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REORIENTATION OF WATER MOLECULES FREE FROM HYDROGEN BONDING

Reorientation of Water Molecules Free from Hydrogen Bonding

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The Mori continued fraction representation of the dipolar memory function $K_m(t)$ has been used to evaluate a spectrum $C(\omega)$ involving a single molecular parameter $K_0(0)$, an intermolecular torque dependent parameter $K_1(0)$ and a frequency parameter γ. Knowing these, it is possible to calculate the orientational correlation function $C(t)$ analytically. These parameters have been evaluated by fitting $C(\omega)$ to far infrared absorption data for very dilute solutions of water in cyclohexane, carbon tetrachloride and benzene. Therefrom $C(t)$ was found to be non-exponential, with correlation times of $\sim$0.1 ps, the corresponding loss curves $\varepsilon''(\omega)$ being asymmetric and peaking at far infrared frequencies. Thus the motion of free, unbonded water molecules cannot be described as rotational diffusion, but rather by a model of large amplitude reorientations, exhibiting distinct solvent dependence.

A considerable amount of detailed investigation has been carried out into the dielectric and far infrared properties of pure liquid water.[1, 2] The hydrogen bonding means that the observed Cole–Cole plot arises from the combined motions of considerably more than one molecule. As is shown in this study of the motion of unbonded individual H_2O molecules dissolved in organic solvents, the dielectric loss curve of the single molecule peaks at far infrared frequencies ($> \sim 100\ \mathrm{cm}^{-1}$). The corresponding reorientational correlation function,[3] $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$, where $\mathbf{u}$ is a unit vector in the direction of the molecular dipole moment, is not exponential, so that the intermolecular dynamics cannot be described by the classical Debye–Stokes–Einstein picture of rotational diffusion, requiring infinitely fast, infinitesimally small changes in the angular orientation of an individual dipole moment. The correlation time, defined by

$$\tau_M = \int_0^\infty \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle \,\mathrm{d}t$$

is of the order of 0.1 ps in the three solutions studied, such a short value being expected for a molecule such as H_2O which has an average moment of inertia of only $\sim 2 \times 10^{-40}\ \mathrm{g\ cm}^2$ about axes perpendicular to that of the dipole.

Loss curves $[\varepsilon''(\omega)]$ and correlation functions are calculated analytically by fitting the far infrared absorption data of Pardoe and Gebbie [4] to a theoretical curve generated using Mori's [5] continued fraction representation of the reorientational memory function.[6] This processing is carried out for very dilute solutions of water in cyclohexane, carbon tetrachloride and benzene.

THEORY

The equation proposed by Langevin [7] to account for translational Brownian motion can be extended to describe the rotational counterpart. Thus

$$\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t} + \beta\boldsymbol{\omega} = \boldsymbol{\Gamma}(t) \tag{1}$$

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where $\mathbf{\Gamma}(t)$ has the properties of angular acceleration and is the stochastic or random torque per unit moment of inertia on a given molecule due to its neighbours, β is a friction tensor with the units of frequency, and ω is the angular velocity (rad s^{-1}). The autocorrelation function which this equation yields upon direct integration is

$$C_{\boldsymbol{\omega}}(t) = \langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(t) \rangle = \exp(-\beta t) \langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(0) \rangle \qquad (2)$$

i.e. is purely exponential. The random torque $\mathbf{\Gamma}(t)$ is stationary and Gaussian and has an infinitely short correlation time, so that

$$\langle \mathbf{\Gamma}(0) \cdot \mathbf{\Gamma}(t) \rangle = D\delta(t) \qquad (3)$$

where $\delta(t)$ is a delta function in time and D is a diffusion tensor. In Langevin's model no correlation exists between the kinetic moment of the particle and the random torque, so that

$$\langle \boldsymbol{\omega}(0) \cdot \mathbf{\Gamma}(t) \rangle = 0. \qquad (4)$$

Fourier inversion [3] of eqn (2) leads to the Debye type complex spectral density $s(\boldsymbol{\omega})$, given by

$$s(\boldsymbol{\omega}) = \frac{D}{|\beta + \mathrm{i}\boldsymbol{\omega}|^2}. \qquad (5)$$

By Doob's theorem [8] the angular velocity probability distribution is rigorously Markovian, so that the conditional probability distribution for the state at any future instant, given the present state, is unaffected by any additional knowledge of the past history of the system.

