the high and low frequencies are very different, the transition of \( C_{ij}^{CC}(k,\omega) \) to the hydrodynamic regime is not sharp. So, two peaks may be observed in the \( C_{L}^{CC}(k,\omega) \) functions for wave vectors approaching the hydrodynamic region. As \( k \) decreases the high-frequency peak decreases while the low-frequency peak increases (the former should disappear at \( k \) equal zero). These findings suggest that \( C_{L}^{11}(k,\omega) \) is composed of two functions with peaks at different frequencies such that in mixtures of nondisparate mass particles, say \( Li_{0.7}Mg_{0.3} \), they are so close that they cannot be distinguished.

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