The collective dynamical properties of HCl: The transverse current correlations

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Results are presented for the transverse current correlation functions and their spectra obtained by molecular dynamics simulation of liquid hydrogen chloride (HCl) at 201 K. To rationalize the results we analyze the data in the framework of the Mori–Zwanig theory and calculate the first order memory functions. This is done both in and exactly from the simulation data and by suitable approximations with one and two decay rates. It is found that the simple viscoelastic approximation with a single relaxation time is not sufficient to describe the dynamics of HCl whereas the extended model with two relaxation-times function accounts quite well for the simulation data in the low wave-number regime. Hydrogen bonding is found to play only a minor role in the dynamics of the liquid and the main features compare well with a simple liquidlike argon [DOI: 10.1063/1.1352643]

I. INTRODUCTION

In recent years considerable efforts have been devoted to the study of hydrogen-bonded liquids both by experimental[1–4] and computer simulation methods.[5–9] Water has naturally been the subject of most investigations, due to its relevance in many physical, chemical, and biological applications. peculiar features have been discovered in the dynamics of collective quantities which have been related to the existence of localized motions of molecular clusters.[10] As a mater of fact, these features are also present in the center of mass (c.m.) velocity autocorrelation function.

In liquid water the spectra of the longitudinal and transverse currents, at wavelengths above a limiting value of ≈ 1 Å^{-1}, show the clear appearance of two distinct peaks.[11] One of them is easily interpretable within the theoretical approaches developed for simple monatomic liquids; namely the presence of longitudinal and shear waves of the acoustic nature. The sound dispersion appears strikingly more marked than that in simple liquids (the so-called fast sound effect).[12] This peculiarity of water follows from the combination of two circumstances. First, owing to the strong hydrogen bond, the main peak of the oxygen–oxgyen pair distribution function corresponds to separations definitely lower than those implied by the size of oxygen ions, a fact that ultimately leads to an unusually high Einstein frequency $\Omega_0 \approx 35\ \text{ps}^{-1}$. Second, the nearly tetrahedral geometry of the network does not allow rapid rearrangements of the molecules.

The second peak indicates the existence of extra modes which can be ascribed to dynamical processes occurring in clusters of molecules, therefore confined to a limited region of space in the liquid. Such interpretation is supported by the observation that the frequency of this second peak does not change by varying the wave vector.

In a recent study, we have shown that similar features are also present in an even stronger hydrogen-bonded liquid; namely hydrogen fluoride (HF).[13] Here in the longitudinal current spectra one can distinguish a low frequency peak associated with acousticlike propagation and a high frequency one at $\approx 50\ \text{ps}^{-1}$, which remains almost constant by changing the wave vector. In contrast with H_2O, the dispersion of the acoustic mode in HF does not show any trace of ''fast sound,'' although the first criterion previously mentioned is equally, or even more easily, met than in water. Even in HF the Einstein frequency is found to be quite large ($\Omega_0 \approx 33\ \text{ps}^{-1}$). However, the peculiar arrangement of HF molecules in topological chains causes the presence of rapid, nearly free, motions of the molecules limiting the magnitude of the sound dispersion which can actually be observed. On the other hand, the high frequency peak, present in both the longitudinal and transverse current spectra, can be explained in terms of local vibrations of the hydrogen-bonded molecules along the above-mentioned chains. A thorough investigation of the molecular motions by an instantaneous normal mode analysis has confirmed such an interpretation.[14]

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In this paper we present the results of the analysis of the transverse current in a system representative of hydrogen chloride (HCl), obtained by computer simulation. Besides being simpler, the consideration of the transverse current instead of the longitudinal one has the advantage of bypassing the problem of the poor knowledge of some thermodynamic parameters such as specific heats and sound velocity.

The aim of this work is to explore the relevance of hydrogen-bonding strength in determining the dynamical properties of molecular liquids. At first, the structural properties of the system are discussed to show that despite the presence of electrostatic forces HCl does not share the peculiar local ordering of other hydrogen-bonded systems (e.g., water and HF). Such a behavior is found to be reflected also in the dynamical quantities so that at the end of our analysis we can concluded that HCl is more similar to a monatomic liquid (like argon) rather than to water.