Unfortunately, the general theory of random functions [9] shows that the second derivative of $C_{\boldsymbol{\omega}}(t)$ must be well-defined at $t = 0$. The quantity $|\ddot{C}_{\boldsymbol{\omega}}(t)|_{t=0}$ of eqn (2) is not so defined, which means that the random variable $\mathbf{\Gamma}(t)$, of infinitely short correlation time, has no physical reality. Experimentally, this is confirmed in the far infrared, where eqn (5) produces a plateau (called the Debye plateau) value of $\alpha(\omega)$, the absorption coefficient per unit path length of absorbing material (*e.g.* a dipolar liquid). In general, it is required that (i) $\mathbf{\Gamma}(t)$ be not necessarily Gaussian, and have a finite correlation time, and (ii) the friction tensor β be dependent on time.

These conditions are fulfilled by a more general form of the Langevin equation (1) proposed by Kubo and others [10]

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(t) \rangle = -\int_0^t K_{\omega}(t-\tau') \langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(\tau') \rangle \, \mathrm{d}\tau' \qquad (6)$$

where the " memory tensor " K is defined by Kubo's second fluctuation-dissipation theorem

$$\langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(0) \rangle K_{\boldsymbol{\omega}}(t) = \langle \mathbf{\Gamma}(0) \cdot \mathbf{\Gamma}(t) \rangle \qquad (7)$$

which compares and contrasts with eqn (3) of the simple theory. The " equilibrium ", or zero-time, properties of the system remain unchanged, so that, for example, with a Maxwell–Boltzmann equilibrium distribution of a unidimensional process of free rotation disturbed by collision, the first order distribution function is still

$$^1f_{\omega} = \frac{I}{2\pi kT} \exp\left(-\frac{I\omega^2}{2kT}\right)$$

with $\langle \boldsymbol{\omega} \rangle = 0$ and $\langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(0) \rangle = kT/I$.

Neglecting cross-correlations,[11] rotational-type far infrared bands of dipolar molecules have their associated orientational auto-correlation functions defined by [12]

$$C_{\mathrm{m}}(t) = \langle \mathbf{u}(0) \,.\, \mathbf{u}(t) \rangle$$
$$= \int_{-\infty}^{\infty} \exp{(\mathrm{i}\omega t)} \frac{3\hbar c}{4\pi^2} \frac{\sigma(\omega)\,\mathrm{d}\omega}{\omega[1-\exp{(-\hbar\omega/kT)}]} \tag{8}$$

where $\sigma(\omega)$ is the absorption coefficient per molecule.

Using $C_{\mathrm{m}}(t)$ in eqn (6) gives:

$$\dot{C}_{\mathrm{m}}(t) = -\int_0^t K_0(t-\tau')C_{\mathrm{m}}(\tau')\,\mathrm{d}\tau'$$

with $K_0(t-\tau')$ as the associated memory or response function whose Fourier transform would be the frequency dependent friction coefficient.

It can be shown [5] that the set of memory functions $K_0(t), \ldots, K_n(t)$ obey the set of coupled Volterra equations such that

$$\frac{\partial}{\partial t} K_{n-1}(t) = -\int_0^t K_n(t-\tau')K_{n-1}(\tau')\,\mathrm{d}\tau$$

with $n = 1, \ldots, N$. Taking Laplace transforms

$$\tilde{C}_{\mathrm{m}}(p) = \frac{C_{\mathrm{m}}(0)}{p+\tilde{K}_0(p)} = \frac{C_{\mathrm{m}}(0)}{p+\dfrac{K_0(0)}{p+\tilde{K}_1(p)}} = \ldots . \tag{9}$$

