NONLINEAR EFFECTS IN MOLECULAR DYNAMICS OF WATER: LARGE SAMPLE COMPUTER SIMULATION OF RISE AND FALL TRANSIENTS

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In one of the largest computer simulations to data of liquid water, the effect of a strong, external, uniaxial electric field on an equilibrium sample of 1372 molecules has been investigated. The orientational rise transient from field-off to field-on equilibrium shows a complex pattern of oscillations in the sub-picosecond range which are neither predicted theoretically nor seen in previous computer simulations. On the other hand, the phenomenon of fall transient acceleration first discovered by computer simulation in a sample of only 108 molecules is confirmed in the present work, indicating that the acceleration effect is independent of sample size, and is a fundamental physical property of liquids, including water.

Early computer simulations of molecular diffusion, using a small sample of 108 molecules, resulted in the observation of field decoupling and fall transient acceleration [1–5]. Subsequent analytical work [5–10] showed that these are fundamental dynamical processes which provide unique information on the statistical properties of the molecular liquid state of matter. The field decoupling effect shows that the molecular ensemble is statistically non-markovian, and the fall transient acceleration can be explained only by using an effective intermolecular potential which is nonlinear in the diffusion coordinate (linear or angular displacement, depending on whether the process is translational or rotational diffusion). A simple diffusion process such as that envisaged by Debye [11] in the original theory of rotational diffusion cannot be used to explain these effects. However, the concept of itinerant oscillation, torsional or linear oscillation superimposed upon rotational or translational diffusion, can be put into mathematical form and in some cases the resulting equations can be solved analytically for observables of interest [12–15]. The itinerant oscillator equations have also been given a rigorous and general framework by Grigolini and Marchesoni [7,16] and by Schneider and Freed [17]. In simple terms, for example, a two dimensional Langevin equation for rotational diffusion is supplemented by an extra term representing the effect of the intermolecular potential $V_0 \sin\theta$ [18]:

$$I\ddot{\theta}+I\beta\dot{\theta}+V_0\sin\theta=W, \tag{1}$$

where β is the friction coefficient, V_0 the potential barrier height, I the moment of inertia, and W the stochastic noise (Wiener process) of the two dimensional rotational Langevin equation. When this equation is solved for the dipole orientational, following upon the instantaneous application of a strong, uniaxial, electric field to a sample of diffusing molecules, rise and fall transients can be observed. As the external electric field strength is increased the theoretical rise transients start to oscillate at sub-picosecond intervals, and the fall transients are accelerated in time dependence with respect to the equilibrium dipole orientational autocorrelation function. Later theoretical work by Grigolini and Marchesoni [16] showed that under certain circumstances the fall transient can be decelerated as well as accelerated by a nonlinear field term. However, the additional term in the Langevin equation must

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be nonlinear in θ for the theoretical description of fall transient acceleration or deceleration. A simple harmonic potential term, proportional to θ^2, produces a fall transient whose time dependence is identical with that of the equilibrium orientational autocorrelation function.

In this Letter we not only provide the first numerical verification of the rise transient oscillation (RT) in real liquid, as predicted from the modified planar-rotational Langevin equation by Coffey, Rybarsch, and Schroer in 1982 [18], but also point out the emergence of more complex patterns as the field strength is increased. Althoug the original theoretical prediction was made with planar rotational diffusion, the present computer simulation, using 1372 water molecules, shows that RTO is also observable numerically in three dimensions. This is supporting evidence for the validity of simple planar dynamics for three dimensional diffusion. In the following the method and the potential for water–water interaction are briefly described before the results.

The translational and rotational equations of motion were integrated numerically for 1372 water molecules interacting through a pairwise additive intermolecular potential approximated with a Lennard-Jones 5 by 5 site–site representation developed by Evans et al. and well tested in the literature [19–21]. The time step used was 0.5 fs at a molar volume of 18.0 cm^3/mole and a temperature of 293 K. Simple cubic periodic boundary conditions with minimum image interactions were employed to simulate an infinite system. Electric field was applied after the system had been equilibrated for about 5000 time steps. The duration of the applied field lasted for 2 ps.

