For Infra-Red Peaks in Molecular Liquids?

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Abstract
Circular diffusion in a multiple cone potential-energy well produces peaks in the far infra-red power absorption coefficient as the rate of escape from these wells becomes slow. The Kramer’s equation governing the dynamics of the system is solved using matrix inversion methods. The dependence of the number, relative intensity and frequency of the far infra-red peaks on matrix size is illustrated, and numerical results are shown describing the development with decreasing rate of escape of far infra-red peaks. The complete analytical form of the peaks is shown to be a broad band of constant half-width 1:2 decades at low frequency, superimposed on which are the high frequency far infra-red peaks. The far infra-red power absorption spectrum in the determinist limit of well-known models corresponding to the first two approximations of the linear Mori continued fraction expansion of the Liouville equation is shown to be composed of delta functions at well-defined frequencies. The number of delta functions increases with approximant order (i.e. number of continued functions)

These theoretical results are discussed in terms of the recent experimental discovery by G. J. Evans of peaks in the far infra-red power absorption spectrum of dipolar and non-dipolar molecular liquids, and in terms of the recent suggestion by Grigorov and co-workers of a phase change in the low frequency limit caused by determinist transition to chaos.

Introduction
The first description of rotational diffusion was given, effective, in terms of a rotational Langlevin equation. In three dimension this is a technically difficult problem [1], and for this reason a simple and clear solution is sought in terms of the equation:

\[
\dot{\theta}(t) + \frac{\beta}{\gamma} \dot{\theta}(t) = \dot{\omega}(t)
\]

where the rotation of the asymmetric top is confined to a plane. \(\dot{\theta}\) is the angular displacement of the principal axis in the plane, \(\dot{\omega}\) the angular velocity, \(\gamma\) the rotational friction constant and \(\beta\) the angular momentum. Expt. (1) provides the autocorrelation functions:

\[
\langle \dot{\theta}(t) \dot{\theta}(0) \rangle = e^{-\beta t}
\]

\[
\langle \cos \theta(t) \cos \theta(0) \rangle = \exp \left[ -\frac{\beta T}{2t} [\beta t - 1 + e^{-\beta t}] \right].
\]

If it is assumed in eq. (1) that:

\[
\beta \geq \frac{\dot{\theta}(t)}{\dot{\omega}(t)} (3)
\]

i.e. the “high friction” limit, then expt. (2) produce:

\[
\cos \theta(t) \cos \theta(0) \approx \exp \left[ -\frac{\beta T}{2t} \right].
\]

In this limit we can define the so-called Debye relaxation time as:

\[
T_D = \frac{\beta}{kT}
\]

Cumbrous solutions for the three dimensional diffusion of the asymmetric top from eqs. (1) have recently become available, but add little physical insight, if any.

This simple “one-particle” model has many short-comings, which have been documented. The need to account for “liquid structure” is probably the most obvious item, and in this context the following modification has been proposed:

\[
\dot{\theta}(t) + \frac{\beta}{\gamma} \dot{\theta}(t) + \nabla(\theta) = \dot{\omega}(t)
\]

\[
V = -V_s \cos (m \theta(t))
\]

and solved by Reid [2] by transforming into the Kramer’s equation:

\[
\frac{\partial p}{\partial t} + \frac{\partial p}{\partial \theta} V_s \frac{\partial p}{\partial \theta} = \frac{\partial^2 p}{\partial \theta^2} + \delta \delta \left( \frac{\partial^2 p}{\partial \theta^2} \right)
\]

(7)

for the conditional probability density function

\[
\rho(\dot{\theta}, \dot{\theta}, \dot{\theta}(0), \theta(0), \theta(t))
\]

(8)

The solution by Reid is much more transparent than others in the literature and opens up several new possibilities in the field of Langlevin dynamics. This paper explores the case \(\beta = 0\), the opposite to the “high friction” limit mentioned already. In the limit \(\beta = 0\) it has been shown recently [3] that the rate of escape from the potential wells defined by eqn. (7) becomes very low, and that this rate of escape becomes proportional to \(\dot{\theta}\) itself. When \(\beta = 0\) eqn. (6) reduces to the deterministic result:

\[
\dot{\theta}(t) + \dot{\omega}(t) = \dot{\theta}(t)
\]

\[
V = -V_s \cos (m \theta(t))
\]

