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MOLECULAR PHYSICS, 1987, VOL. 61, NO. 1, 15–22

On the existence of far-infrared absorption peaks in the complex polarizability of the itinerant oscillator model of polar fluids

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(*Received 31 July 1986; accepted 20 September 1986*)

The complex polarizability of the itinerant oscillator model in the case where the stochastic torques are weak in comparison with the deterministic ones may be evaluated analytically in terms of a series involving the modified Bessel functions. This clearly shows the existence of a harmonic peak structure at high frequencies. In the case where the stochastic torques are significant the complex polarizability may not easily be evaluated analytically but may be calculated to a high degree of accuracy using numerical Fourier transform techniques developed by Corcoran. These techniques show that the harmonic peak structure still persists when the friction in the system is significant, but those peaks of higher order with respect to the fundamental frequency are so small in amplitude when friction acts on both dipole and cage of the model system that they are almost imperceptible. If on the other hand frictional torques are supposed to act only on the cage as in earlier versions of the model a distinct peak structure still persists.

1. Introduction

The possible existence of resonant absorption peaks in the far-infrared spectrum of polar fluids has aroused considerable interest, both theoretically [1] and experimentally [2]. The theoretical investigation of the existence of these peaks has been very considerably hampered by the mathematical intractability of models such as the itinerant oscillator [3], which are used to calculate the theoretical far-infrared spectrum. Farley [4] has recently suggested that the itinerant oscillator model should be analysed again in terms of normal modes of vibration. This has resulted in closed-form expressions (i.e. not in the form of roots of polynomial equations, etc. [5]) for all the time correlation functions of the itinerant oscillator model for the special case where all the friction coefficients per unit inertia in the model are equal [6]. This simplification has allowed us great insight into the physics of the model. The time correlation functions of orientation for the model, which are now available in closed form for the special case cited above, always have the form of double transcendental functions.

It is the purpose of this paper to show that the double transcendental form of the orientational correlation functions predicts theoretically the existence of high-frequency peaks, but that in general the peaks at frequencies higher than the fundamental are very small for typical ranges of molecular parameters. This result suggests that it may be very difficult to observe such peaks in practice as borne out by the work of G.J. Evans *et al.* [7], who have recently obtained evidence for the peak structure in liquid crystals.

2. Complex polarizability for the equal friction itinerant oscillator model

The equations of motion of the itinerant oscillator model are

$$\ddot{\phi}_1 + \beta_1\dot{\phi}_1 + \omega_0^2(\phi_1 - \phi_2) = g_1(t), \tag{1}$$

$$\ddot{\phi}_2 + \beta_2\dot{\phi}_2 - \Omega_0^2(\phi_1 - \phi_2) = g_2(t). \tag{2}$$

Note that ϕ_1, ϕ_2 are the angles the dipoles make with an arbitrary unit vector $\mathbf{e}$ while $I_1\beta_1\dot{\phi}_1$ and $I_2\beta_2\dot{\phi}$ are the frictional torques and $I_1 g_1$ and $I_2 g_2$ are white noise torques. Quantities subscripted by a 1 refer to the inner or disk dipole while those subscripted by 2 refer to the outer or annulus dipole.

By analysing these equations in terms of normal modes for the case $\beta_1 = \beta_2 = \beta$ but I_1 not in general equal to I_2, Coffey *et al.* [6] were able to show that the decay of the dipole moment of the system following on the removal of a unidirectional electric field of unit magnitude at time $t = 0$ is of the form

$$\begin{aligned}\langle(\mathbf{m}(0)\,.\,\mathbf{e})(\mathbf{m}(t)\,.\,\mathbf{e})\rangle_0 &= M(t)\\ &= \frac{C_\chi(t)}{kT}\{\mu_1^2 \exp(-a_1^2\gamma_1(1-x)) + \mu_2^2 \exp(-a_2^2\gamma_2(1-x))\\ &\quad + 2\mu_1\mu_2 \exp(-\tfrac{1}{2}(a_1^2 + a_2^2)\gamma_1) \exp(-a_1 a_2 \gamma_1 x)\},\end{aligned} \tag{3}$$

$$\gamma_1 = \frac{kT}{8V_0}, \tag{4}$$

$$a_1 = \frac{2I_2}{I_1 + I_2}, \tag{5}$$

$$a_2 = \frac{2I_1}{I_1 + I_2}, \qquad 0 < a_1 < 2, \quad 0 < a_2 < 2, \tag{6}$$

$$x = \exp\left(\frac{-\beta t}{2}\right)\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right), \tag{7}$$

$$\omega_1 = \left(\frac{2V_0}{J} - \frac{\beta^2}{4}\right)^{1/2}, \qquad J = \frac{I_1 I_2}{I_1 + I_2}, \tag{8}$$

$$C_\chi(t) = \tfrac{1}{2}\exp[-a(\beta t - 1 + \exp(-\beta t))], \qquad a = \frac{kT}{(I_1 + I_2)\beta^2}. \tag{9}$$