The paper is organized as follows: in Sec. II we present the model used to perform the molecular dynamics (MD) simulations along with the relevant radial distribution functions which illustrate the structural arrangement of the molecules; in Sec. III we report the results for the transverse current and the comparison with the analysis performed in terms of viscoelastic approximation. Section IV reports some concluding remarks.

II. MOLECULAR DYNAMICS SIMULATION AND STATIC PROPERTIES

The simulation of HCl has been performed by using the C^* potential model implemented by Klein and McDonald.[15] It consists of interaction sites over the hydrogen and chlorine atoms which accounts for repulsive forces and short range dispersive contributions. Fractional charges, which give rise to long range interactions between the molecules, are distributed over the hydrogen, chlorine, and an intermediate site to account in an effective way for the electronic distribution in the molecule. These long range interactions are treated by the reaction field method. A reasonable agreement with the thermodynamic properties is achieved and the essential features of the experimental structure factors are reproduced.[16]

Molecular dynamics simulations were carried out at a liquid density $\rho = 1.186$ g/cm^3 and at an average temperature $\langle T \rangle = 201$ K. The time step of integration was 2 fs, which leads to a good conservation of the total energy. The system under consideration consists of 512 molecules which were enclosed in a cubic box with periodic boundary conditions. The box length, $L = 29.681$ Å, fixes the minimum wave-vector compatible with the system size to $k_{\min} = 2\pi/L = 0.2117$ Å^{-1}.

The radial distribution functions evaluated during the run are reported in Fig. 1. It is apparent that hydrogen bonding is present in the liquid, since the H–Cl distribution has a fist maximum at a distance shorter than the position of the first peaks of both H–H and Cl–Cl correlations. However, the relatively low strength of the hydrogen bond is deduced from the fact that the first peak position of the Cl–Cl pair distribution function, at 3.8 Å, does not differ too much from the size of a chlorine ion, 3.62 Å.[17] In HCl the Einstein frequency ($\Omega_0 \approx 13$ ps^{-1}) is consequently found to be considerably lower than in water ($\Omega_0 \approx 35$ ps^{-1}) and HF ($\Omega_0 \approx 33$ ps^{-1}). The short range arrangement of molecules does not present any peculiar feature. For example, the number of first neighbors for each molecule turns out to be ≈12, close to the value expected for a simple monatomic liquid.

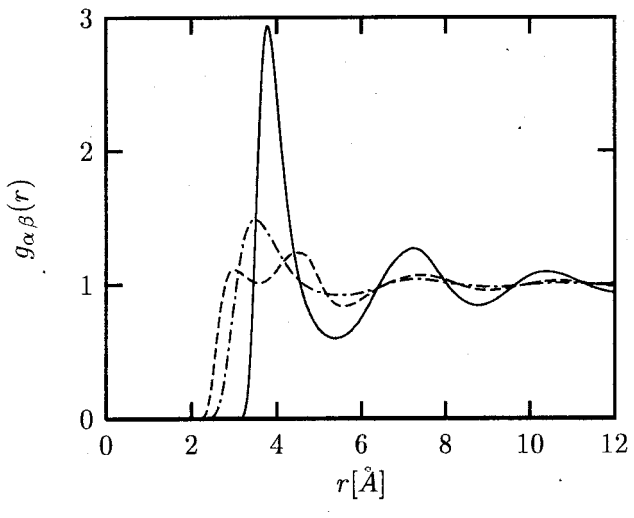

FIG. 1. The radial distribution functions of the HCl simulated by C^* model potential: Cl–Cl, solid line; Cl–H, dashed line; H–H, dotted–dashed line.

III. DYNAMICAL QUANTITIES

The key quantity, we dwell on is the transverse current correlation function, defined by

$$C_T(\mathbf{k},t) = (1/N)\langle \mathbf{j}_T^*(\mathbf{k},0) \cdot \mathbf{j}_T(\mathbf{k},t) \rangle \tag{1}$$

with

$$\mathbf{j}_T(\mathbf{k},t) = \sum_i^N \hat{\mathbf{k}} \times \mathbf{v}_i(t) \exp(i\mathbf{k}\cdot\mathbf{r}_i(t)). \tag{2}$$

Here $\hat{\mathbf{k}}$ is the unit vector along the wave vector $\mathbf{k}$, whereas $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ represent the position and the velocity of center of mass of the ith molecule, respectively.

