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BROWNIAN MOTION IN POTENTIAL WELLS: i) FINE STRUCTURE IN THE FAR INFRA-RED ABSORPTION OF DIPOLAR LIQUIDS

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ABSTRACT

The theory of Brownian motion in cosine potential wells is used to produce fine structures in the far infra-red power absorption coefficient of dipolar liquids in the low friction limit for finite barrier heights. The broad far infra-red absorption profile evolves into many sharp, resonance peaks as the friction coefficient, $\beta \to o$. The theory lends qualitative support to the recent experimental observation of fine structure in the far infra-red power absorption of acetonitrile - a highly structured liquid whose viscosity is, nonetheless, low in comparison with other molecular liquids at room temperature.

INTRODUCTION

The far infra-red power absorption profile of dipolar liquids usually takes on the appearance of a broad band of about 100 cm^{-1} half width [1]. This is the high frequency adjunct of the complete dielectric loss profile, which stretches to zero frequency. The relation between the far infra-red power absorption coefficient ($\alpha(\omega)$ in neper cm^{-1}) and the dielectric loss ($\varepsilon''(\omega)$) is given by:

$$\alpha(\omega) = \frac{\omega\varepsilon''(\omega)}{cn(\omega)} \tag{1}$$

Where ω is the angular frequency in radians sec^{-1}; c the velocity of light in vacuo and $n(\omega)$ the frequency dependent refractive index. The angular

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frequency ω is related to the wavenumber ($\bar{\nu}$ in cm^{-1}) by:

$$\omega = 2\pi c\bar{\nu} \tag{2}$$

It is clear from eqns (1) and (2) that a theory for $\alpha(\omega)$ is also one for $\varepsilon''(\omega)$ and vice-versa, i.e. these quantities are merely different ways of accounting for the same molecular dynamical process.

It is well-known [2] that a molecular dynamical theory for the far infra-red absorption of dipolar liquids must take into consideration the nature of inter-molecular energy wells. The original Debye theory for the dielectric loss does not do this and the result in terms of $\alpha(\omega)$ is an unrealistic plateau absorption stretching out to $\omega\to\infty$. The simplest way of modelling the potential well is:

$$V = - Vo \cos N\theta(t) \tag{3}$$

where θ is the angular coordinate for planar libration of the dipole moment, N the well multiplicity and Vo the barrier height between wells. "Planar libration" means that we consider [1] the rotational motion of an asymmetric top whose dipole moment oscillates torsionally in a plane. This artificial constraint is applied for the sake of simplicity, i.e. to "linearise" the Euler equations.

If the molecular motion in a liquid is treated in terms of Brownian motion, the governing equation is the rotational Langevin equation:

$$I\ddot{\theta}(t) + I\beta\dot{\theta}(t) = \dot{W}(t) \tag{4}$$

where I is the molecular moment of inertia, and W(t) is the Wiener process. The effect of a potential well of the form (3) may be incorporated as:

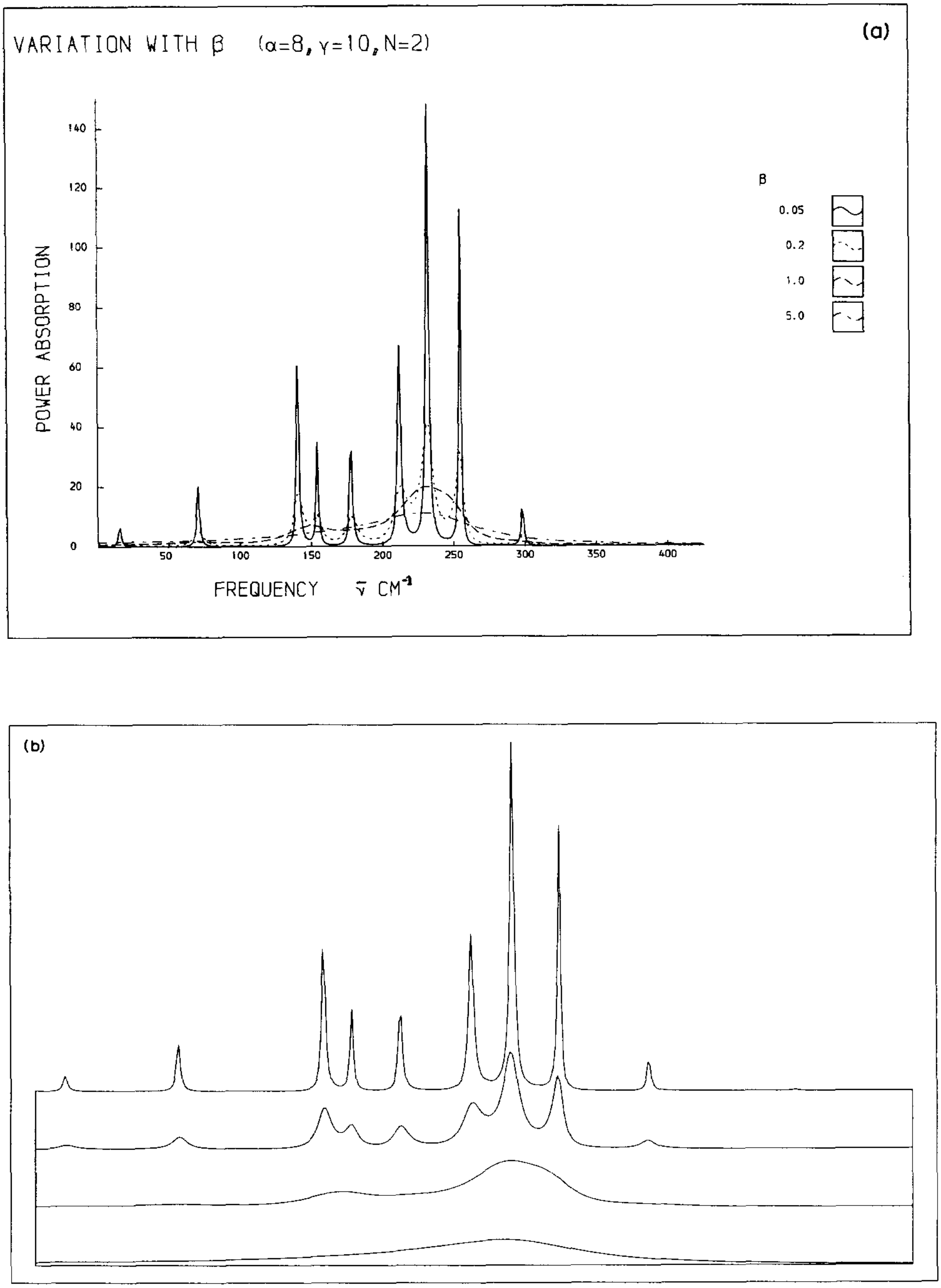
$$I\ddot{\theta}(t) + I\beta\dot{\theta}(t) + V'(\theta) = \dot{W}(t) \tag{5}$$

where the derivative V' is taken with respect to the coordinate θ.

Figure (1)