When an electric field is turned on, it is assumed to produce a torque on each molecule of the type $-\boldsymbol{\mu}\times\boldsymbol{E}$ where $\boldsymbol{\mu}$ is the molecular dipole moment and E the external field strength applied in the z direction. This is the type of torque considered analytically by Coffey, Rybarsch, and Schroer [18]. More complicated types of field–dipole interaction could be coded if necessary, e.g. as in previous work [4,5] on the generation of second order Langevin functions (known as Kielich functions) by computer simulation.

As in previous work with a small sample of 108 molecules the rotational and translational kinetic energies of the sample at field-off and field-on equilibrium are the same on average. During the rise transient time interval, however, the sample is in the process of re-equilibration so that a temperature rescaling process is utilized to control the effective rotational and translational kinetic energies.

Temperatures rescaling in our simulations takes place at irregular intervals defined by a limit over which the temperature is allowed to fluctuate (usually about ±50 K). Rescaling is automatic and takes place sometimes over successive time steps and sometimes once every ten, hundred, or even thousand, time steps. Its effect, if present, is usually manifested as cusps in the transients and correlation functions [7,18]. The observed maxima and minima in the rise transients of this work, as will be seen, are quite different in nature, being regularly periodic, differentiable, continuous, and field dependent, and thus are not to be attributed to the artifacts of the temperature rescaling.

Rise transients were defined at each time step as the simple average over 1372 molecules of the z component of the dipole unit vector and were computed over about 500 time steps after the instantaneous application of the z-axis external field; and fall transients similarly calculated after its instantaneous removal. FTA is detected by comparing the normalized orientational fall transient with the equivalent orientational autocorrelation function at field-free equilibrium, and for this purpose the latter was computed using standard running time averaging techniques.

Fig. 1 exemplifies rise transient oscillations with a field of sufficient strength ($\sim 5\times10^9$ V/m) to nearly saturate the Langevin function. The equivalent energy being pumped into the system by the field is 20.0 kJ/mole, which lifts the field-of equilibrium potential energy of -35.5 kJ/mole to a field-on equilibrium level of -15.5 kJ/mole. The oscillations in fig. 1 occur at regular intervals as predicted by the theory. Below the saturation, both the amplitude and the oscillation frquency are seen to decrease with decreasing external field strength, as predicted essentially in the original paper by Coffey et al. [18]. However, if the externally applied field strength is doubled, the oscillations in the rise transient deepen and split as illustrated in fig. 2. This is an effect which is not predicted by the simple two

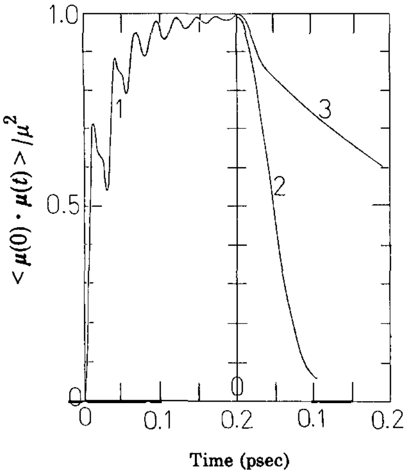

Fig. 1. Rise and fall transients of the dipole (μ) autocorrelation functions for an external field energetically equivalent to +20.0 kJ/mole: Rise transient (1) showing oscillations; Fall transient (2) accelerated with respect to the equilibrium orientational autocorrelation function (3).

dimensional diffusion theory of Coffey, Rybarsch, and Schroer [18] and which is reported here for the first time. The simple diffusional theory predicts one RTO frequency only, which is deepened by increasing the field strength. In our large sample simulation, on the other hand, increasing the field strength results in extra RTO peaks as in fig. 2 compared with fig. 1.

The number of peaks in the rise transients is plotted against field strength in fig. 3, which clearly shows that the former is roughly proportional to the latter at fixed temperature and molar volume. The dependence of numbers of peaks on field strength has never been predicted theoretically (much less experimentally), an indication that the simple sine potential in eq. (1) is not an adequate description of the actual intermolecular potential effective in controlling the diffusion dynamics. A more realistic potential would be the one suggested from a Fourier expansion in θ.

