Viscous versus Elastic Response of Hydrogen-Bonded Liquids: Collective Dynamics in HF

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The role of hydrogen bonding in the determination of the dynamical properties of liquids is investigated by a computer simulation of HF, and compared with water. Sound dispersion is found to be much smaller and interpretable in terms of the viscoelastic approximation. Some dynamical solidlike features are found even in this liquid and interpreted in terms of localized motions of molecules along topological chains present in the liquid. The present investigation answers some relevant questions concerning the dynamical behavior of associated liquids. [S0031-9007(98)07004-5]

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A full understanding of the dynamical properties of hydrogen-bonded liquids has certainly not yet been achieved, since the appearance of features not present in simple monatomic liquids has still to be given a robust physical basis. Water is certainly the liquid which has been more extensively investigated both experimentally [1–3] and by computer simulation [4–7], and the presence of modes at wave vectors $k > 1\ \mathrm{nm}^{-1}$, propagating with a velocity 2.5 times larger than the ultrasonic sound velocity, has been the subject of a large debate. It is now currently believed that this extraordinary large anomalous dispersion can be explained by the fact that, on a length scale of a few molecular clusters, the behavior of water is more similar to that of a solid rather than of a liquid. Therefore the dynamical features at short wavelengths are dominated by the elastic response, which appears to be much more rigid than in simple liquids. This effect has been traced back to the structure set up by the presence of hydrogen bonds [8]. Nearest neighbor oxygen atoms can approach at an average distance smaller than that characteristic of the atomic radius determined by the repulsive part of the potential (e.g., σ in the Lennard-Jones potential). This implies that the second moment of the longitudinal current [9] is much higher than one would expect in a simple liquid. Correspondingly C_∞ turns out to be very high ($\approx$4500–5000 m/s), i.e., the same magnitude of the velocity of propagation of the longitudinal acoustic modes in ice. This argument is supported by the observation that at $k > 2\ \mathrm{nm}^{-1}$ transverse waves can propagate in the liquid, as demonstrated by computer simulations [7,10,11].

The presence of an optical-like mode, which appears at $k \approx 10\ \mathrm{nm}^{-1}$ both in the longitudinal and transverse spectra at $\omega \approx 10\ \mathrm{ps}^{-1}$, reinforces the overall picture that the response of water is similar to that of a solid at length scales of the order of 1 nm. A collective excitation at the same energy has been measured in ice close to the melting point both by neutron [2] and x-ray [3] scattering experiments. Regarding the nature of these dynamical properties several important questions remain to be answered: Are these features peculiar of water? What is the role of hydrogen bonding?

In the present Letter we try to answer these fundamental questions in order to pave the way to a more general understanding of the dynamical properties of hydrogen-bonded liquids. To this end we have analyzed in detail by computer simulation the relevant dynamical correlation functions of a model system of liquid HF. Here the hydrogen bond energy ($\approx -25\ \mathrm{kJ\,mol}^{-1}$) between two molecules is even stronger than in water ($\approx -20\ \mathrm{kJ\,mol}^{-1}$) so that its role should appear even more evident [12].

Recently we have implemented both a nonpolarizable [13] and a polarizable [14] model and analyzed the structural properties [12,14]. The results were compared with *ab initio* calculations [15], and we found that, even if the polarizable model gives better results for the partial radial distribution functions, the nonpolarizable model is sufficiently realistic when compared with neutron diffraction data [16]. In view of these results we have chosen to adopt the nonpolarizable model in the present study of the dynamical quantities, since it appears less demanding from the point of view of computational time.

In our computer simulation of HF we have studied a system of 512 molecules interacting through the three-site model developed in Ref. [13]. The trajectory length was

450 ps where a time step of integration of 2 fs was applied. Periodic boundary conditions with a tapered reaction field method were used to take long range interactions into account. For the computation of the spectra of the correlation functions we used time intervals ranging between 1 and 6 ps (depending on the convergence) leading to minimum frequencies $\omega_{\min} = 0.167\ \mathrm{ps}^{-1}$ or $\omega_{\min} = 1\ \mathrm{ps}^{-1}$.

