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ITINERANT OSCILLATION WITH A COSINE POTENTIAL

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The equations of motion of the planar itinerant librator are extended to involve a cosine potential rather than a harmonic form for interaction, and are solved numerically to produce the angular velocity autocorrelation function and its Fourier transform (real and imaginary parts). The behaviour of the cosine potential is matched with that of the harmonic potential through these functions and in general conforms more closely to the indication of zero-THz spectroscopy and computer simulation.

1. Introduction

In this paper we deal with an extension of the model of itinerant oscillation to include potential interaction forms other than the harmonic function used by Coffey and Calderwood [1] in their original paper. The assumption made by these authors is that the binding (or potential interaction) between the inner molecule and cage is harmonic. This is an approximation introduced for the sake of analytical tractability. More realistically the potential has a cosine dependence so that the equations of motion are [2]:

$$I_2\,\ddot{\theta}(t) + I_2\,\omega_0^2 \sin[\theta(t) - \phi(t)] = 0, \qquad (1)$$

$$I_1\,\ddot{\phi}(t) + I_1\,\beta\dot{\phi}(t) - I_2\,\omega_0^2 \sin[\theta(t) - \phi(t)] = I_1\,\dot{W}(t). \qquad (2)$$

In these equations $W(t)$ is a Wiener process representing the effect of brownian noise on the rotating cage, of moment of inertia I_1. The moment of inertia of the reference (encaged) molecule is I_2 and ω_0^2 is a coupling constant between molecule and cage. The friction coefficient β is a scalar governing the brownian motion of the cage and θ and ϕ are orientation angles defined by Coffey and Calderwood [1].

There is no known analytical solution to eqs. (1) and (2) except in the case $\sin[\theta(t) - \phi(t)] \doteqdot \theta(t) - \phi(t)$, i.e. the harmonic case. However, Ferrario and Evans [2] have recently solved these equations numerically by the use of matrix diagonalisation techniques, and in consequence it is of interest to recalculate the experimental best fit harmonic results of Reid and Evans [3].

2. Computer simulation

An algorithm written originally by Renaud and Singer [4] has been modified to produce the Legendre polynomial $\langle P_n \rangle$ orientational autocorrelation functions for n up to 5, together with the angular momentum autocorrelation function, $\langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle$. These data can then be analysed with the model equations (1) and (2) in the harmonic limit of Coffey and Calderwood [1] as discussed lately by Ferrario et al. [2].

This was carried out as follows. With the original concept of $\sin[\theta(t)-\phi(t)] \doteq \theta(t)-\phi(t)$ the simulated $\langle P_2 \rangle$ function was fitted with a non-linear least mean squares method, iterating on β, ω_0^2 and $(I_1/I_2)\omega_0^2$ as parameters. Using these it is possible to calculate $\langle P_2 \rangle$ to $\langle P_5 \rangle$ analytically, using the theorem of Calderwood and Coffey [1]. It is also possible to calculate $\langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle$ with the same set of parameters. A self-consistent comparison is therefore possible. By fitting the function $\langle P_2(t) \rangle$, the second Legendre polynomial autocorrelation function (acf) of orientation, $\theta(t)$, the first acf $\langle P_1(t) \rangle$ is reproduced fairly accurately [2], especially at long times, where the decay of both P_1 and P_2 with time is roughly exponential. The functions $\langle P_2 \rangle$ and $\langle P_5 \rangle$ are followed less closely, possibly because these are always markedly non-exponential in nature. The harmonic assumption $\sin[\theta(t)-\phi(t)] \doteq \theta(t)-\phi(t)$ is therefore fairly restrictive in the original model. This is shown clearly by comparing the simulated and analytical angular momentum acf's using the set of parameters derived from $\langle P_2 \rangle$. The model $\langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle$ is *far too oscillatory.*

It is therefore essential to consider whether the replacement of a harmonic potential by a cosine one would succeed in damping out these oscillations to a sufficient degree, or whether the basic concept of itinerant oscillation is at odds with the results.