(5)

\[
T_D = \frac{\beta}{kT}
\]

(6)

\[
V = -V_s \cos (m \theta(t))
\]

(7)

\[
\frac{\partial p}{\partial t} + \frac{\partial p}{\partial \theta} V_s \frac{\partial p}{\partial \theta} = \frac{\partial^2 p}{\partial \theta^2} + \delta \delta \left( \frac{\partial^2 p}{\partial \theta^2} \right)
\]

(8)

\[
\rho(\dot{\theta}, \dot{\theta}, \dot{\theta}(0), \theta(0), \theta(t))
\]

(9)

\[
\dot{\theta}(t) + \dot{\omega}(t) = \dot{\theta}(t)
\]

(10)

\[
V = -V_s \cos (m \theta(t))
\]

(11)

\[
\frac{\partial p}{\partial t} + \frac{\partial p}{\partial \theta} V_s \frac{\partial p}{\partial \theta} = \frac{\partial^2 p}{\partial \theta^2} + \delta \delta \left( \frac{\partial^2 p}{\partial \theta^2} \right)
\]

(12)

\[
\rho(\dot{\theta}, \dot{\theta}, \dot{\theta}(0), \theta(0), \theta(t))
\]

(13)
Furthermore, if the temperature is very low, the motion is
confined to the bottom of the potential well, and:
\[ \sin \theta + \cos \theta = 0, \]
so that eqn. (9) gives the familiar Hooke's law:
\[ F = -k \theta. \]

In this respect eqn. (6) is preferably different from eqn. (1),
although superficially similar in appearance. There is no way
of obtaining Hooke's law from eqn. (3). The link between the
modified Langevin equation (6) and Hooke's law (eqn. (11)) is
an important one, for it provides a route from liquid state
molecular dynamics to the dynamics of molecular crystals. It
is well-known [4] that the harmonic approximation (eqn. (11))
forms the basis for the available descriptions of the far infra-red
lattice modes of crystalline solids. Eqn. (11) would describe the
elementary oscillatory motion pasting rise to one rotational
lattice mode - a delta function of frequency. In contrast, Red.
[2] has shown clearly that eqn. (6) produces for the far infra-
red power absorption coefficients a broad band for the relatively
high values of \( \beta \) given in his paper [see Fig. (3)].

It follows naturally from these considerations that the
transition from eqns. (6) to eqns. (11) describes the phase tran-
sition from molecular liquid to molecular crystal. This apparent-
ly obvious and superficial remark has profound implications for
the theory of Langevin dynamics, because such a phase change
must be generated by the simple process:
\[ \beta = 0. \]

This means that solutions of eqn. (6) for molecular dynamics
must produce lattice modes in the 'low-friction limit'. It follows
that there is no fundamental difference between liquid and
crystal dynamics in the framework of the modified Langevin
equations and the equivalent Kramers equation (9).

This paper solves eqn. (5) in the limit \( \beta = 0 \) for various types of
potential \( V \), and for the parameters defined by Red. [2]:
\[ \alpha = \frac{k}{2m}, \]
\[ \gamma = \frac{\nu_0}{2kT}. \]

The product \( \alpha \gamma = \nu_0/2kT \) is therefore a measure of the
well depth in terms of the molecular moment of inertia. The paper
shows that this rate of escape is too low to be of any practical
interest.

Numerical Solution of Eqns. (8).

Eqn. (8) can be written as:
\[ ma(t) = A(t). \]

The square matrix \( A(t) \) is an asymmetric complex, banded tri-
diagonal, which must be inverted for the column vector \( A(t) \),
where \( x \) is the Laplace variable. The column vector \( A(t) \) is
the vector of initial values, arranged in the order:
\[ \ldots , A(t)_0 , A(t)_1 , \ldots , A(t)_0 , \ldots , A(t)_1 , \ldots , A(t)_0 , \ldots , A(t)_1 , \ldots , A(t)_0 , \ldots , A(t)_1 , \ldots , A(t)_0 , \ldots , A(t)_1 , \ldots , A(t)_0 , \ldots , A(t)_1 , \ldots . \]