If we proceed now to the limit

$$\beta_1 = \beta_2 = \beta = 0 \tag{10}$$

and also for convenience we assume that the dipole moment of the disk is equal to that of the annulus, so that $\mu_1 = \mu_2$, we find that

$$\left(\Omega = \sqrt{\frac{2V_0}{J}} = \sqrt{\Omega_0^2 + \omega_0^2}\right)$$

$$M(t) = \frac{\mu^2}{2kT}\,[\exp(-a_1^2\gamma_1)\exp(a_1^2\gamma_1\cos\Omega t) + \exp(-a_2^2\gamma_1)\exp(a_2^2\gamma_1\cos\Omega t)$$
$$+ 2\exp(-\tfrac{1}{2}(a_1^2 + a_2^2)\gamma_1)\exp(-a_1 a_2\gamma_1\cos\Omega t)] \tag{11}$$

Let us now recall that [8]

$$\exp(iz\sin\theta) = \sum_{n=-\infty}^{n=\infty}\exp(in\theta)J_n(z) \tag{12}$$

where J_n is the Bessel function of first kind of order n, and n is an integer. By simple algebra

$$\exp(-z\cos\theta) = \sum_{n=-\infty}^{n=\infty}\exp\left(i\frac{n\pi}{2}\right)\exp(in\theta)J_n(iz), \tag{13}$$

$$\exp(z\cos\theta) = \sum_{n=-\infty}^{n=\infty}\exp\left(-i\frac{n\pi}{2}\right)\exp(-in\theta)J_n(iz). \tag{14}$$

These are the Fourier series expansions of $\exp(\pm z\cos\theta)$. It is now possible to work out the complex polarizability exactly for this particular case. We first recall that

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(\pm ixy)\,dx = \delta(y) \tag{15}$$

where $\delta(y)$ is the Dirac delta function. Using equations (13) and (14) to expand the double transcendental functions in equation (11) as a Fourier series and substituting the result into the complex polarizability formula, namely

$$\alpha(\omega) = \alpha'(0) - i\omega\int_0^{\infty}M(t)\exp(-i\omega t)\,dt, \tag{16}$$

we find that the complex polarizability is

$$\alpha(\omega) = \frac{\mu^2}{2kT}\Bigg([1 + \exp(-2\gamma_1)] - i\omega\sum_{n=-\infty}^{n=\infty}\Big\{[\exp(-a_1^2\gamma_1)J_n(ia_1^2\gamma_1)$$
$$+ \exp(-a_2^2\gamma_1)J_n(ia_2^2\gamma_1)]\exp\left(-i\frac{n\pi}{2}\right)\delta(\omega + n\Omega)$$
$$+ 2\exp(-\tfrac{1}{2}(a_1^2 + a_2^2)\gamma_1)J_n(ia_1a_2\gamma_1)\exp\left(i\frac{n\pi}{2}\right)\delta(\omega - n\Omega)\Big\}\Bigg). \tag{17}$$

These Bessel functions of imaginary argument may be written in terms of the modified Bessel function of real argument defined by Sneddon [8]

$$I_n(z) = i^{-n}J_n(iz)$$

The most interesting feature of equation (17) is that the spectrum is a series of delta functions at $\omega = \pm n\Omega$. The amplitude of each function is determined by the modified Bessel functions. These delta functions represent peaks in the far-infrared spectrum. If, as is often done in attempting to derive analytic expressions for the complex polarizability from correlation functions such as equation (3), we assume that the time correlation function, equation (11), is truncated after the first two terms of the series, then the only peak that will survive is the one at $\omega = \Omega$, i.e. the fundamental frequency. Although the above calculation is valid only for the undamped motion it indicates that simple analytic formulae derived by truncating (after the first two terms) a series expansion for $\alpha(\omega)$ analogous to the method of deriving the Rocard equation [9] cannot predict the peak structure in the polarizability.