This is Mori's continued fraction representation of the correlation function $C_{\mathrm{m}}(t)$, p being the Laplace variable. The associated spectrum of frequencies, $C_{\mathrm{m}}(\mathrm{i}\omega)$, which is the Fourier–Laplace transform of $\tilde{C}_{\mathrm{m}}(p)$, can now be obtained by truncating the series of eqn (9) using a convenient form for $K_n(t)$. The equilibrium averages $K_0(0)$, $K_1(0)$ *etc.* are related [6] to the terms in the even time expansion of $C_{\mathrm{m}}(t)$, so that, for a linear molecule [12, 13] or a symmetric top, $K_0(0) = 2kT/I_B$ (where I_B is the component of the moment of inertia perpendicular to the axis containing the dipole moment) *i.e.* is a single molecule property, and $K_1(0)$ is related to the intermolecular mean square torque, $\langle \mathrm{O}(V)^2 \rangle$. Any truncation of the series of eqn (9) which leaves out $\tilde{K}_1(p)$ cannot adequately account for their torque. Such is the termination $K_0(t) = K_0(0)\exp(-\gamma_0 t)$, which corresponds [11] to the M-diffusion model [14] of instantaneous collisions when the torque becomes infinite at the moment of encounter. One of the simplest ways of introducing a finite $\langle (\mathrm{O}V)^2 \rangle$ is to use [15] the truncation

$$K_1(t) = K_1(0)\exp(-\gamma t)$$

so that

$$\tilde{C}_{\mathrm{m}}(p) = \frac{K_1(0)+p^2+p\gamma}{p^3+p^2\gamma+p[K_0(0)+K_1(0)]+\gamma K_0(0)}. \tag{10}$$

The absorption coefficient, $\alpha(\omega)$, can now be extracted from eqn (10) by Fourier–Laplace transformation, giving

$$\alpha(\omega) = \frac{\Lambda(\varepsilon_0-\varepsilon_\infty)}{n(\omega)c} \frac{\omega^2 K_0(0)K_1(0)\gamma}{\gamma^2[K_0(0)-\omega^2]^2+\omega^2\{\omega^2-[K_0(0)+K_1(0)]\}^2} \tag{11}$$

where Λ is a correction [16] for the internal field, $n(\omega)$ is the frequency dependent refactive index, $(\varepsilon_0-\varepsilon_\infty)$ is the total dispersion and c is the velocity of light.

Inverse Laplace transformation of eqn (10) yields the correlation function as

$$\begin{aligned} C_{\mathrm{m}}(t) &= \langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle \\ &= \left[\frac{\cos\beta t}{1+\Gamma}+\frac{1}{\beta}\left(\frac{\alpha_1+\Gamma\alpha_2}{1+\Gamma}\right)\sin\beta t\right]\exp(-\alpha_1 t)+\frac{\Gamma}{1+\Gamma}\exp(-\alpha_2 t) \end{aligned} \tag{12}$$

where

$$\Gamma = \frac{2\alpha_1(2\beta^2-\alpha_1^2)}{\alpha_2(3\alpha_1^2-\beta^2-\alpha_2^2)},$$

with

$$\alpha_2 = -S_1-S_2+\gamma/3\,;\ \alpha_1 = \tfrac{1}{2}(S_1+S_2)+\gamma/3\,;\ \beta = \tfrac{1}{2}\sqrt{3}(S_1-S_2).$$

The parameters S_1 and S_2 are defined by

$$S_1 = \left[-\frac{B}{2}+\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}}$$

$$S_2 = \left[-\frac{B}{2}-\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}},$$

with

$$A = K_0(0)+K_1(0)-\gamma^2/3$$

$$B = \frac{\gamma}{3}\left[\frac{2\gamma^2}{9}+2K_0(0)-K_1(0)\right].$$

The correlation time, τ_{m}, defined by:

$$\tau_{\mathrm{m}} = \int_0^\infty \langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle\,\mathrm{d}t \tag{13}$$

is evaluated from eqn (12) as

$$\tau_{\mathrm{m}} = \frac{1}{(1+\Gamma)}\left(\frac{2\alpha_1+\Gamma\alpha_2}{\alpha_1^2+\beta^2}+\frac{\Gamma}{\alpha_2}\right). \tag{14}$$