In this paper eqn. (15) is solved using the algorithm written
by Red. [7], and also with a new algorithm written by M. W.
Evens to incorporate potentials of the general type exemplified
by eqn. (17). The latter algorithm inverts \( A(t) \) by Cholesky
factorisation and partial pivoting, with extended precision arithmetic
for the inner products on the CDC 7600 and CDC Cyber-205
computers of U.M.R.E.C., using the Numerical Algorithm
Group's routine F04ADF. This algorithm was implemented in
an efficiently vectorized form on the Cyber 205 with Pacific
Centre Integral Behaviour, \( \alpha=10, \beta=0.1, \gamma=5 \)

![Graph showing Centre Integral Behaviour](image)

Sierra Research Incorporated's V.A.S.T. utility. This enabled the inversion of a $1000 \times 1000$ complex matrix \( m \) in under 300 seconds. C.P.U. Cyber time. The integrals in eqn. (20) were evaluated using the N.A.G. routine D01GAF. The precision of these integrations was checked by this routine for every integral, and also by using the fact that the complex part of eqn. (20) should vanish by symmetry. In respect of initial conditions it is important to note the relation:

\[
\cos \theta \left( \mathbf{A}^T(0) \right) = \mathbf{0}, \quad m \neq 0,
\]

so that only the fifty or so centre integrals of the type (20) need to be evaluated in the column vector \( \mathbf{A}(0) \).

Convergence effects and numerical artifacts

It is clear from inspection of eqns. (11) or (17) that in the limit \( \beta \to 0 \) peaks will appear in the far infra-red power absorption from modified Langeron equations and their equivalent Kramers equations. However, great care must be taken in calculating \( \alpha(u) \) of eqn. (19) by inversion of \( m \), especially in the limit \( \beta \to 0 \). Reid has discussed [2] the convergence of eqn. (15) for relatively high values of \( \beta \), where the far infra-red spectra is a broad band. In this section the behaviour of the Crout factorisation algorithm is reported for complex matrices \( m \) of the following dimensions:

- (i) 1000 x 1000;
- (ii) 200 x 200;
- (iii) 400 x 400;
- (iv) 1000 x 1000.

The dimensionality of matrix \( m \) (see Table 1) is defined by the product \( \text{NCMAX} = 2 \text{NC} = 1 \), where \( \text{NC} \) defines the number of centre integrals \( \mathbf{A}(r) \) (either side of \( \mathbf{A}(0) \)). The behaviour of the \( \mathbf{A}(0) \) coefficients depends on the ratio \( \gamma \). Convergence is much more rapid when this ratio is less than one. For \( \gamma < 0.1 \text{THz} \), the convergence behaviour as a function of \( r \) is illustrated in Fig. (1). Centre integral behaviour is independent of \( \beta \), and, for \( V = -V_{c} \cos 2 \theta \), Fig. (1) shows that the terms \( \mathbf{A}(0), \mathbf{A}(\gamma), \mathbf{A}(\gamma) \) dominate. The numerical integration produces within the uncertainty perfectly symmetrical results, i.e. \( \mathbf{A}(0) = \mathbf{A}(\gamma), \mathbf{A}(\gamma) = \mathbf{A}(\gamma) \). (It is interesting to speculate in this context a one to one correspondence between the number of significant centre integrals and number of significant peaks in the final far infra-red spectrum.) At \( r = 0 \), the uncertainty in the numerical integration is 2.9 x 10^{-4}, and at \( r = 12 \) it is 1.6 x 10^{-2}. The value of the second integral in eqn. (20) is $< 10^{-4}$ for all $12 < r < 12$, with an uncertainty for all $r < 0.2$ x 10^{-7}. These results were obtained with 100 quadrature input mesh points per integral. The value of $r$ was used with machine precision work N.A.G. X01AAF.

The parameter NCMAX defines how many blocks of the type illustrated in Tables 1 and 2 are used to build up \( m \), which is always a square matrix.
The numerical method is based on the assumption [2] that the solution of eqn. (8) takes the general form:

\[ \rho = \exp \left( -\frac{\Delta^2}{\Delta \sigma} \right) \sum D_n(\theta) \phi_n(\theta, r) \]  

(22)

where \( D_n \) are modified Hermite polynomials - the Weber polynomials and \( \phi_n(\theta, r) \) are expanded in a Fourier series:

\[ \phi_n(\theta, r) = \sum \frac{d_l}{2^l l!} \exp(i\lambda n) \]  

(23)

(\( p = 0, 1, \ldots, \pi \)). The parameter INCMAX therefore has the effect of truncating the series \( \phi_n(\theta, r) \) of eqn. (23). It is also clear from the structure of Tables 1 and 2 that the values chosen for NC and INCMAX determine the level of truncation in eqns. (23).