The spectrum of $C_T(k,t)$ can be written as

$$C_T(k,\omega) = \frac{1}{\pi} \mathrm{Re}[\tilde{C}_T(k, z = i\omega)], \tag{3}$$

where $\tilde{C}_T(k,z)$ is the Laplace transform

$$\tilde{C}_T(k,z) = \int_0^\infty dt\, C_T(k,t) e^{-zt}. \tag{4}$$

Within the Mori–Zwanzig formalism the Laplace transform of $C_T(k,t)$ can be written as

$$\tilde{C}_T(k,z) = \frac{C_T(k,t=0)}{z + \tilde{K}_T(k,z)}, \tag{5}$$

where $\tilde{K}_T(k,z)$ is the Laplace transform of the first memory function of $C_T(k,t)$. Using this relation, it turns out that the spectrum of the transverse current can be written as

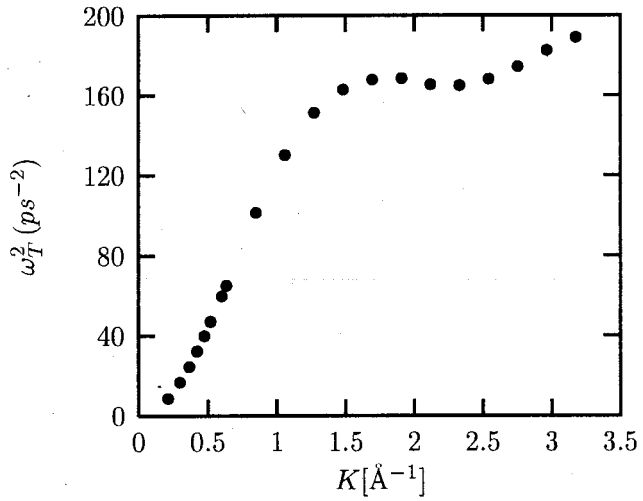

FIG. 2. $\omega_T^2(k)$ by fitting the MD data for $C_T(k,t)/C_T(k,0)$ on $t\to 0$ at small times.

$$\frac{C_T(k,\omega)}{C_T(k,t=0)}=\frac{1}{\pi}\frac{K_T'(k,\omega)}{[\omega-K_T''(k,\omega)]^2+[K_T'(k,\omega)]^2}, \tag{6}$$

where $K_T'(k,\omega)$ and $K_T''(k,i\omega)$ are defined as

$$\tilde{K}_T(k,z=i\omega)=\int_0^\infty dt\cos\omega t K_T(k,t)-i\int_0^\infty dt\sin\omega t K_T(k,t)$$
$$\equiv K_T'(k,\omega)-iK_T''(k,\omega). \tag{7}$$

A simple approximation of $K_T(k,t)$ is given by the viscoelastic model which assumes an exponentially decaying memory function,

$$K_T(k,t)=K_T(k,0)e^{-t/\tau_{Tk}}. \tag{8}$$

Here $K_T(k,t=0)=\omega_T^2(k)$ is the normalized second frequency moment of the transverse current spectrum $C_T(k,\omega)$ which can be expressed as

$$\omega_T^2(k)=-\frac{1}{2}\frac{[\ddot{C}_T(k,t=0)]}{C_T(k,t=0)}, \tag{9}$$

where a dot indicates a time derivative.

We have obtained $\omega_T^2(k)$ by fitting the MD data for $C_T(k,t)/C_T(k,0)$ at short times via $C_T(k,t)=C_T(k,0)[1-\omega_T^2(k)t^2]$.[18] The result for this function is shown in Fig. 2. Within the viscoelastic model (8), Eq. (6) is transformed into

$$\frac{C_T(k,\omega)}{C_T(k,t=0)}=\frac{1}{\pi}\frac{\omega_T^2(k)(1/\tau_{Tk})}{[\omega^2-\omega_T^2(k)]^2+[\omega(1/\tau_{Tk})]^2}. \tag{10}$$

Calculating $\omega_T^2(k)$ via Eq. (9), this expression contains only one unknown quantity, τ_{Tk}, which is the relaxation time of the memory function.

The quality of the fitting procedure is shown in Fig. 3, where the approximated data are compared with the MD results for several wave vectors. The agreement is not very good, especially in the range of small frequencies. The disagreement becomes more pronounced when increasing the wave number k.