One can say qualitatively how equation (3) will be affected if damping is included. Essentially the delta function spikes will be flattened, and indeed it would seem that for acceptable values of the parameters I_1, I_2, β, etc., only the peak at $\omega = \Omega$ is significant. This is not however the case for the original version of the I.O. model, where there are no stochastic torques acting on the inner dipole or disk [3].

In this version of the model, the correlation function of the inner dipole is all that is supposed to contribute to the polarizability. The dipole correlation function is given by Coffey *et al.* [10, p. 117]

$$\frac{\mu^2}{kT}\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 = \frac{\mu^2}{2kT}\exp\left(-\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0\right) \tag{18}$$

where

$$\begin{aligned}\langle(\Delta\phi_1)^2\rangle_0 &= \mathscr{L}^{-1}\left\{2\frac{kT}{I_1}\frac{s(s+\beta)+\Omega_0^2}{s^2[s^3+\beta s^2+(\omega_0^2+\Omega_0^2)s+\beta\omega_0^2]}\right\}\\ &= K_1 + K_2 t + K_3\exp(-\lambda_3 t) + K_4\exp(-\lambda_4 t)\\ &\qquad + K_5\exp(-\lambda_5 t)\end{aligned} \tag{19}$$

where $K_1, \ldots, K_5$ are the residues at the poles $(0, 0, -\lambda_3, -\lambda_4, -\lambda_5)$ of $s^2[s^3 + \beta s^2 + (\omega_0^2 + \Omega_0^2)s + \beta\omega_0^2]$.

This version of the model in which $\beta_1 = 0$ shows a sharp peak at $\omega = \Omega$ followed by a smaller peak at 2Ω (see below). Apropos of this one may criticize equation (11) on the grounds that it does not contain frictional terms and in consequence does not have any dissipative mechanism. In writing down such an equation we assert that we are simply proceeding to the limit where the damping and stochastic torques are assumed to be very small in comparison with the deterministic ones. We simply use equation (11) to get some insight into the high-frequency behaviour. In the two-friction case however it would seem that for realistic values of the parameters of the model the only significant peak is that at the fundamental frequency Ω.

3. Numerical analysis of the polarizability

In order to Fourier transform equations (3) and (18) numerically according to the complex polarizability formula, equation (16), it is convenient to introduce the parameters

$$\hat{\alpha} = \sqrt{\left(\frac{kT}{I_1}\right)}, \qquad \hat{\gamma} = \frac{V_0}{I\hat{\alpha}}, \qquad I_r = \frac{I_2}{I_1}, \qquad b = \frac{\beta_1}{\beta_2}, \tag{20}$$

where it is useful to note that (see [11])

$$\omega_0^2 = 2\hat{\alpha}\hat{\gamma}, \qquad \frac{V_0}{kT} = \frac{\hat{\gamma}}{\hat{\alpha}}. \tag{21}$$