The numerical results show that for any reasonable size of matrix \( m \) sensible results are obtained as \( \beta = 0 \) from an expansion of the type (23) only if the ratio \( \gamma / \sigma \) does not exceed approximately two. If this ratio becomes too high the far infrared absorption \( \alpha(\nu) \) from eqn. (19) starts to show unphysical negative regions from both algorithms - the Rad method and Crouz factorisation. This suggests that in this case the series (22) and (23) need many terms to converge. If they converge at all, this problem can be overcome by using \( \gamma / \sigma < 1 \), even for very small \( \sigma \) (of the order 100 x 100).

The question now arises of how the peaks in the far infrared power absorption coefficient depend on the size of the matrix \( m \). The numerical results given in this section attempt to answer this question for \( NC = 12 \), and for various values of INCMAX, i.e. blocks of the type illustrated in Tables 1 and 2. The parameters employed are \( a = 10 \) THz, \( \beta = 0.1 \) GHz, \( \gamma = 5 \) GHz, for a potential of the type \( V = V_0 \cos 2\pi f \). (For 40 blocks the matrix size is 1000 x 1000.)

For INCMAX = 8 (4 blocks) these major peaks appear in the far infrared spectrum from eqn. (8), or equivalently, eqn. (6). These are illustrated in Fig.2(a). There is a further very small peak at 206 cm\(^{-1}\). The matrix size is now 100 x 100. With INCMAX = 8 (200 x 200 matrix), there are five peaks visible in Fig. 2(b), whose position and relative intensities have changed noticeably to Fig. 2(a). In Fig. 2(c), INCMAX = 16 (400 x 400 matrix), and five major peaks are visible. The two peaks at 118 cm\(^{-1}\) and 181 cm\(^{-1}\) stay roughly in the same position, those at 10 mm\(^{-1}\) and 51 cm\(^{-1}\) shift slightly to higher frequency. The obvious difference between Fig. 2(b) and Fig. 2(c) is the greatly diminished height of the peak at 146 cm\(^{-1}\) (\( m = 200 \times 200 \)).

![Figure 2: Convergence of the far infrared power absorption spectrum for \( a, \beta \) and \( \gamma \) of Fig. 11. (a) \( m = 100 \times 100 \); (b) \( m = 200 \times 200 \); (c) \( m = 400 \times 400 \); (d) \( m = 1000 \times 1000 \); (e) the same spectrum from Reid's algorithm, for \( a = 10.0 \) THz; \( \beta = 0.05 \) THz; \( \gamma = 5.0 \) THz. Ordinate: power absorption.]

[Image: Figure 2]
If we make a rough, order of magnitude, estimate of the parameter for water, we have 1 = 2 × 10^{-10} \text{ cm}^{-1}, so that at 300 K, a = 150 \text{ THz}. A value of 0.1 \text{ THz} for the parameter \( a \) means, very roughly speaking, an increase every 10 ps or so, i.e., a H-bond is broken and reformed, on the average, in this interval of time. This is a simplistic picture, but nevertheless acceptable as a rough description of what happens to an individual water molecule, which then makes a temporary but sizeable contribution to the overall reaction rate. For H-bonds involving 4 water molecules, this is known to be far too simple for water. We have already mentioned how more realistic intermolecular potential can be obtained by Fourier synthesis, and how each term in the Fourier sum generates more peaks in the far infrared spectrum. The Kramer's equation is therefore fully capable of generating all the peaks listed in Table 3. It is probable that further observation will reveal yet more far-infrared peaks in liquid water. Matching these peaks to the appropriate Fourier series will provide information on the effective intermolecular potential and its spatial symmetry projected on to the plane of rotation (i.e., the "orbit" described by the angle \( \theta \)). With computer simulation of Langevin dynamics, these dimensional analyses should be feasible.