3. Numerical solution

This has been described elsewhere [2], but the salient points are reproduced here for convenience. The first stage is to write down the Fokker–Planck equations describing the process, that is:

$$\partial P(\psi_1, \psi_2, \dot{\theta}, \dot{\phi}, t \,|\, 0)/\partial t = LP, \tag{3}$$

where the Fokker–Planck operator L is:

$$\begin{aligned} &\frac{1}{2}\frac{\partial}{\partial \psi_1}(\dot{\theta}+\dot{\phi}) + \frac{1}{2}\frac{\partial}{\partial \psi_2}(\dot{\theta}-\dot{\phi}) - \frac{1}{2I_2}\frac{\partial}{\partial \dot{\theta}} V'(\psi_2) \\ &+ \frac{1}{2I_1}\frac{\partial}{\partial \dot{\phi}} V'(\psi_2) + \frac{\partial}{\partial \dot{\theta}}\dot{\theta} + \frac{kT}{I_2}\frac{\partial^2}{\partial \dot{\theta}^2} + \frac{\partial}{\partial \dot{\phi}}\dot{\phi} \\ &+ \frac{kT}{I_1}\frac{\partial^2}{\partial \dot{\phi}^2}. \end{aligned}$$

The boundary conditions for θ and ψ are $-\pi < \theta < \pi$ and $-\pi < \phi < \pi$, which result in $-\pi < \psi_1 \leqslant \pi$ and $-\pi < \psi_2 \leqslant \pi$.

Here

$$\psi_1 \equiv (\theta+\phi)/2; \qquad \psi_2 \equiv (\theta-\phi)/2;$$

$$V(\psi_2) = -I_2\,\omega_0^2 \cos(2\psi_2).$$

The equilibrium solution of eq. (3) is:

$$P_{\mathrm{eq}}(\psi_1, \psi_2, \dot{\theta}, \dot{\phi}) = \frac{1}{N'} \exp\left[-\frac{\dot{\theta}^2 I_2}{2kT} - \frac{\dot{\phi}^2 I_1}{2kT} + \frac{I_2\omega_0^2}{kT}\cos(2\psi_2)\right]. \tag{4}$$

Eq. (3) can be solved by a method which is generally applicable and is described by Risken and Volmer [5]. This allows us to compute any correlation function of interest by the integral:

$$\langle \alpha_1, (0)\, \alpha_2(t) \rangle = \int \chi_1(\Omega, 0)\, \chi_2(\Omega, t)\, \mathrm{d}\Omega, \tag{5}$$

where $[\Omega] = [\psi_1, \psi_2, \dot{\theta}, \dot{\phi}]$ are physical observables of the system and can be expressed in terms of $[\Omega(t)]$.

$\chi_2(\Omega, t)$ is the solution of the equation

$$\partial \chi / \partial t = L_{\mathrm{F}} \chi, \tag{6}$$

with the diffusion operator:

$$L_{\mathrm{F}} = \psi^{-1}(\Omega) L(\psi(\Omega)) \tag{7}$$

and

$$\psi(\Omega) = (N')^{-1/2} \exp[-(I_2\dot{\theta}^2 + I_1\dot{\phi}^2)/4kT + (I_2\omega_0^2/2kT)\cos(2\psi_2)]. \tag{8}$$

Subjected to the initial condition:

$$\Phi_2(0, \Omega) = \alpha_2(\Omega)\, \psi(\Omega).$$

The solution is achieved numerically by using the following expansion on the basis set of Hermite polynomials and on the plane waves of the function Φ:

$$\Phi(\Omega) = \sum_{\substack{n=0\\ n_1,n_2}}^{\infty} \sum_{-\infty}^{\infty} A_{kq}^{n_1 n_2}(t)\, \mathrm{He}_{n_1}(\dot{\theta})\, \mathrm{He}_{n_2}(\dot{\phi}) \times \exp(\mathrm{i}k\psi_1 + \mathrm{i}q\psi_2)\psi(\Omega), \tag{9}$$

which transforms eq. (6) into a linear differential matrix equation:

$$\dot{\boldsymbol{A}}(t) = \mathbf{C}\boldsymbol{A}(t), \tag{10}$$

where

$$\boldsymbol{A}(t) = \begin{bmatrix} A_{00}^{00}(t) \\ A_{00}^{10}(t) \\ \vdots \\ A_{\tilde{k}\tilde{q}}^{\tilde{n},\tilde{n}_2} \end{bmatrix}, \tag{11}$$

and $\mathbf{C}$ is the matrix expansion of the operator L_{F} on the basis set given by eq. (9).