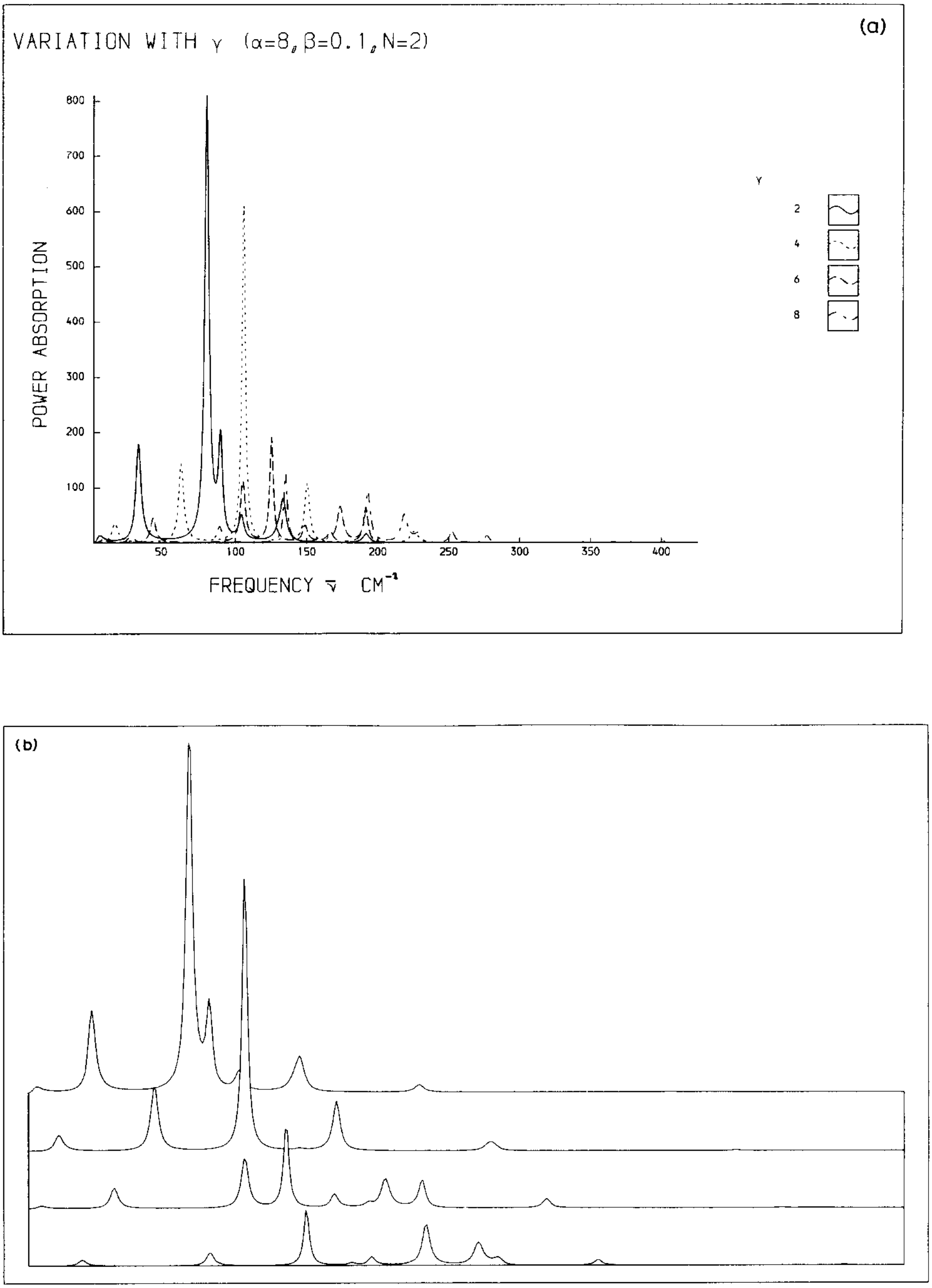
(a) Appearance of peaks as $\beta\to o$.

(b) Schematic of fig 1(a) for clarity.



3-D PLOT TO SHOW THE EMERGENCE OF ULTRA FINE STRUCTURE
WITH DECREASE IN BETA
VALUES OF BETA ARE 5.0.1.0,0.2 AND 0.05

Fig. 1.



3-D PLOT TO SHOW THE SHIFT AND DIMUNITION IN HEIGHT OF PEAKS
WITH INCREASE IN GAMA
VALUES OF GAMA ARE 2,4,6 AND 8.

Fig. 2.

Eqn. (5) as it stands has no known analytical solution. It may be solved numerically however by transformation [1,2] into the Kramers equation [3] for the conditional probability density function

$$\rho(\dot\theta,\theta,t|\dot\theta(o), \theta(o), o):$$

$$\frac{\partial\rho}{\partial t} + \dot\theta \frac{\partial\rho}{\partial\theta} - \frac{V'}{I} \frac{\partial\rho}{\partial\dot\theta} = \beta \frac{\partial}{\partial\dot\theta} (\dot\theta\rho + \frac{kT}{I} \frac{\partial\theta}{\partial\dot\theta}) \qquad (6)$$

The first successful numerical solution of this equation for a potential of the form (3) was accomplished recently by Reid [4].

In this letter we use Reid's method to investigate theoretically the appearance of fine structure in the far infra-red power absorption of liquids. As far as we are aware, this is the first investigation of its kind into a new phenomenon of general validity.