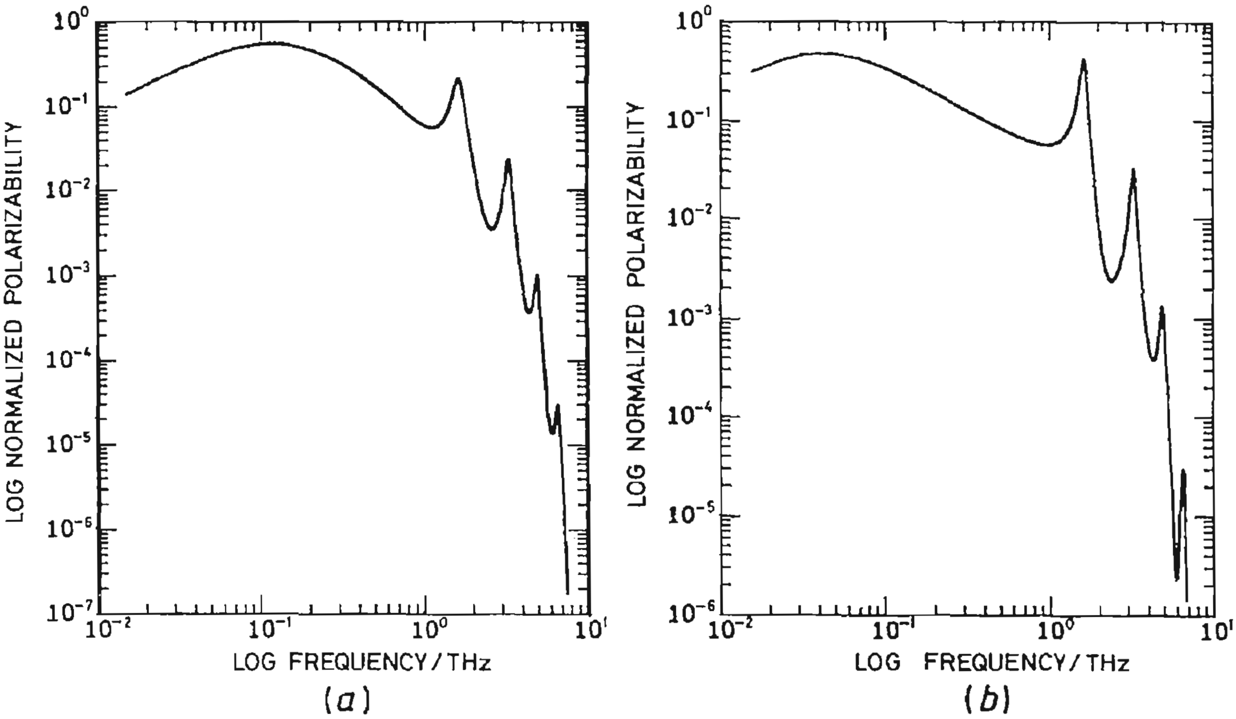


Figure 1. Normalized polarizability showing the occurrence of four distinct peaks in the FIR region of the spectrum for $b = 0$ and (*a*) $\hat{\alpha} = 5$, $\beta = 4$, $\hat{\gamma} = 10$ and $I_r = 8$, (*b*) as for (*a*), but with $\beta = 12$. *x*-ordinate: log frequency (THz), *y*-ordinate: log normalized polarizability.

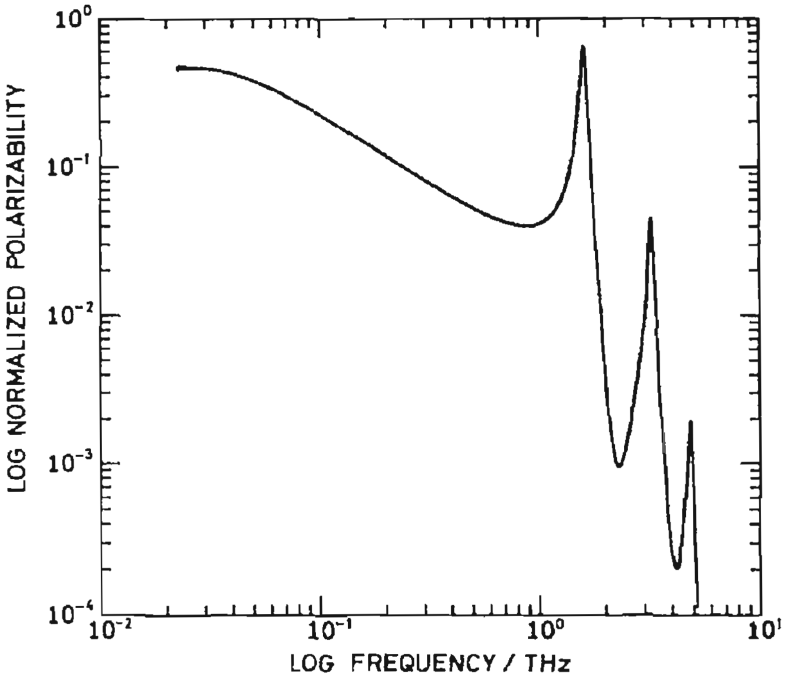
We further note that the scalar determinant or characteristic equation of the I.O. model in the general case where $\beta_1 \neq \beta_2$, which result covers all possibilities in the model, is [12, 13]

$$s\{s^3 + \beta_2(1 + b)s^2 + [2\hat{\alpha}\hat{\gamma}(1 + I_r^{-1}) + \beta_2^2 b]s + \omega_0^2 \beta_2(1 + bI_r^{-1})\}. \quad (22)$$