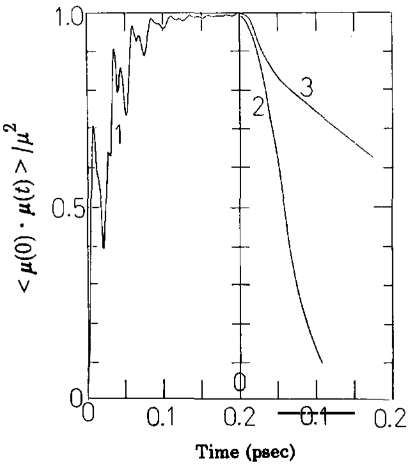

Fig. 2. As for fig. 1, but field is increased in intensity by 2 times.

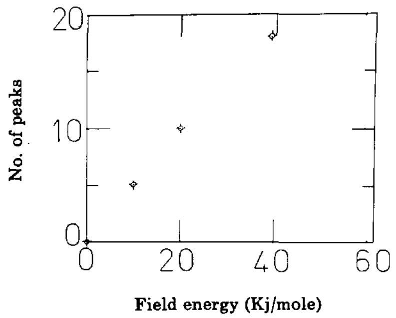

Fig. 3. Number of peaks in the rise transient plotted as a function of equivalent applied field energy in kJ/mole.

In previous simulations [1–5] of RTO with only 108 water molecules the oscillations were unobservable, being either too low in amplitude or masked by noise. Therefore there is a pronounced effect of sample size, large samples are essential in eliminating statistical noise, which tended to dominate the rise transients obtained with only 108 molecules [1–5]. Furthermore, the field induced rise transient oscillations are easily distinguishable from noise by their regularity and field dependence. The RTO increases with external electric field strength whereas statistical noise in the rise transients decreases.

In contrast, the fall transient acceleration (FTA) effect is clearly observable in small samples of 108 molecules, and is confirmed in this work with 1372 water molecules after the instantaneous removal of the uniaxial electric field. Both field strengths shown in figs. 1 and 2 are sufficient to produce a very large fall transient acceleration as illustrated there. The fall transients are free of oscillations but decay far more quickly to zero than the equivalent equilibrium orientational autocorrelation function. FTA was also explained analytically by Grigolini using a type of planar intinerant oscillator where the effective intermolecular potential was represented by a cosine term, nonlinear in the rotational coordinates [22]. A full description of this theory is available [23], and confirms that FTA appears analytically only through the use of nonlinear potential terms. This also means that such terms must be used at field free equilibrium in a more complete description of diffusion processes than allowed for in the original work of Debye, where there is no representation of the effective intermolecular potential. Experimental verification of the analytical and numerical work would provide unique and novel information on the role of the effective intermolecular potential in the context of liquid state diffusion.

As in smaller samples of 108 molecules, the FTA effect is also dependent on field strength: the stronger the applied field the more rapid is the decay of the fall transient in comparison with the equilibrium orientational autocorrelation function.

The observation of rise transient oscillation (RTO) and fall transient acceleration (FTA) in our computer simulation shows that a simple harmonic potential term is insufficient for a realistic discription of rotational diffusion in the presence of intermolecular pair potentials. On the other hand, a two dimensional theoretical treatment of rotational diffusion seems to be an adequate approximation of the essentials of three dimensional molecular dynamics in the liquid state of matter. Essentially similar effects are generated both by two dimensional analytical diffusion theory and by three dimensional large sample numerical computer simulation of liquid water, although further theoretical work is required to explain the appearance of extra peaks as the field strength is increased beyond the saturation point.

The RTO and FTA effects have now been predicted theoretically and confirmed numerically by large sample simulation. To observe these effects experimentally requires an aligning field sufficient to saturate the Langevin function. One possible way of achieving this without the use of intense laser fields and elaborate back up apparatus would be to monitor rise and fall transients in room temperature or supercooled liquid crystals with electric or magnetic aligning fields of low intensity. The orientational transients in supercooled liquid crystals can be slowed to the nanosecond time scale and monitored with the fast response detectors of a probe laser system, such as a submillimeter laser, or of a Fourier transform interferometer. Alternatively, saturation of the Langevin function could be achieved with powerful pulses of laser radiation, and the second Legendre polynomial rise and fall transients monitored with optical Kerr effect apparatus.

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