Eq. (10) is solved by diagonalising the matrix $\mathbf{C}$. The solution is:

$$\boldsymbol{A}(t) = \exp(\mathbf{C}t)\boldsymbol{A}(0) = \sum_i \boldsymbol{F}_i \exp(\boldsymbol{C}_i t)[\tilde{\boldsymbol{F}}_i, \boldsymbol{A}(0)], \tag{12}$$

where $\boldsymbol{F}_i$ and $\tilde{\boldsymbol{F}}_i$ are the right and left eigenvectors and $\boldsymbol{C}_i$ the eigenvalues of the matrix $\mathbf{C}$, and the brackets [,] mean the scalar product. In evaluating the integrals (5) we have used the fact that:

$$g_q = \int \cos(qx) \exp((I_2\omega_0^2/kT)\cos 2x)\, \mathrm{d}x$$

$$= 0 \text{ if } n \text{ is odd;}$$

$$= B_{q/2}(I_2\omega_0^2/kT) \quad \text{if } n \text{ is even or zero.}$$

Here $B_n(z)$ is the modified Bessel function of integer order, $n = 0, 1, 2, \ldots$.

4. Results and discussion

Reid and Evans [3] have recently estimated the coefficients β, ω_0^2 and $(I_1/I_2)\omega_0^2$ for twenty-three dipolar solutes in decalin using data in both frequency and time domains. We have recomputed the theoretical angular momentum acf's and in this section some of the results are illustrated in the low and high damping extremes.

The computational problem of solving eqs. (1) and (2) involves multi-dimensional matrix diagonalisation [eq. (11)] and therefore an unusually large amount of storage. In consequence it is not possible on the system available to us (UMRCC CDC 7600) to compute the orientational autocorrelation functions $\langle P_n \rangle$ because of lack of storage space.

However, using the best fit parameters of Reid and Evans [3] it is possible to compare directly the harmonic and cosinal angular momentum autocorrelation functions. We have chosen four solute/decalin systems out of the original twenty-three with which to do this in as representative a manner as possible. The corresponding zero-THz spectra are listed elsewhere [3, 6] in the harmonic limit.

The purpose of replacing the harmonic potential with a cosine potential is to generalise the itinerant librator model. There is no known *truncation* of the Mori continued fraction which corresponds to the use of a cosine potential although theoretically the use of an *infinite* continued fraction with the appropriate equilibrium averages should lead to a proper description of three-dimensional angular motion even when the intermolecular potential interaction is arbitrary in form [6–8]. The Mori continued fraction is linear in nature but so is *two*-dimensional angular motion, in contrast to the three-dimensional case, where the nonlinearities of the Euler equations are projected into the noise term of the generalised Langevin equation. Debye used the same device in the development of his original rotational diffusion equation for isotropic motion [9], because the Euler/Langevin equations for a spherical top are inherently non-linear in three dimensions.

The systems considered are [3] (10% V/V in decalin at 293 K): toluene, pentafluorobenzene, α-picoline, nitrobenzene (two alternative sets of parameters), bromobenzene (two alternative sets), aniline, benzonitrile, chloronaphthalene (two alternative sets), and bromonaphthalene. The parameters β, ω_0^2 and $(I_1/I_2)\omega_0^2$ of eqs. (1)

and (2) used in these calculations are listed by Reid and Evans [3] in their table 1.

The harmonic and cosinal versions of the it~~inerant librator model~~ are illustrated in figs. 1 to 4, ~~in terms of the~~ normalised angular ~~momentum acf.~~

$$\frac{\langle \boldsymbol{J}(t)\cdot \boldsymbol{J}(0)\rangle}{\langle \boldsymbol{J}(0)\cdot \boldsymbol{J}(0)\rangle} \equiv \frac{\langle \dot{\theta}(t)\,\dot{\theta}(0)\rangle}{\langle \dot{\theta}(0)\,\dot{\theta}(0)\rangle}$$

and the real and imaginary parts of its Fourier transform (in the frequency domain).

The $\langle \dot{\theta}(t)\dot{\theta}(0)\rangle$ function for toluene/decalin is oscillatory in the harmonic limit but damped when we solve eqs. (1) and (2). For reasons of storage restriction on the CDC 7600 it is not possible to extend the computation past 5.0 reduced units in the time domain (fig. 1a), but the full effect of the damping can be brought out by Fourier transformation (fig. 1b). The top panel of fig. 1b, is *approximately* similar to the far infrared power absorption coefficient,

$$\alpha(\omega) \propto \int_0^\infty \langle \dot{\theta}(t)\dot{\theta}(0)\rangle \cos \omega t \, \mathrm{d}t,$$

although the latter is more accurately the Fourier transform of the rotational velocity autocorrelation function [6–8]. It can be seen from fig. 1b that use of the cosinal potential has the effect on the spectrum of moving the peak to lower frequencies and to develop a secondary feature in the dispersion (bottom panel). The spectrum in the cosinal case is the broader. At higher frequencies both representations become identical.