The memory function corresponding to $C_{\mathrm{m}}(t)$ is given by

$$\tilde{K}_{\mathrm{m}}(p) = p+\tilde{C}_{\mathrm{m}}^{-1}(p) \tag{15}$$

so that

$$\left.\begin{aligned} K_{\mathrm{m}}(t) &= K_0(0){}_{\mathrm{e}}^{-\gamma t/2}[\cos at+(\gamma/2a)\sin at] \\ &\text{if } K_1(0) > \gamma^2/4 \\ &= K_0(0){}_{\mathrm{e}}^{-\gamma t/2}\,[\cosh bt+(\gamma/2b)\sinh bt] \\ &\text{if } K_1(0) < \gamma^2/4 \\ &= K_0(0){}_{\mathrm{e}}^{-\gamma t/2}(1+\gamma t/2) \\ &\text{if } K_1(0) = \gamma^2/4 \end{aligned}\right] \tag{16}$$

where $a^2 = -b^2 = [K_1(0)-\gamma^2/4]$.

This form of $K_{\mathrm{m}}(t)$ is the same as that for the orientational correlation function deduced from the *M*-diffusion model of a vibrator perturbed by a Poisson distribution of collisions randomising the angular momentum vector in direction only.

By fitting the far-infrared $\alpha(\omega)$ data to eqn (11), thereby determining γ and $K_1(0)$, it is possible to calculate the vectorial correlation function $C_{\mathrm{m}}(t)$ and the memory function $K_{\mathrm{m}}(t)$ using eqn (12) and (16). Without the use of eqn (11), it would be difficult, if not impossible, to evaluate $C_m(t)$ by numerical Fourier transformation of of the far infrared data, because these have not the necessary accuracy needed in the region 0.1-10 cm^{-1} for this operation.

RESULTS AND DISCUSSION

The far infrared absorption data of Pardoe and Gebbie [4] for very dilute solutions of water in cyclohexane, carbon tetrachloride and benzene were fitted to eqn (11) using the N.A.G. least mean squares program EO4 FAA. The results are illustrated in fig. (1), where are displayed also the corresponding correlation functions $C_m(t)$ of eqn (12). The table shows the values of $K_1(0)$ and γ needed for each fitting, together with the correlation time τ_m of eqn (14). The memory functions $K_m(t)$ are displayed in fig. (2), together with the dielectric loss curves $\varepsilon''(\omega)$ calculated from eqn (11) using the Maxwell relation:

$$\alpha(\omega) = \omega\varepsilon''(\omega)/n(\omega).$$

Here, $\varepsilon''(\omega)$ is the dielectric loss, and $n(\omega)$, the frequency dependent refractive index, is virtually constant, near the D-line value, for these low absorbing systems.

TABLE 1.—PARAMETERS USED IN EQN (12) AND (16)

solution	T/K	$\left(\frac{2kT}{I_B}\right)^{-1} K_0(0)$	$\left(\frac{2kT}{I_B}\right)^{-1} K_1(0)$	$\left(\frac{2kT}{I_B}\right)^{-1/2} \gamma$	τ_M/ps
H_2O+cyclohexane (0.011 % w/w)	296	1.11	3.00	2.58	0.10
H_2O+CCl_4 (0.01 % w/w)	300	1.18	3.39	2.37	0.08
H_2O+benzene (0.06 % w/w)	300	1.16	6.19	2.82	0.09

The value of $K_0(0)$ is in each case close to the theoretical symmetric top value of $2kT/I_B$, the water molecule being in reality an asymmetric top. In contrast, the torque dependent parameter $K_1(0)$ displays a distinct solvent dependence, being higher in benzene than in the other two solvents. It might be significant that the latter each form a plastic crystalline, or rotator phase, so that their van der Waals profiles are by implication spheroidal in contrast to the plate-like benzene molecule.