In this context, the use of parameters equivalent to \( a = 150 \text{ THz}, b = 0.1 \text{ THz} \) provides a new and simple explanation for the observed dielectric loss peak of liquid water, even though the Knudsen effect is significantly different from 10^{-6} \text{ cm}^{-1}. It is thus important to realize that eqn (6) is therefore capable of reproducing two apparently quite different experimental aspects of liquid water molecular dynamics self-consistently and simply by using the limit \( \beta > 0 \). In other words, the predictions of eqn (6) offer both the observed (Debye type) dielectric loss peak [5] and far infrared peaks in the limit \( \beta = 0 \). Peaks have now been reported by G. J. Evans [9, 11] in several other dipolar and non-dipolar molecular liquids, including chlorobenzene, bromobenzene and benzene, where the position of the lattice modes in the equivalent molecular crystals are well-known. These results await corroborative, but it is clear that the liquid state peaks occur closer to the vicinity of the crystal lattice modes. The agreement is particularly striking for chlorobenzene and benzene. There seem to be more peaks in the molecular liquid than in the corresponding crystal. This pattern is repeated for chloroform, deuterated chloroform, benzene, the (+) enantiomer and racemic mixture of 2-chlorobutane, carbon tetrachloride, nitromethane, acetone, and, of course, liquid water, where the liquid peaks (Table 3), are far more numerous than the lattice modes of ice I h at I less than just below the melting point [5]. These observations can be explained quite straightforwardly in terms of the symmetry of a such as eqn. (17). The greater the number of terms the lower the effective symmetry, and the more the number of far infrared peaks. The effective symmetry in the liquid is known to be less than that in the crystalline solid, although recent diffraction studies [13] imply that the difference in local order is smaller than expected. Similar conclusions come from the computer simulations of Rahman [13] on atomic liquids.

### Table III. Liquid water: Far-infrared peaks with different instruments (6 cm^{-1})

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**Some numerical results from Eqn. (6)**

Figure (3) illustrates the development of peaks from Reid's
algorithm [2] as $\beta = 0$. The parameters are: $\alpha = 0.00 T$, $\beta_1 = 0.1 T$, and $\gamma = 0.00 T$, and the potential $V = V_1 \cos 2\beta$. Some of the equivalent loss curves are illustrated in Fig. (3). Figures (4) show clearly that the complex loss profile from eq. (5) is a low frequency broad band together with a series of peaks in the far infrared. It is important in the light of Fig. (2) to estimate how many of these peaks are likely to be present for an effectively infinite matrix as, when convergence has been attained. In this context it is known [2] that convergence is more rapid the larger the parameter $\beta$. It seems safe to assume therefore that the peaks, when first resolved in Fig. (3), for $\beta = 1.00 T$, have come from a converged solution. Again, for a potential $V = V_1 \cos 2\beta$, these are five visible peaks in Fig. (3) as for the larger matrices in Fig. (2). As $\beta$ is lowered from 1.0 to 0.5 T, further peaks are resolved (Fig. (3)) but thereafter the number does not increase. Nine peaks only result at $\beta = 0.05 T$ (Fig. (3)), and at exactly the same frequencies as with $\beta = 0.5 T$. For a given matrix size, therefore, there is no dependence on $\beta$ of the number of peaks in the spectrum.

The dependence of the number of peaks on the size of the matrix $M$ is illustrated in Fig. (2) and has also been investigated recently by P. Grigolini and co-workers [14], who came to the important conclusion that in the low friction limit the deterministic character of the system becomes dominant. For a potential of the type $V = V_1 \cos \beta \theta(t)$, at low temperature, so that only the first two terms in the McLaurin expansion of $\cos \beta \theta(t)$ are retained the so-called Duffing oscillators, two peaks appear for an effectively infinite matrix $M$. These are also described by Voigtlaender and Rükken [15], who claim that their numerical results agree with the deterministic limit $\beta = 0$ calculated using an independent analytical method. The same two peak frequencies are observed by Grigolini and co-workers [14] using a continued fraction method, but the use of analogue circuit simulation [15] suggests the presence of a residual linewidth, and importantly, a phase transition to deterministic chaos as $\beta = 0$. Voigtlaender and Rükken [15], on the other hand, argue that the peaks survive unaltered by deterministic chaos even for $\beta$ as low as 0.01 for precisely the same system as described by Grigolini et al. [14].