The situation for pentafluorobenzene/decalin (fig. 2) is similar, and the "as infrared" spectrum (fig. 2b, top panel) shows the characteristic shift to lower frequencies. This implies that the effective mean square torque is lower when using a cosine potential. The damping out of $\langle \dot{\theta}(t)\dot{\theta}(0)\rangle$ illustrated in figs. 1a and 2a produces an angular velocity acf more in line with that produced by computer simulation [6–8].

These characteristics are exhibited also by the 10% V/V solution of α-picoline in decalin. The

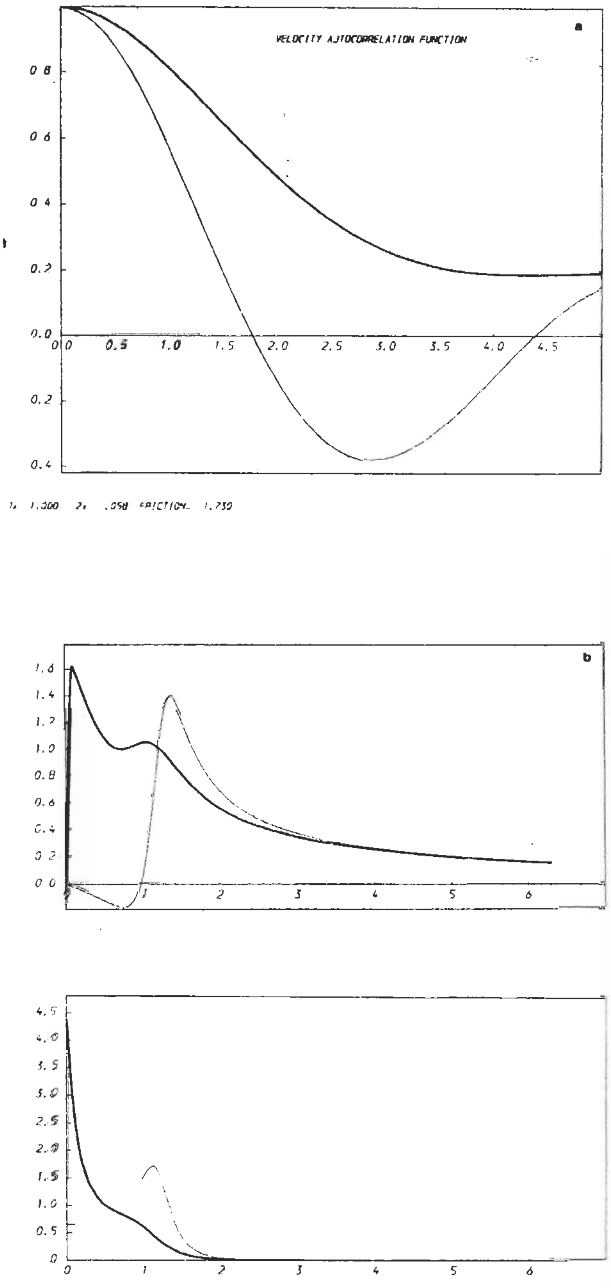

Fig. 1. Best fit for toluene in decalin. (a) —— (thick line) cosine potential. —— harmonic potential. We have $\beta_1 = 17.3\ (kT/I_r)^{1/2}$ THz, $\omega_0^2 = 100.0\ (kT/I_r)\ (\mathrm{THz})^2$, $(I_1/I_2)\ \omega_0^2 = 112\ (kT/I_r)\ (\mathrm{THz})^2$ with $(I_r/kT)^{1/2} = 0.69$ ps. Here I_r is a reduced moment of inertia described by Reid and Evans [3] $T = 293$ K. (b) Fourier transformation. Bottom panel dispersion, top panel "far infrared" spectrum (approximate). Ordinates and abscissae in reduced units.