The motion of the dipolar water molecule cannot be described as rotational diffusion, since the correlation functions, $C_m(t)$ are not exponential. In cyclohexane [fig. 1(*b*)], there is a probability that a majority of molecules will have jumped through greater than $\pi/2$ rad at $\gtrsim 0.11$ ps because $C_m(t)$ becomes negative before oscillating to zero at ~ 0.4 ps. The overall correlation time is 0.10 ps, much shorter than the Debye relaxation time in pure liquid water,[1, 2] where many molecules, linked together by hydrogen bonding, are simultaneously contributing to the relaxation process. The loss curve in cyclohexane [fig. 2(*b*)] is asymmetric when plotted on a log scale, and peaks at ~ 140 cm^{-1}.

Oscillations in $C_m(t)$ are apparent also in solution in carbon tetrachloride, but here the correlation function remains positive, implying that the H_2O molecule has slightly less angular freedom [$K_1(0)$ is slightly higher] than in cyclohexane, and that jumps of smaller amplitude are possible. This conclusion is open to uncertainty since the original fit [fig. 1(*c*)] is not as satisfactory as for the solution in cyclohexane.

The oscillations in $C_m(t)$ are damped out almost completely in the benzene solution, but the semi-logarithmic plot of fig. 1(*f*) shows that the correlation function is not exponential, so that Debye-type relaxation is not taking place. The loss curve [fig. 2(*f*)] is highly asymmetric, and peaks at 70 cm^{-1}, considerably lower than in cyclohexane and carbon tetrachloride solutions.