The wave-number dependence of τ_{Tk}^{-1} as obtained by fitting Eq. (10) to the MD results is reported in Fig. 4.

In the range between $k_{\min}=0.21$ Å^{-1} and 0.367 Å^{-1} the spectrum of $C_T(k,t)$ does not present any peak at $\omega\neq 0$, thus revealing that below 0.367 Å^{-1} the system cannot support shear waves. Beyond 0.367 Å^{-1} an inelastic peak appears in the spectra but a single relaxation time model cannot reproduce all the features. From the knowledge of the relaxation time τ_{Tk} we have calculated the wave-vector-dependent viscosity coefficient.[19]

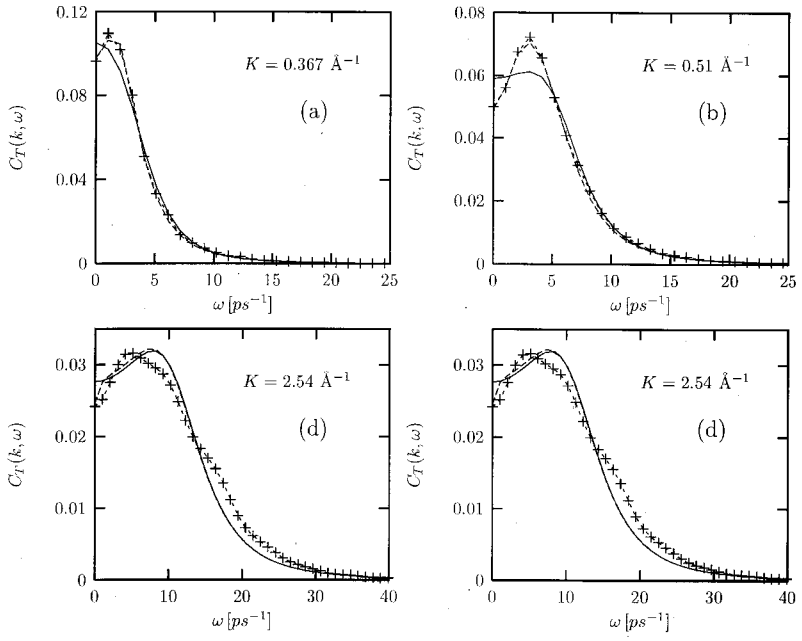

FIG. 3. Results for $C_T(k,\omega)$ from (i) MD simulation (dashed–crossed line), (ii) the viscoelastic model (solid line), and (iii) the two-relaxation-times model (dashed line).

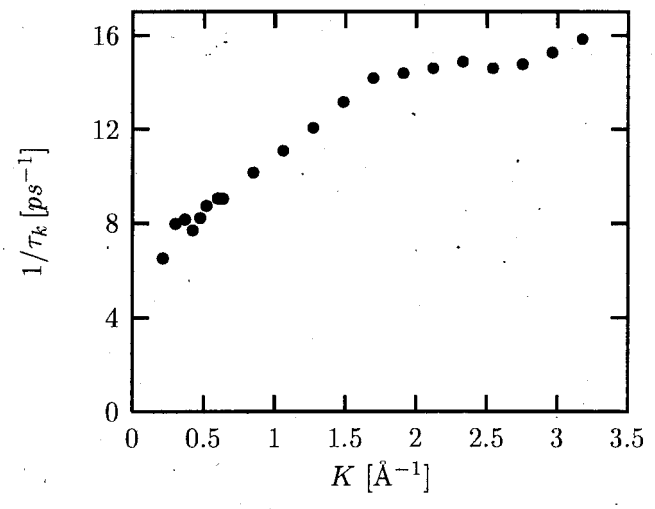

FIG. 4. Relaxation time $1/\tau_{Tk}$: dots are obtained fitting the current spectrum on Eq. (10).