We have evaluated the correlation functions of the longitudinal $[\mathbf{J}_L(\mathbf{k}, t)]$ and transverse $[\mathbf{J}_T(\mathbf{k}, t)]$ currents

$$\begin{aligned} \mathbf{J}_L(\mathbf{k}, t) &= \frac{1}{\sqrt{N}} \sum_i \hat{\mathbf{k}}(\hat{\mathbf{k}} \cdot \mathbf{v}_i) \exp[\mathrm{i}\mathbf{k}\mathbf{r}_i(t)]; \\ \mathbf{J}_T(\mathbf{k}, t) &= \frac{1}{\sqrt{N}} \sum_i \hat{\mathbf{k}} \times \mathbf{v}_i \exp[\mathrm{i}\mathbf{k}\mathbf{r}_i(t)], \end{aligned} \tag{1}$$

where $\hat{\mathbf{k}}$ indicates the unit vector along $\mathbf{k}$, $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ are the position and velocity of the center of mass of the ith molecule, respectively, and N is the number of molecules in the sample. The range of wave vectors which was explored starts from the minimum accessible value $2.5\ \mathrm{nm}^{-1}$. Two thermodynamic states have been investigated: state point A at $\rho = 1.178\ \mathrm{g/cm}^3$, $T = 203$ K and B at $\rho = 1.015\ \mathrm{g/cm}^3$, $T = 273$ K.

The spectra of the longitudinal and transverse current correlation functions are presented in Fig. 1 for state point A. The presence of collective modes is signaled by the appearance of peaks in the spectra. By reporting the frequency of these peaks as a function of k (as shown in Fig. 2) one can start to make an assignment of the nature of these collective modes. One notices that the low frequency longitudinal mode changes almost linearly at small wave vectors, thus indicating its *acoustic* origin. The corresponding sound velocity is reported in Fig. 3 and compared with what one would expect for the corresponding isothermal counterpart $C_0 = \sqrt{k_B T / M S(k)}$ [17], where M is the mass of the molecule and $S(k)$ is the center of mass structure factor. Since the experimental adiabatic sound velocity is found to be $C_s = 483.3$ m/s at state point B, one can conclude that a slight sound dispersion is present, but nothing similar to what is found in water. We have evaluated $C_\infty(k)$ through the second moment of the longitudinal current correlation function and compared it with $C(k)$ in Fig. 3. One can surely conclude that the propagation of this collective longitudinal mode is dominated by the viscous rather than elastic response of the system, contrary to what happens in water (it is instructive to see a similar comparison for water reported in Fig. 5 of Ref. [8]). An analogous situation is found even at state point A, as shown in Fig. 3. An experimental value at this state point is not known but since at $T = 240$ K, $C_s = 623.8$ m/s we may safely state that again at increasing wave vector (i.e., out of the hydrodynamic regime) a slight increase of this velocity is present which remains in any case much smaller than $C_\infty(k)$.

As far as the transverse current spectra are concerned, only at low temperature a low frequency peak appears at relatively high wave vector. The fact that transverse modes cannot be supported (at least at small wave vectors) is again an indication that the collective excitations are dominated by the viscous response.

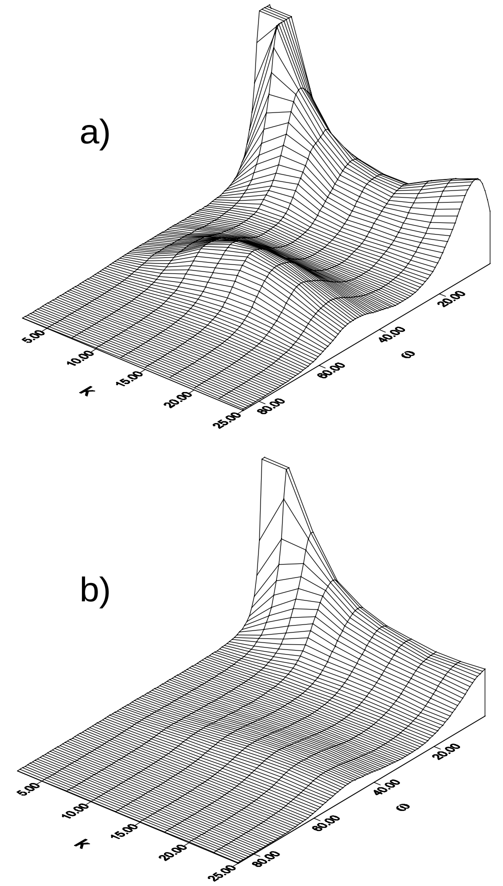

FIG. 1. Surface plots of the longitudinal (a) and transverse (b) current spectra of HF at state point A. Units are nm^{-1} (for k) and ps^{-1} (for ω). The amplitude is in arbitrary units.