The question of how many peaks survive for an infinite matrix $M$ is therefore a matter for further investigation and of great interest. In our opinion the peaks in Figs. (2–4) are real, although some may diminish in intensity (see Fig. (2)) or shift in frequency as $M$ is increased. One of the many interesting consequences of this work is that seemingly deterministic equations such as (17) show the phenomenon of so-called "transition to chaos", i.e. the trajectories defined by such equations become exceedingly complicated [16]. "Coupled pendulums" equations are well-known to show deterministic transition to chaos, a type of phase transition.

To end this discussion we look at two simple linear models, and provide a simple proof that more than one peak must exist in the far infrared as the friction coefficient $\beta$ vanishes. This proof is independent of the considerations by Grigolini et al. [14] and by Voigtlaender and Rükken [15].

The harmonic oscillator [1, 2]

This is eq. (6) in the limit $\sin \theta(t) = \theta(t)$, i.e.:

$$\dot{\theta}(t) + g_0 \theta(t) + M V_1 \cos \theta(t) = 0$$

(24)

i.e. Hooke's law perturbed with friction and noise. If we write:
Fig. 4. As for Fig. (3), dielectric loss $\omega = 0.0$ THz, $\gamma = 10.0$ THz: (a) $\beta = 50.0$ THz; (b) $\beta = 1.0$ THz; (c) $\beta = 0.5$ THz; (d) $\beta = 0.2$ THz; (e) $\beta = 0.1$ THz. Note that the complete dielectric loss spectrum is a broad band of constant half-width at low frequencies, with a series of peaks developing on the high frequency side (in the far infra-red range). Abcissa: log 10 (w) = -12.

$$\omega_{\text{loss}} = \frac{m^2 v^2}{l}$$  \hfill (25)

cps. (24) is well-known [2] to provide the following results:

$$\theta(t) = \frac{1}{\beta_0} \left[ \cos \left( \frac{\beta_0 t}{2} \right) + \frac{\beta_0}{2} \sin \left( \frac{\beta_0 t}{2} \right) \right]$$  \hfill (26),

for underdamped motion. Hvev:

$$\beta_0 = 2 \left[ \omega - \frac{\omega_i}{\alpha_2} \right]^{1/2}$$  \hfill (27)
In eqn. (26), the term on the l.h.s., $\psi(t)\Theta(t)$, is the equilibrium, thermodynamically averaged, angular velocity correlation function, from which Fourier transform is therefore a spectrum in the usual way. In the limit $\beta = 0$ eqn. (26) gives:

$$\psi(t)\Theta(t) = \cos \frac{2}{2} \beta$$

The angular velocity spectrum is therefore two delta functions (i.e. an infinitely sharp peak) at the frequencies $\pm \omega_0/\beta$. In the limit $\beta = 0$, on the other hand, it is more instructive to look directly at the analytical Fourier transform of eqns. (26) i.e., the complete spectrum. In this respect it is necessary to consider $0 < \omega < \infty$, so that the single-sided Fourier transform is defined as:

$$\mathcal{F}\{\psi(t)\Theta(t)\} = \int_0^\infty e^{-i \omega t} \psi(t)\Theta(t) \, dt = \frac{1}{2} \left\{ \sin \frac{2}{2} \beta + \frac{\beta}{ \beta + \omega} \right\}$$

+ \frac{1}{2} \left\{ \sin \frac{2}{2} \beta + \frac{\beta}{ \beta + \omega} \right\} + \frac{1}{2} \left\{ \sin \frac{2}{2} \beta + \frac{\beta}{ \beta + \omega} \right\}

+ \frac{1}{2} \left\{ \sin \frac{2}{2} \beta + \frac{\beta}{ \beta + \omega} \right\}

(29)

The complete analytical spectrum from eqn. (24) therefore consists of several peaks. In the range of physical interest, i.e. $0 < \omega < \infty$, there are three peaks in the real part of eqn. (29). One of these is situated at $\omega_0 = \beta/2$ and is a positive peak of approximate height $+1/\beta$ and half-width $\beta$. As $\beta \rightarrow 0$ this therefore becomes the delta function mentioned already. However, there are two more peaks for finite $\beta$ whose intensities are proportional to $\beta/\omega$ for all $\omega > 0$. These disappear if and only if $\beta$ vanishes (i.e. $\beta = 0$). The approximate heights of these peaks are $1/4\beta$, with half-width $\beta$; and they are situated at $\omega = \beta/2, \pm \beta$. In the simple linear case of eqn. (24) the three peaks in the limit $\beta \rightarrow 0$ therefore happen to be situated at the same frequency. In the non-linear case this might well no longer be so.