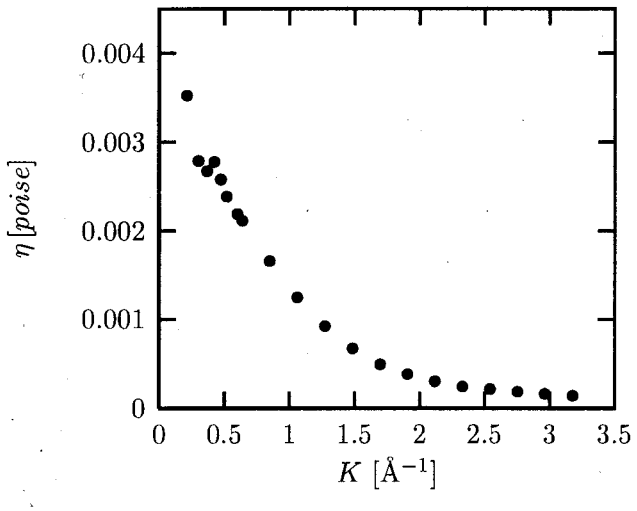

FIG. 5. *k*-dependent viscosity coefficient.

$$\eta(k)=\frac{nm}{k^2}\omega_T^2(k)\tau_{Tk}, \tag{11}$$

where *n* and *m* are the number density and mass of a molecule, respectively. The results are reported in Fig. 5.

In order to improve the agreement with the MD data we follow Levesque *et al.*[20] in their analysis of the transverse current correlation function in a Lennard-Jones liquid, i.e., a second exponential relaxation mechanism is introduced. The presence of two well-separated time scales, rather than being a mere empirical attempt to improve the quality of the fitting, reflects the presence of physically different decay mechanisms:[19] a fast initial decay (''collisional'' mechanism) and a considerably slower long-time tail, associated with structural relaxation processes, and accounted for by ''mode-coupling'' frameworks.

In this approximation the transverse memory function is written as

$$K_t(k,t)=\omega_T^2(k)[(1-\alpha_k)e^{-t/\tau_{1k}}+\alpha_k e^{-t/\tau_{2k}}] \tag{12}$$

and consequently $C_T(k,t)$ becomes

$$\frac{C_T(k,\omega)}{C_T(k,t=0)}=\frac{1}{\pi}\frac{\omega_T^2(k)(A_1/\tau_{1k}+A_2/\tau_{2k})}{[\omega_T^2(k)\cdot(A_1/\tau_{1k}+A_2/\tau_{2k})]^2+[\omega\cdot[1-\omega_T^2(k)(A_1+A_2)]]^2}, \tag{13}$$

where

$$A_1=\frac{(1-\alpha_k)}{\omega^2+(1/\tau_{1k})^2}, \tag{14}$$

$$A_2=\frac{\alpha_k}{\omega^2+(1/\tau_{2k})^2}. \tag{15}$$

As in the Lennard-Jones liquids,[20] the fitting turns out to be very good at small and intermediate wave vectors as shown in Fig. 3 (dashed line). Beyond $k=1$ Å^{-1} the agreement progressively worsens and above 1.5 Å^{-1} the second relaxation channel becomes so weak that the one- and two-relaxation-times approximations become indistinguishable. As a matter of fact $\alpha_k \sim 0$ for $k>1.5$ Å^{-1} as shown in Fig. 6. These discrepancies at large frequencies are likely to be due to the oversimplified form of the exponential approximation, since it is well known that the exact $K_T(k,t)$ must have a zero slope at $t\to 0$.[18]

We notice that the contribution of the longest time relaxation is relatively small since α_k is always <0.1. The values of the relaxation times are reported in Fig. 7. The *k* dependence of τ_{1k} and τ_{2k} appears to be quite similar to what is found for liquid argon.[20]

This observation and the quality of the fitting indicates that the overall behavior of liquid HCl is similar to that of a simple monatomic liquid. The only noticeable difference appears at intermediate wave vectors, where the MD data show a larger contribution at frequency around 18 ps^{-1}. This extra intensity, which appears as a shoulder in the spectra at rather large wave vector, parallels the result of other hydrogen-bonded liquids (H_2O, HF, methanol)[11,14] where a clear second peak appears in the transverse spectra. If this is really the case, the shoulder can be traced back to much more localized excitations with a nearly flat dispersion relation.