The second peak present in both longitudinal and transverse spectra appears to be almost at the same frequency and not much affected by the temperature change ($\omega = 40\ \mathrm{ps}^{-1}$ at $T = 273$ K and $\omega = 45\ \mathrm{ps}^{-1}$ at $T = 203$ K). Moreover, it results to be almost constant at increasing wave vectors. In order to understand its origin, we compare these findings with light and neutron scattering results for solid HF.

As is well known HF crystallizes in the orthorhombic structure with two molecules per primitive cell (in the ferroelectric configuration) [18]. The molecules form infinitely long zigzag chains. Raman and infrared spectra have been measured [19,20]; in particular, two bands have been observed centered at $\omega = 35$ and $67\ \mathrm{ps}^{-1}$, both of them infrared active. They have been attributed to translational motions of the molecules, where the low frequency mode involves oscillations perpendicular to the chain, whereas the higher frequency mode involves oscillations in the direction of the chain. Both these modes are then characterized by a stretching of the hydrogen bond. Because the

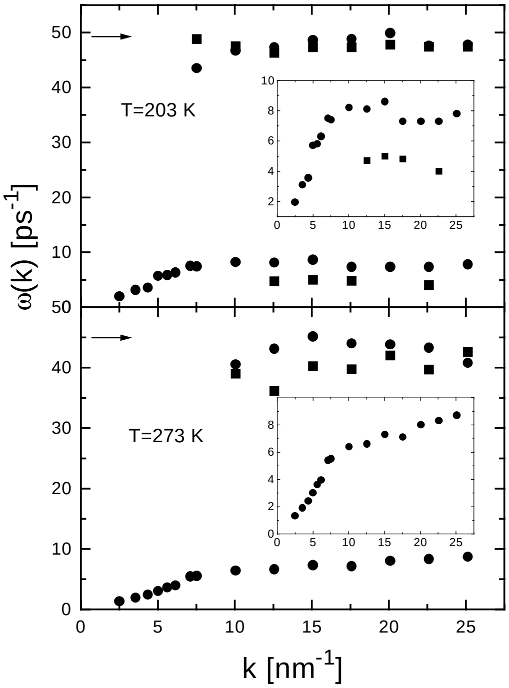

FIG. 2. Frequency values of the peak positions of the longitudinal (dots) and transverse (squares) current spectra. Upper figure: state point A. Lower figure: state point B. The insets show the details of the longitudinal and transverse acoustic modes. The arrows indicate the high frequency peak position of the VACF spectrum.

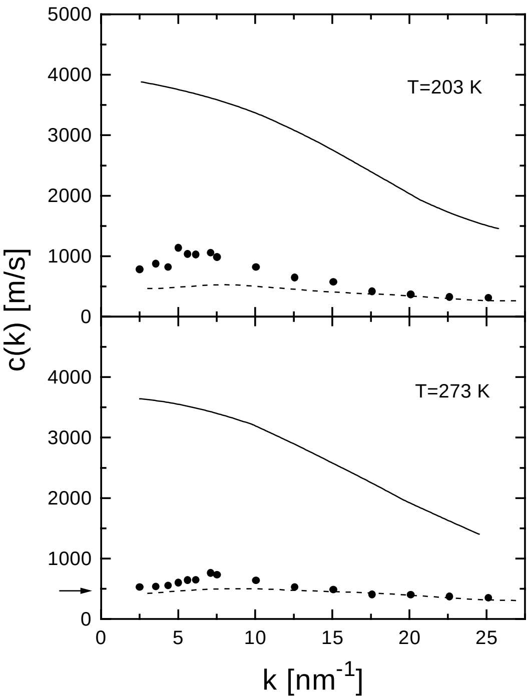

FIG. 3. Sound dispersion of HF at two state points A (upper figure) and B (lower figure). Dashed line: $C_0(k)$ isothermal sound velocity. Solid line: $C_\infty(k)$ evaluated through the second moment of the longitudinal current correlation function. The arrow indicates the value of the experimental sound velocity.