RESULTS AND DISCUSSION

Reid solves eqn. (6) in terms of parameters [4] $\alpha = (kT/I)^{1/2}$;β; and $\gamma = Vo/(2(IkT)^{1/2})$. He provides results in terms of the dielectric loss $\varepsilon''(\omega)$ and power absorption coefficient [1] $\alpha(\omega)$. His method has been used to investigate the behaviour of these quantities for structured liquids such as acetonitrile whose viscosity is low. The original theory [2] of Debye results in a simple linear relation between β and the viscosity (η) through Stokes's law. The introduction of the term V' into eqn. (5) modifies this result considerably, so that β from eqn. (5) may be varied through two orders of magnitude for constant α and γ, the Debye relaxation time remaining the same to within a few percent. However, it can be argued that the lower the actual, measured, macroscopic viscosity of a fluid the lower will be its macroscopic coefficient of friction, the precise relation between the two being a secondary

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Figure (2)

(a) Variation of peak structure with γ for constant α and β.

(b) Schematic of fig 2(a) for clarity.

consideration. On this simple basis the recent report [5] of detail in the far infra-red absorption of liquid acetonitrile could be linked theoretically, with the limit $\beta \to o$ in eqn. (6), the Kramers equation.

This expectation is corroborated in fig. (1), which illustrates the far infra-red power absorption from eqn. (6) for α = 8.0 THz; γ = 10.0 THz; and β = 0.05, 0.2, 1.0 and 5.0 THz. A series of sharp, well-defined peaks appears as $\beta \to o$. (In terms of $\varepsilon''(\omega)$, the dielectric loss profile appears approximately in the region of the observed Debye relaxation time [6] τ_D = 3.3 ps for this range of β). The variation of these peaks with barrier height, γ, for constant α and β is illustrated in fig. (2). There is a dimunition in intensity and overall shift to higher frequency as γ increases. The dependence on β of the number of peaks is illustrated in fig. (3), and of the maximum peak height in fig. (4). Details of peak position, peak height and separation, maximum peak position, maximum peak height and trough amplitude, position and separation are tabulated (table 1(a) to 1(f)) for various β at N = 2, α = 8.0 THz and γ = 10 THz, parameters chosen to provide a Debye relaxation time close to that observed. (τ_D = 3.3 ps).

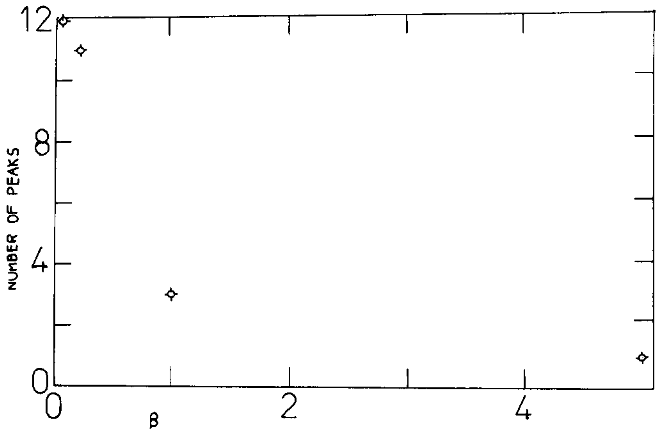

Figure (3)

Variation of number of peaks with β (THz)

TABLE 1

Data on peaks and troughs for different parameter values of the parameters.

(a) ALFA = 8.0 BETA = 0.05 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	1.50	0.36	
2.	16.00	0.39	14.50
3.	71.00	20.12	55.00
4.	140.50	60.61	69.50
5.	154.50	34.97	14.00
6.	178.50	32.08	24.00
7.	212.00	67.16	33.50
8.	232.00	148.02	20.00
9.	244.00	2.67	12.00
10.	255.00	112.75	11.00
11.	298.00	12.27	43.00
12.	369.00	0.52	71.00

MAXIMUM PEAK IS AT NUBAR = 232.00

MAXIMUM PEAK HEIGHT IS 148.02

	TROUGH POSITION (CM^{-1})	TROUGH HEIGHT	SEPARATION (CM^{-1})
1.	5.99	0.16	
2.	40.00	0.08	34.01
3.	100.00	0.08	60.00
4.	148.50	2.26	48.50
5.	165.50	0.61	17.00
6.	193.00	0.69	27.50
7.	221.00	4.34	28.00
8.	243.00	2.65	22.00
9.	246.00	2.52	3.00
10.	281.00	0.16	35.00
11.	350.00	0.02	69.00
12.	396.50	0.01	46.50