The linear inertial oscillator

This is well-known to be the next approximate [5] of the same linear Mori continued fraction [17] which generates the harmonic oscillator. The angular velocity c.e.f. in this case can be written as:

$$\psi(t)\Theta(t) = \frac{e^{-\alpha t} \cos \omega_0 t}{1 + \Lambda} + \frac{\alpha_1}{\omega_0} \frac{e^{-\alpha t} \sin \omega_0 t}{1 + \Lambda}$$

(30)

The complete Fourier transform of eqn. (30) therefore consists, on the positive frequency side, of several peaks defined as follows:

(1) A Lorentzian centred at the frequency origin ($\omega = 0$) of height $1/4\alpha$ and half-width $\alpha$.

(2) A Lorentzian centred at $\pm \omega_0$ of height $1/4(1 + \Lambda)^2\alpha$ and half-width $\omega_0$.

(3) Positive and negative peaks at $\omega_0, \pm \omega_0$, respectively, of approximate height (or depth)

$$\psi(t)\Theta(t) = \frac{1}{4\alpha} (1 + \Lambda)^2$$

(31)

The low frequency limit of the linear inertial oscillator, eqn. (30), means that both $\alpha$ and $\omega_0$ tend to zero. When $\alpha = 0$ we recover the deterministic spectrum, which consists of two delta functions, one at the origin (with $\omega = 0$) and one at $\omega = \omega_0$. (In this respect note that the deterministic angular velocity spectrum from the zeroth linear Mori approximant, eqn. (1), is a single delta function at $\omega = 0$.)

In summary, therefore, the deterministic spectra from the linear Mori continued fraction consist of delta functions. For approximate zero [eqn. (1)] there is one delta function at the origin. For approximate one [eqn. (24)] there is one delta function at $\pm \beta_2$. For approximate two [eqn. (30)] there are two delta functions: one at $\omega = 0$ and one at $\omega = \omega_0$. In general it is known that the angular velocity correlation function from the linear Mori continued fraction is an infinite sum of complex exponentials. This leads to the conclusion that the deterministic angular velocity spectrum from high order linear Mori approximants [18] must consist of a large number of delta functions (see appendix). Therefore, in the linear case, peaks are expected in the far infra-red power absorption in the low frequency limit.

Grigolini et al. [14] have, however, just made the important discovery that when the analysis is extended to the non-linear case, the deterministic trajectories themselves become so intricately complicated [16] that, even near the stable states of "deterministic chaos". Grigolini et al. [14] have therefore discovered a fundamentally new phenomenon of deterministic physics in the low frequency limit.

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Appendix

It has been shown [18] that the angular velocity a.c.f. from the grid linear Mori approach takes on three general forms, i.e.:

$C(t) = \frac{2}{\pi} \int_{0}^{\infty} \frac{e^{-\omega t}}{\omega} \left( \cos \omega \eta + \sin \omega \eta \right) \frac{\Omega}{\Omega + \omega} d\omega$  

(A1)

where the coefficients can be described in terms of the roots:

$(\alpha_1 \pm i \beta_1), (\alpha_2 \pm i \beta_2), (\alpha_3 \pm i \beta_3),$ and $(\alpha_4 \pm i \beta_4); or:$

$C(t) = \frac{1}{\pi} \int_{0}^{\infty} e^{-\omega t} \cos \omega \eta d\omega$  

or

$C(t) = \frac{1}{\pi} \int_{0}^{\infty} e^{-\omega t} \sin \omega \eta d\omega$  

(A2)

or

$C(t) = \sum_{k=1}^{4} D_k \exp(-\alpha_k t)$  

(A3)

In the deterministic limit eqn. (A1) provides two distinct peaks; two delta functions at $\omega = \beta_1$ and $\omega = -\beta_1$. Eqns. (A2) provides three peaks; two delta functions superimposed at the origin, $(\omega = 0)$, and another at $\omega = \beta_2$. Eqn. (A3) provides four delta functions, superimposed at $\omega = 0$.

This argument can be extended to higher approximations.