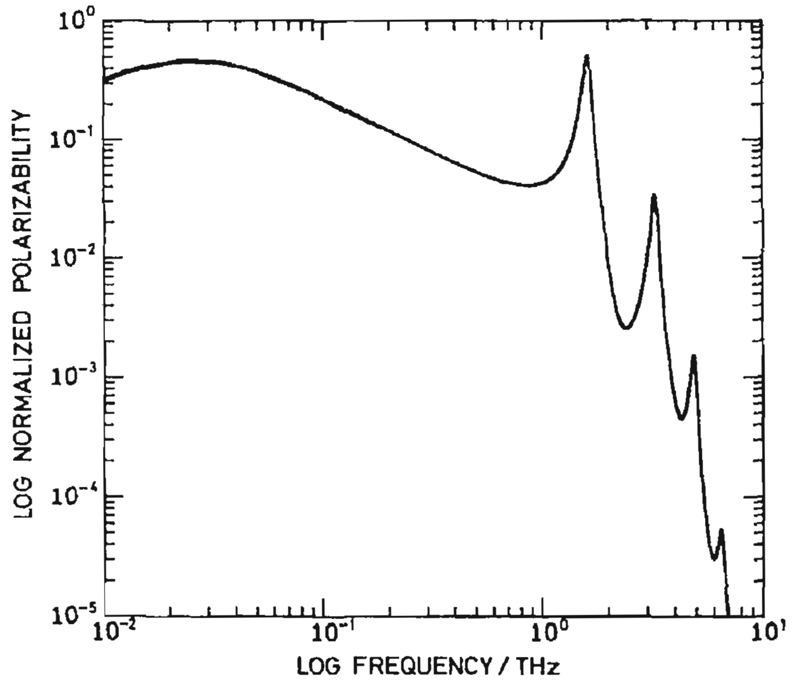
The original version of the I.O. model where there is no friction on the inner dipole corresponds to the case $b = 0$. The case where $\beta_1 = \beta$ corresponds to $b = 1$ (equation (3)). Using a fast Fourier transform program which we have described elsewhere [11, 13] it is possible to evaluate the complex polarizability to a high order of accuracy. In order to illustrate our results, we show in figures 1 and 2 normalized polarizability spectra plotted on a log scale against the frequency (THz), also on a log scale. Figure 1 shows the effect of varying the friction on the outer dipole. As this is increased, the microwave (MW) and far-infrared (FIR) peaks become more widely separated and the multiple peaks in the FIR region are noticeably enhanced. This lends some support to the hypothesis that a multiple peak structure will not be observed experimentally in the FIR region unless the broadband (MW) spectrum of the system under observation can be shifted to lower frequencies. In figure 2, we show the effect of allowing a very small amount of friction to act on the inner dipole. The multiple peak structure is evidently very much affected by small amounts of friction on the inner dipole. Finally, we note that only three peaks are shown in figure 2(*a*) because of the numerical inaccuracies due to rounding errors in our algorithm for these parameter values. Also, we have not yet calculated spectra over more than three decades of frequency. Such calculations should be possible, but would require the use of more sophisticated numerical techniques than have been employed in the present work.

4. Discussion

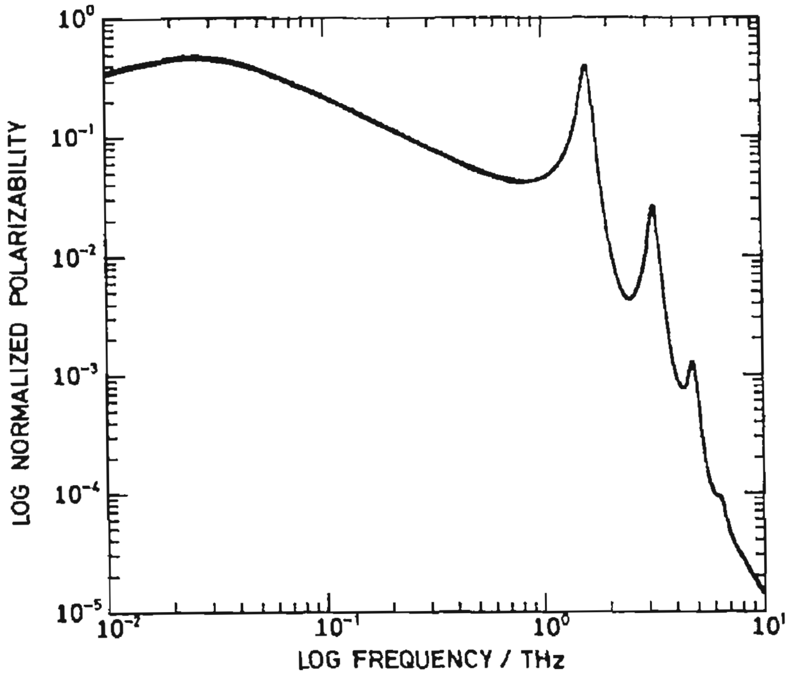
The theoretical methods described above have led to the conclusion that peaks can be expected in the far-infrared power absorption of dipolar materials in the condensed molecular state of matter. It is therefore interesting to look for the conditions under which these peaks might be observed experimentally. From careful and repeated measurements of the far-infrared absorption of molecular liquids, both by interferometry and by sub-millimetre laser spectroscopy, it now seems certain that the peak structure will not be visible in dipolar liquids at ambient temperature