(b) ALFA = 8.0 BETA = 0.20 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	15.50	1.85	
2.	70.50	5.34	55.00
3.	141.50	17.76	71.00
4.	154.50	10.80	13.00
5.	178.50	10.17	24.00
6.	213.50	20.00	35.00
7.	231.50	41.16	18.00
8.	254.50	31.30	23.00
9.	298.50	3.69	44.00
10.	369.50	0.17	71.00
11.	425.50	0.25	56.00

MAXIMUM PEAK IS AT NUBAR = 231.50

MAXIMUM PEAK HEIGHT IS 41.16

	TROUGH POSITION (CM^{-1})	TROUGH HEIGHT	SEPARATION (CM^{-1})
1.	39.50	0.30	
2.	99.50	0.34	60.00
3.	148.50	7.25	49.00
4.	165.50	2.28	17.00
5.	192.50	2.60	27.00
6.	220.50	14.20	28.00
7.	244.50	8.91	24.00
8.	281.50	0.62	37.00
9.	351.50	0.07	70.00
10.	396.50	0.05	45.00

(c) ALFA = 8.0 BETA = 1.00 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	70.50	1.71	
2.	149.50	6.94	79.00
3.	231.00	19.82	81.50

MAXIMUM PEAK IS AT NUBAR = 231.00

MAXIMUM PEAK HEIGHT IS 19.82

	TROUGH POSITION (CM^{-1})	TROUGH HEIGHT	SEPARATION (CM^{-1})
1.	94.50	1.36	
2.	170.50	5.37	76.00
3.	395.50	0.21	225.00

(d) ALFA = 8.0 BETA = 5.00 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	228.50	11.05	

MAXIMUM PEAK IS AT NUBAR = 228.50

MAXIMUM PEAK HEIGHT IS 11.05

(e) ALFA = 8.0 BETA = 10.00 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	218.00	7.44	

MAXIMUM PEAK IS AT NUBAR = 218.00
MAXIMUM PEAK HEIGHT IS 7.44

(f) ALFA = 8.0 BETA = 50.00 GAMA = 10. N = 2

	PEAK POSITION (CM^{-1})	PEAK HEIGHT	SEPARATION (CM^{-1})
1.	157.50	3.22	

MAXIMUM PEAK IS AT NUBAR = 157.50
MAXIMUM PEAK HEIGHT IS 3.22

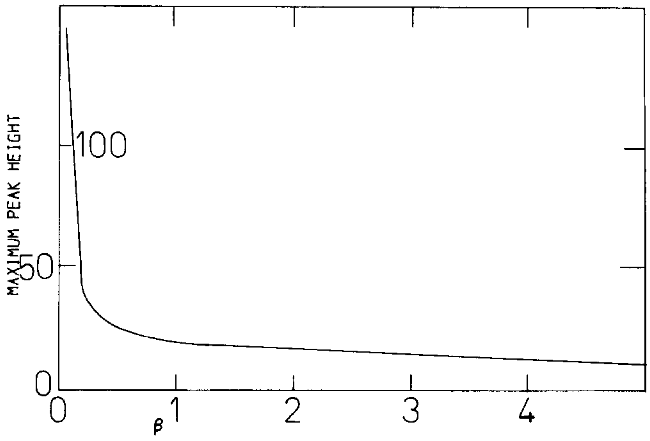

Figure (4)

Variation of maximum peak intensity (in neper cm^{-1}) with β in THz.

COMPARISON WITH EXPERIMENTAL DATA

The fine structure in the far infra-red power absorption coefficient reported [5] for acetonitrile is denser in appearance than that produced theoretically in this paper, but a greater number of peaks could be produced from eqn. (5) in a number of ways [7]. One of them would be through the use of a discrete thermodynamically weighted distribution over the well depth parameter γ. This will be the subject of future work.

CONCLUSION

The main conclusion is that a theory of molecular dynamics based on Brownian motion in potential wells is capable of describing resonance processes in the far infra-red that result in the appearance of fine structure in the power absorption coefficient of a dipolar liquid.

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