In order to corroborate the above findings we have evaluated directly the memory function from the transverse current spectrum. As is well known, the real and imaginary

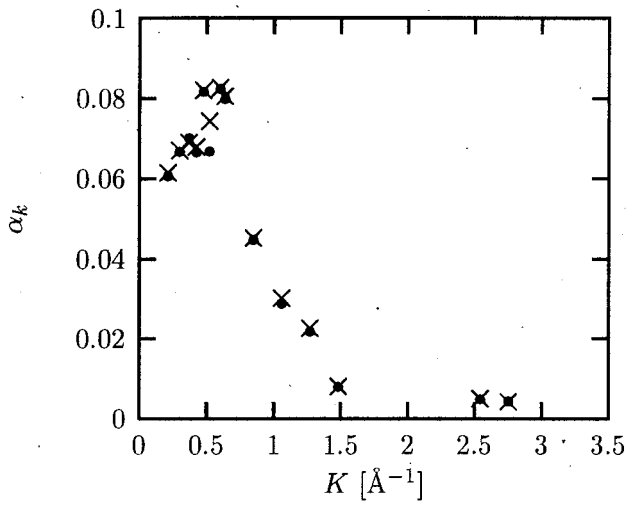

FIG. 6. Resutls for the coefficient α_k obtained by (i) fitting the current spectrum according to Eq. (13); (ii) fitting directly the memory function in time on Eq. (12).

part of the Laplace transform of $K_T(k,t)$ can be expressed in terms of $C_T'(k,\omega)$ and $C_T''(k,i\omega)$ [the real and imaginary part of $\tilde{C}_T(k,i\omega)$, respectively] by relations

$$K_T'(k,\omega)=\frac{C_T(k,t=0)\cdot C_T'(k,\omega)}{C_T'(k,\omega)^2+C_T''(k,\omega)^2}, \tag{16}$$

$$K_T''(k,\omega)=\omega-\frac{C_T(k,t=0)\cdot C_T''(k,\omega)}{C_T'(k,\omega)^2+C_T''(k,\omega)^2}. \tag{17}$$

Thus, the spectrum of the memory function of the transverse current correlation function reads

$$K_T(k,\omega)=\frac{1}{\pi}K_T'(k,\omega) \tag{18}$$

$$=\frac{1}{\pi}\frac{C_T(k,t=0)\cdot C_T'(k,\omega)}{C_T'(k,\omega)^2+C_T''(k,\omega)^2}. \tag{19}$$

The corresponding $K_T(k,t)$ obtained by the inverse Fourier transform of Eq. (18) is shown in Fig. 8. We have fitted the memory functions, so obtained, with Eq. (8) and with Eq. (12). In Fig. 8 the results of these fittings are reported. The fitting parameters are compared with those obtained from the current spectrum in Figs. 7 and 6.

IV. CONCLUSIONS

In the present work we have reported and analyzed several simulation data for the collective dynamics of liquid HCl, a system in which a scarce amount of experimental results is available. Neutron diffraction measurements[21–23] appear to indicate that in this liquid the hydrogen bond, although undoubtedly present, is rather weak. Our structural data are consistent with these findings, thus indicating that the potential model implemented in Ref. 15 is sufficiently realistic. However, from this evidence one cannot *a priori* infer any conclusion on the actual relevance of H bond effects in the dynamics.