two modes are infrared active they can safely be labeled as *optical.*

We believe that the high frequency mode apparent in both the longitudinal and transverse spectra can be ascribed to the same type of oscillating motion of the molecules. By examining the structure of liquid HF we have found [12] that *topological* chains still persist in the liquid phase. In fact, an overwhelming percentage ($\approx 82\%$) of molecules has two nearest neighbors, and by a combined geometrical and energetic definition of the hydrogen bond we found that HF molecules are arranged in paths that resemble long chains, even if not strictly linear. The oscillatory motion of the molecules along these chains is therefore responsible for the appearance of the well defined second peak in the longitudinal and transverse current spectra.

This conclusion is confirmed by the analysis of the center of mass velocity autocorrelation (VACF) function and its corresponding spectrum for the two examined state points. A well defined peak is present at a frequency which is marked as an arrow in Fig. 2. Since the VACF spectrum is a measure of the density of states, it is useful to compare the present result with that obtained by inelastic neutron diffraction measurements from solid and liquid HF [21]. The spectrum of solid HF presents a shoulder at about 26.82 meV (i.e., $\omega = 40.6$ ps^{-1}) in close agreement with the present finding. In the liquid phase a large plateau is present at the same energy.

The present study shows that even in the case of liquid HF, when the system makes a transition from the solid to the liquid phase, some topological features persist, in particular, the arrangement of molecules in the form of linear chains, which determine the dynamical behavior. The chains are found to move rather free, so that the viscosity is much lower than in other molecular liquids (e.g., in water). This observation is confirmed by the fact that the isothermal compressibility of HF is very high as shown by the $k \longrightarrow 0$ behavior of the structure factor $S(k)$ reported in Fig. 4 for state points A and B.

An estimate of the shear viscosity can be made by the time dependence of the transverse current correlation function at small wave vectors which shows a monotonic decay, typical of the hydrodynamic regime. One can assume that

$$C_T(k,t) = \frac{k_B T}{M} \exp\left(-\frac{\eta(k)k^2}{nM}\,t\right) \tag{2}$$

[$\eta(k)$ being a generalized shear viscosity coefficient and n the number density] and derive a value for η of $\approx 0.16 \times 10^{-3}$ Pa s at $T = 203$ K, about 10 times smaller than the corresponding value for water close to the melting point [22]. This result can explain the different behavior of HF with respect to water. In fact, by adopting a simple viscoelastic model for the analysis of the dynamics of the transverse current it turns out that the Maxwell relaxation

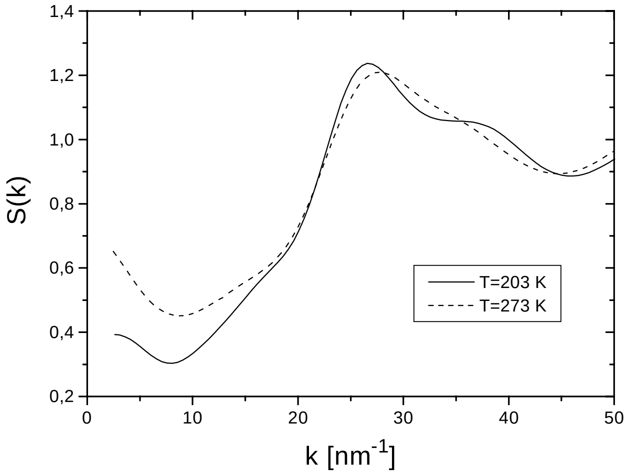

FIG. 4. Center of mass structure factor of HF at the two state points.

time $\tau_M(k) = \eta(k)/G_\infty(k)$ [$G_\infty(k)$ being the wave vector dependent rigidity modulus proportional to the normalized second moment of the transverse current, $\langle\omega_T^2(k)\rangle$] is so short that $\langle\omega_T^2(k)\rangle\tau_M^2$ is always $\ll 1$. Consequently in this liquid the dynamics of collective properties is dominated by the viscous response. Evidently the difference between water and HF has to be found in the fact that, whereas G_∞ is only a few percent smaller in HF than in water, the shear viscosity η is 10 times smaller.