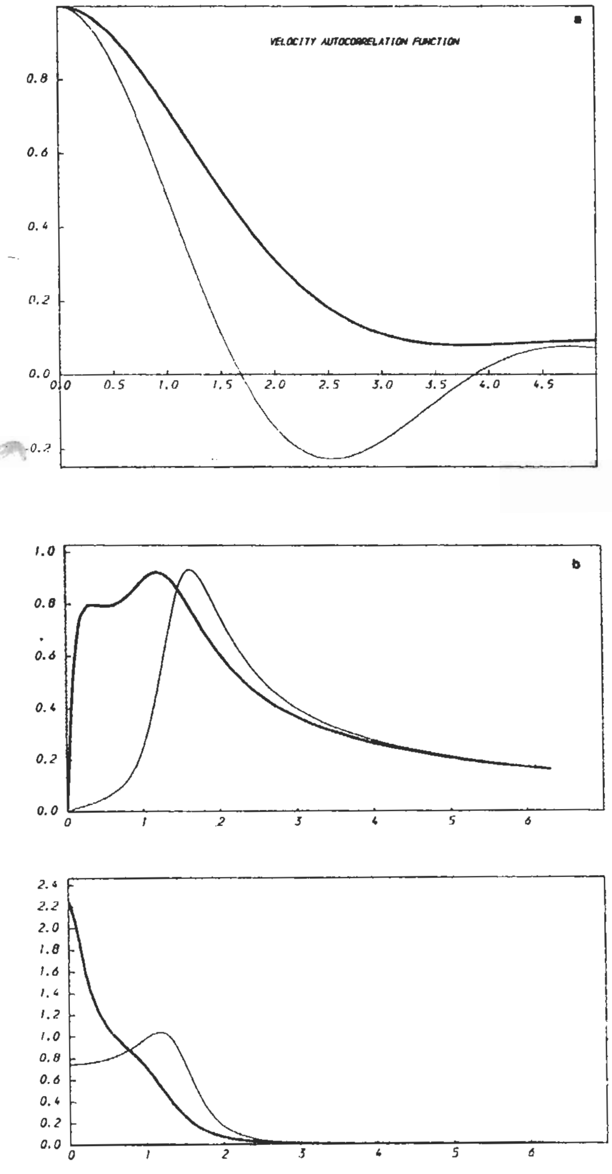

Fig. 2. Pentafluorobenzene in decalin, as for fig. 1. $(I_r/kT)^{1/2} = 1.04$ ps. In the units and order of fig. 1a the parameters are: 24, 129, 232.

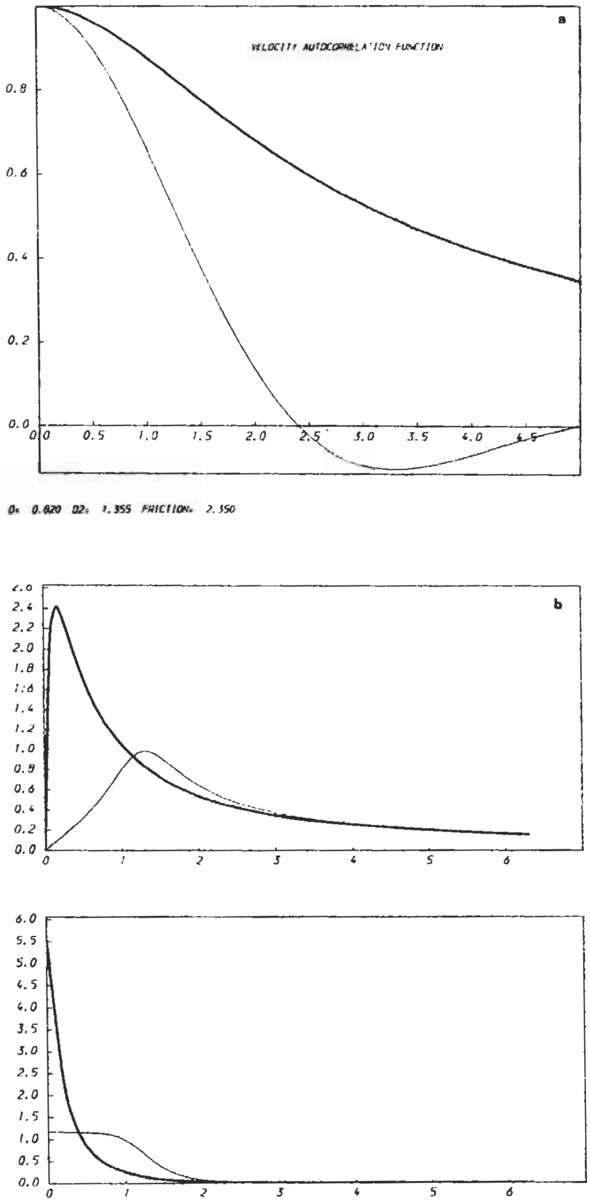

Fig. 3. Bromobenzene/decalin (first set of parameters [3]). $(I_r/kT)^{1/2} = 1.04$ ps. Parameters: 23.5, 82, 224.