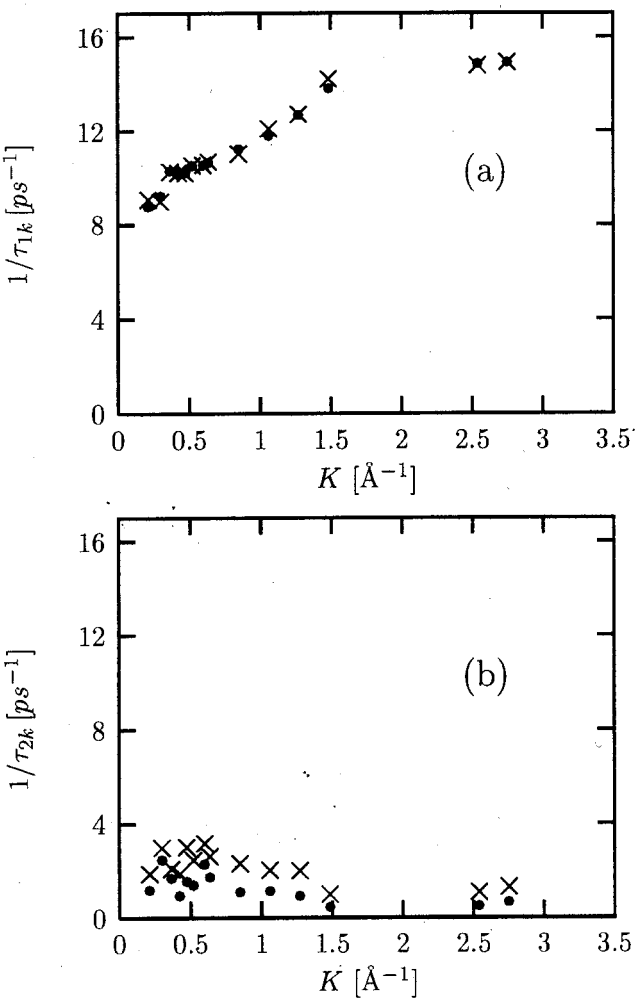

FIG. 7. The fitting parameter $1/\tau_{1k}$ (a) and $1/\tau_{2k}$ (b): dots are obtained by fitting the current spectrum on Eq. (13); crosses are obtained by fitting directly the memory function in time on Eq. (12).

To this goal, we have purposely chosen to investigate the simplest case of collective dynamics, namely the transverse current correlation functions and their associated spectra. This choice also has the additional advantage of providing a rather accurate test of the combined role of structural and H bond effects. For instance, although water and liquid HF have strong H bonds of comparable magnitude, their transverse current spectra show noticeable differences for wave vectors just outside the hydrodynamic regime: in particular, the H_2O spectra appear to exhibit transverse inelastic peaks already at relatively small wave vectors, where the HF spectra are still characterized by a hydrodynamiclike behavior with a central peak at zero frequency.

As discussed in the text, the features obtained for liquid HCl in this wave-vector range are much less drastic, and follow a more gradual evolution very similar to the one observed in monatomic Lennard-Jones liquids.[20] As in the latter systems, the spectra can be analyzed in terms of a viscoelastic model characterized by a single relaxation time. However, as already noted in Ref. 20, a better account of most spectral features can only be obtained by adopting a

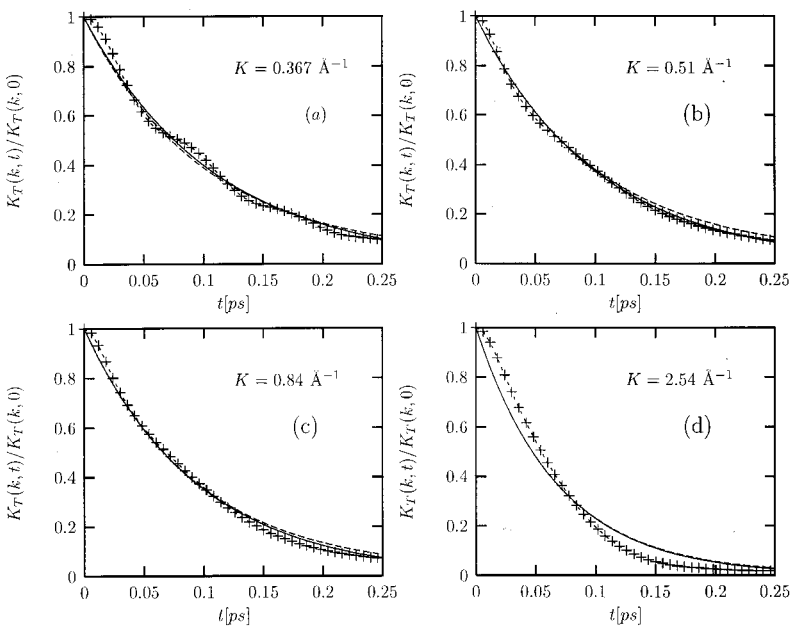

FIG. 8. $K_T(k,t)$: dashed–crossed line is the molecular dynamics data, line is the fit on Eq. (8), and the dashed line is the fit on Eq. (12).

memory function characterized by two different relaxation times.

Having established this, it is worthwhile to point out that some signature of H-bond effects can persist even in liquid HCl. For example, the shoulder present in the transverse spectra at rather large wave vectors resembles a similar feature present in much stronger H-bonded systems, such as H_2O and HF. A clearcut analysis of this weak spectral feature present in our data has, however, not been attempted. Further insight in this respect can be gained by pushing up the accuracy of the simulation and by considering additional probes of collective dynamics, such as the spectra of density fluctuations and the associated longitudinal currents.

ACKNOWLEDGMENTS

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