This argument can also be applied to the analysis of the longitudinal currents. Here the relaxation time $\tau_L(k)$ starts from a value [23]

$$\tau_L(0) = \frac{1}{nM}\,\frac{\frac{4}{3}\eta + \eta_B}{C_\infty^2 - C_0^2}\,, \qquad (3)$$

where η_B is the bulk viscosity. Again comparing with water, whereas C_∞ is of the same order of magnitude, the shear viscosity of HF (and most likely even the bulk viscosity) is much smaller so that in the case of HF this relaxation time is shorter and the liquid cannot respond in a rigid fashion in contrast to water [8].

In conclusion, the so-called *fast sound* phenomenon is not a common feature of hydrogen-bonded liquids, but it is strictly dependent on the actual connectivity properties of the system. This phenomenon appears evident in water, a three dimensional percolating system, whereas in HF, where the presence of topological chains reduces the percolating character to one dimension, the velocity of sound away from the hydrodynamics region does not show such an exceedingly large dispersion. On the other hand, the appearance in HF of the *optical-like* high frequency mode in both the longitudinal and transverse spectra confirms the fact that on a length scale characteristic of molecular clusters hydrogen-bonded liquids exhibit common features which can be understood in terms of the dynamical behavior of the corresponding solid.

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[1] J. Teixeira, M.C. Bellissent-Funel, S.H. Chen, and B. Dorner, Phys. Rev. Lett. **54**, 2681 (1985).
[2] F.J. Bermejo, M. Alvarez, S.M. Bennington, and R. Vallauri, Phys. Rev. E **51**, 2250 (1995).
[3] F. Sette, G. Ruocco, M. Krish, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Phys. Rev. Lett. **75**, 850 (1995).
[4] A. Rahman and F.H. Stillinger, Phys. Rev. A **10**, 368 (1974).
[5] M. Wojcik and E. Clementi, J. Chem. Phys. **85**, 6085 (1986).
[6] M.A. Ricci, D. Rocca, G. Ruocco, and R. Vallauri, Phys. Rev. A **40**, 7226 (1989).
[7] F. Sciortino and S. Sastry, J. Chem. Phys. **100**, 3881 (1994).
[8] U. Balucani, G. Ruocco, A. Torcini, and R. Vallauri, Phys. Rev. E **47**, 1677 (1993).
[9] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).
[10] U. Balucani, J.P. Brodholt, and R. Vallauri, J. Phys. Condens. Matter **8**, 9269 (1996).
[11] M. Sampoli, G. Ruocco, and F. Sette, Phys. Rev. Lett. **79**, 1678 (1997).
[12] P. Jedlovszky and R. Vallauri, Mol. Phys. **93**, 15 (1998).
[13] P. Jedlovszky and R. Vallauri, Mol. Phys. **92**, 331 (1997).
[14] P. Jedlovszky and R. Vallauri, J. Chem. Phys. **107**, 10 166 (1997).
[15] U. Röthlisberger and M. Parrinello, J. Chem. Phys. **106**, 4658 (1997).
[16] M. Deraman, J.C. Dore, J.G. Powles, J.H. Holloway, and P. Chieux, Mol. Phys. **55**, 1351 (1985).
[17] The ratio $\gamma = c_p/c_v$ of the specific heat is experimentally found to be ≈ 1.1. This is in agreement with our simulation value which remains close to one at increasing wave vectors. We then may safely compare the isothermal and adiabatic sound velocities.
[18] M.W. Johnson, E. Sandor, and E. Arzi, Acta Crystallogr. Sec. B **31**, 1998 (1975).
[19] J.S. Kittelberger and D.F. Hornig, J. Chem. Phys. **46**, 3099 (1967).
[20] A. Anderson, B.H. Torrie, and W.S. Tse, Chem. Phys. Lett. **70**, 300 (1980).
[21] H. Boutin, G.J. Safford, and V. Brajovic, J. Chem. Phys. **39**, 3135 (1963).
[22] D. Bertolini and A. Tani, Phys. Rev. E **51**, 1091 (1995); **52**, 1699 (1995).
[23] J.P. Boon and S. Yip, *Molecular Hydrodynamics* (Dover Publications, Inc., New York, 1991).