(a)



(b)



(c)

Figure 2. Normalized polarizability showing the effect on the peak structure of allowing friction to act on the inner dipole. (a) $\hat{\alpha} = 5$, $\beta = 20$, $\hat{\gamma} = 10$, $I_r = 8$ and $b = 0$; (b) as for (a), but $b = 0{\cdot}01$; (c) as for (a), but $b = 0{\cdot}025$. Note that only three FIR peaks are shown in (a) because the numerical algorithm could not satisfactorily resolve the fourth peak. x-ordinate: log frequency (THz), y-ordinate: log normalized polarizability.

and pressure. In terms of the I.O. this is because friction acts on both the inner particle and the surrounding cage. However, in the crystalline molecular solid state it is well known that the broad band in the far-infrared liquid spectrum gives way to a number of phonon modes. These are generated by the cooperative rotational and/or translational motion of the molecules in the crystal. Thus it might be expected that the I.O. normal modes would be visible in a material wherein the experimental conditions were intermediate between those of the ambient molecular liquid and the crystalline solid. Recent work by G. J. Evans on liquid crystals has shown the presence of structure in the far-infrared power absorption which might be attributable to I.O.-type normal modes [2]. In this context it seems significant that the liquid crystalline state of matter is intermediate between that of the molecular liquid and the crystalline solid (since the liquid crystal flows but is birefringent under the influence of an external electric or magnetic field).

The present theoretical work also supports the indications of previous numerical work [1] using a single particle cosine potential model analysed by means of the Kramers equation. This model gave evidence for the appearance of far-infrared peaks in the low friction limit. Some of the peaks derived numerically in the latter work may coincide in origin with those illustrated in figures 1 and 2 from the I.O., but on the other hand some of them were probably artifacts arising from a premature truncation of the matrices involved in the numerical analysis. It seems from the present work that the peaks must be distributed harmonically, and are at their most pronounced when the encaged or inner molecule is bound harmonically to its surroundings with no friction acting between inner molecule and cage. In order to resolve the normal modes of the I.O. it is also necessary to assume that the friction between the outer cage and surrounding medium is low enough to separate the peaks from the broad-band absorption background characteristic of molecular liquids.

Unambiguous experimental evidence for the existence of peaks has also been obtained in the case of a dipolar molecule encaged in a clathrate [14 and references therein]. These are attributed to normal modes of an encaged oscillator and are usually regarded as quantum mechanical in origin [14, 15], derived using a particle in the box analysis. However, the I.O. of this paper is a purely classical model which could be regarded as the rotational equivalent of the translational oscillator as described by R. Davies [14, 15]. Thus it would be interesting to repeat the analysis of this paper when the initial equations of motion are set up for translational itinerant oscillators. It ought to be possible in this case for a heavy rigid cage and a harmonically encaged particle to observe classical resonance modes which are infrared-active because the translational motion of the dipole modulates the infrared-active dipole moment. In other words the encaged translational oscillator acts like a modulator of the probe infrared radiation. The motion of a small dipolar molecule in a clathrate lattice may therefore lend itself to the first experimental recognition of peaks in an infrared spectrum generated by purely classical equations of motion.

We thank Professor F. J. M. Farley for helpful conversations. Trinity College Dublin and the Irish Department of Education are thanked for the award of a Research Studentship to PMC, and the Nuffield foundation is thanked for a travel grant.

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