angular momentum acf's for nitrobenzene/decalin were computed with the two different sets of parameters chosen by Reid and Evans [3] to represent extremes in their time-domain fitting procedures in this case (table 2 of ref. [3]). In the second case the effect of using the cosine potential is not as pronounced, the angular momentum acf's remaining oscillatory. The first case corresponds to curve 4 of Reid and Evans, fig. 3c, and the second to curve 2 of the same figure, the curve which peaks at the higher frequency in the far infrared.

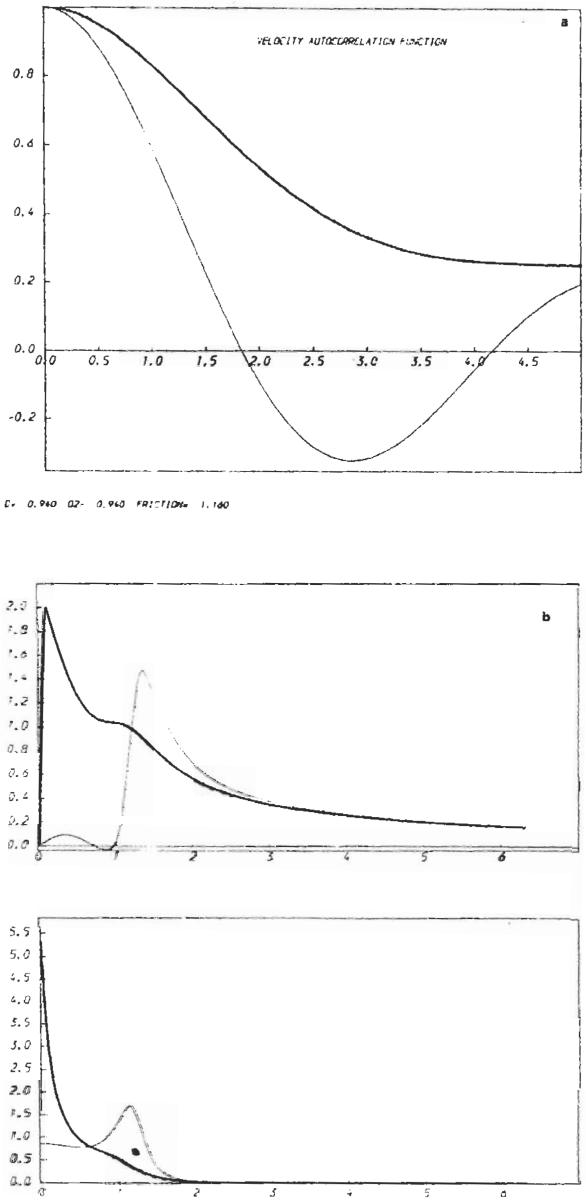

Fig. 4. Aniline/decalin. $(I_r/kT)^{1/2} = 0.69$ ps. Parameters: 11.6, 94.5, 94.3.

Similarly, two sets of best fit parameters [β_1, ω_0^2, and $(I_1/I_2)\omega_0^2$] were deduced in the harmonic limit by Reid and Evans for bromobenzene/decalin. Fig. 3 illustrates that the effect on the autocorrelation function and spectrum in this case is very pronounced.

Reid and Evans discussed the case of aniline in decalin as one where molecular association is an important consideration [3, 6], and the effect of the cosine potential (fig. 4) is significant, the peak of the theoretical spectrum in the harmonic limit being removed and replaced by a shoulder (fig. 4b, top panel). The breadth of the spectrum is now more in line with what is observed experimentally (Reid/Evans) and the damped angular velocity acf is more like that produced typically in a computer simulation [6].

The pattern is similar in benzonitrile/decalin, and in the large, flat, asymmetric diffusers 1-chloronaphthalene/decalin and 1-bromonaphthalene/decalin.

In conclusion therefore we can see that the inclusion of a cosine type of angular dependence in the equations of motion produces results more in line with known spectral features and with those of computer simulation. The amount of computer power involved in solving eqs. (1) and (2) is, however, prohibitive, and further developments should be pursued with care, and in close association with the results of computer simulation, which works in three dimensions with more realistic interaction potentials.

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