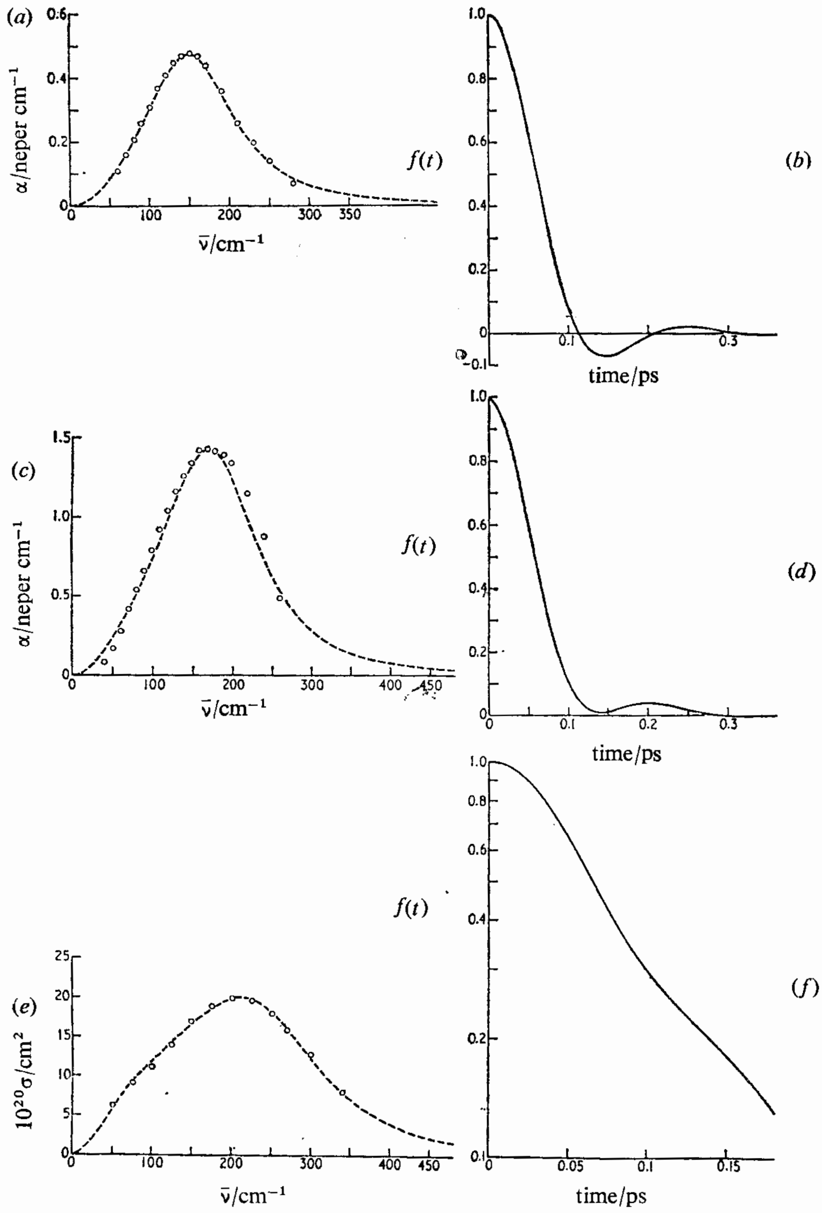

FIG. 1.—(*a*) Absorption [4] of a 0.011 % w/w solution of water in cyclohexane at 296 K, corrected for solvent; – – – eqn (11) l.m.s. best fit. (*b*) Orientational correlation function $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ for the absorption of fig. 1(*a*) calculated from eqn (12). (*c*) Absorption [4] of a 0.01 % w/w solution of water in CCl_4 at 300 K, corrected for solvent; – – – eqn. (11) l.m.s. best fit. (*d*) $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ of eqn (12) for H_2O+CCl_4. (*e*) Absorption [4] of a 0.06 % w/w solution of water in benzene at 300 K, corrected for solvent; – – – eqn (11) l.m.s. best fit. (*f*) $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ of eqn (12) for H_2O+benzene.

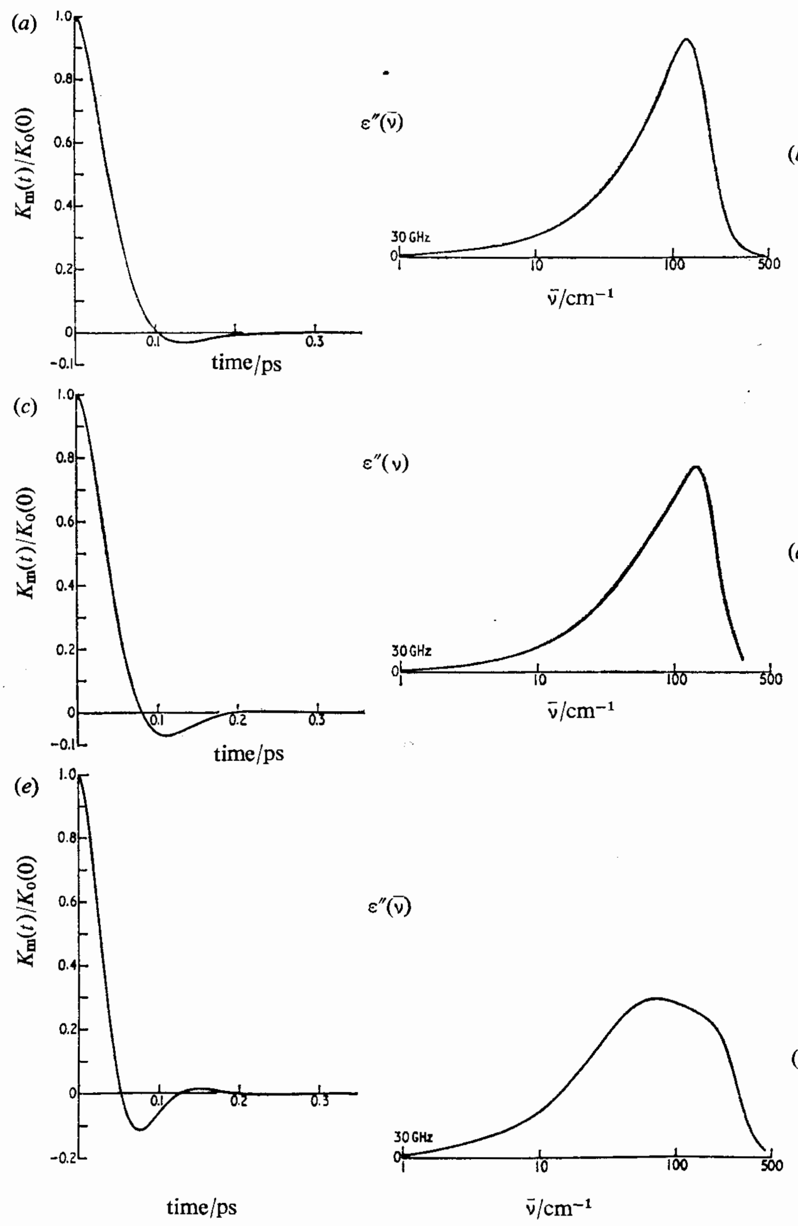

FIG. 2.—(*a*) Normalised memory function [$K_m(t)/K_0(0)$] for H_2O + cyclohexane, calculated from eqn (16). (*b*) Loss curve for H_2O + cyclohexane, calculated from eqn (11). (*c*) Normalised memory function for $H_2O + CCl_4$ at 300 *K*. (*d*) Loss curve for $H_2O + CCl_4$ solution. (*e*) Normalised memory function for H_2O + benzene at 300 K. (*f*) Loss curve for H_2O + benzene solution.

Memory functions were calculated for the three systems using eqn (16), and are displayed in fig. 2(*a*), (*c*) and (*e*), being normalised to unity at $t = 0$ by division by $K_0(0)$. The shape of $K_m(t)$ is independent of $K_0(0)$, and depends upon the torque

$K_1(0)$ and the width parameter γ only at each time t. Using the second fluctuation-dissipation theorem, we have

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(0)\rangle K_{\mathrm{m}}(t) = \langle F(0) \cdot F(t)\rangle \tag{17}$$

where $F(t)$ is a generalised torque, orthogonal to $\mathbf{u}(0)$, *i.e.* $\langle \mathbf{u}(0) \cdot (t)\rangle F = 0$. The torque $F(t)$ is not Markovian, since $K_{\mathrm{m}}(t)$ is not a pure exponential, therefore the autocorrelation function $C_{\mathrm{m}}(t)$ and its associated memory function $K_{\mathrm{m}}(t)$ describe a system of molecular reorientations where past events have a bearing on what happens at future times, unlike Debye relaxation, where $\mathbf{u}(t)$ is Markovian and $\langle \mathbf{u}(0) \cdot \mathbf{u}(t)\rangle$ purely exponential.

Since $C_{\mathrm{m}}(t)$ is an even, equilibrium function of time, it can be shown that the memory function $K_{\mathrm{m}}(t)$ must also have the same property, and subsequently, its Maclaurin expansion must ideally contain even powers of t only. Our $K_{\mathrm{m}}(t)$ [eqn (16)] is even up to t^2, but contains a term in t^3, and $C_{\mathrm{m}}(t)$ contains a term in t^5; therefore both are approximations to the theoretically even functions, but judging from the good fit to the experimental data of the associated spectrum $C_{\mathrm{m}}(\omega)$ [fig. 1(*a*), (*c*), (*e*)], are reasonably adequate for present needs.

Very few computed memory functions are available for comparison with those of fig. 2(*a*), (*c*) and (*e*), but Kushick and Berne [17] have fairly recently computed normalised memory functions for the velocity of self-diffusion of an argon molecule in a Lennard–Jones fluid at several number densities. These functions can be regarded as arising from the extended Langevin theory of translational Brownian motion. The overall form of these functions of argon molecular diffusion and our rotational memory functions for the isolated water molecule are similar. For lower molecular number densities, the translational memory function for argon has a shallow negative region and is damped to zero with slight oscillations. These features are reproduced in our rotational $K_{\mathrm{m}}(t)$, the oscillation being most pronounced in the benzene solution. The memory function becomes negative after 0.10 ps in cyclohexane, 0.08 ps in CCl_4 and 0.05 ps in benzene, suggesting that the " collision " process in the latter solution is shortest lived, since instantaneous inertialess events would correspond to a delta function for $K_{\mathrm{m}}(t)$ at $t = 0$. This is evidence for the effect of the anisotropy of solvent molecules on the motion of the solute H_2O.

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