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# NEW RESONANCE METHOD FOR ANALYZING ANISOTROPIC SOLVENTS IN SOLUTIONS *

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ABSTRACT

A new physical effect is described for the behaviour of magnetically (electrically) anisotropic objects in an alternating external field. These objects (large molecules or clusters of molecules in solutions) acquire an induced moment in a direction different from that of the field. The resulting driving force is the cause of periodic vibrations and rotations as well as of chaotic motion. Only objects of special size confined from above and below are able to execute non-damped motion and to transfer energy from an external field to the medium. The statistical properties of the linearized equation of motion are analyzed in detail. It turns out that the peculiarities of the mechanical motion manifest themselves also in the statistical description.

For a long time I have been aware of the results of the following very peculiar qualitative experiment [1]. The electromagnetic absorption at acoustic frequencies has been observed throughout the melting and crystallization of benzene. This absorption was observed only during the phase transformation process rather than in the solid or liquid phases. In an attempt to explain the amazing results of this experiment, I focussed my attention on the distinctive anisotropy of the benzene molecule which pertains to solid benzene as well. In fact, the $\pi$-electrons in the six-ring molecule of benzene are able to move in an external magnetic field almost exclusively in the plane of the rings rather than in the direction perpendicular to the plane. Accordingly, the diamagnetic susceptibility $\chi$, which describes the magnetic moment $M_i$ ($i = 1, 2, 3$) induced in the external field $F_i$, $M_i = \chi_i F_i$, is very anisotropic. That is, $\Delta\chi = \chi_{\perp} - \chi_{\parallel}$ is very large, which in fact serves as the clue to an explanation of the experiment described above.

In isotropic systems an induced magnetic (dielectric) moment appears due to the induction law in the direction opposite to that of an external field. However, anisotropic systems in an external field acquire an induced mo-

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ment of direction different, in general, from that of a field. In benzene, for instance, the induced moment will be directed perpendicular to the six-ring plane, irrespective of the direction of an external field. In an effort to decrease the interaction energy, the system will start to rotate. However, by the time the induced moment reaches the direction antiparallel to the field, the external (alternating) field may, in turn, change its direction, and the system will continue to rotate in order to reach a new energetically favourable position, and so on. Hence, for an alternating external field and a dissipative medium, this should lead, under certain conditions, to the periodic rotations of a system thereby transferring the energy of an external field to the medium. Moreover, one can understand the reasons why the energy absorption has been observed experimentally only during the melting or crystallization of benzene. There is no effect in the solid phase because the entire system is too heavy and the huge inertia prevents rotation. On the other hand, in the liquid phase the individual molecules are able to follow an external field without any phase lag, i.e. without absorption of energy.

Our theoretical analysis is more general than that needed for an explanation of the benzene experiment. First of all, an anisotropy is usually the rule rather than the exception in organic chemistry and biology. The great majority of dilute solutions of polymers, polymer liquid crystals, aromatic components, viruses, proteins, etc. contain rodlike "one-dimensional", or quasi-two-dimensional molecules or clusters of molecules. Therefore, the suggested effect is a widely occurring phenomenon. Moreover, this effect has a strongly resonant character: only clusters (molecules) of special size are able to rotate in an external field of given frequency and amplitude. The resonant frequency of the external field is basically dependent on the cluster size. The smaller the size of clusters, the higher is the frequency of an external field needed for the resonance absorption. These frequencies cover the bright spectrum starting from a few hundred Hz for a cluster of aromatic compounds floating in a fluid during melting and reaching a few GHz for solutions of the tobacco mosaic virus about a size of a few thousand Ångstroms. Such great sensitivity of this resonance phenomenon to the size of system offers many possibilities for practical applications, such as analysis of the size distribution of anisotropic objects in solution, analysis of the dynamics of first-order phase transitions by the measurement of the cluster size of aromatic components during melting and/or solidification, etc.

After a short review of the mechanical analysis, we shall consider the statistical properties of an ensemble of anisotropic clusters in an alternating external field.

The equation of motion describing the rotation of a cluster has the form

$$\frac{\mathrm{d}L}{\mathrm{d}t} = M \times F - \beta\omega \tag{1}$$

where $L$ is the angular momentum, $\omega$ is the angular velocity of rotation, $\beta$

is the damping torque in a viscous solution, $M_i = \chi_i F_i$ is the magnetic (dielectric) moment induced by the external field $F$, and $\chi$ is the tensor of the magnetic (dielectric) susceptibility.

The usual complication with vector equations of type (1) is the existence of two coordinate systems, one of which is the laboratory system where the external field is defined, and the other being the moving coordinate system with the principal axes of inertia. It is just the latter system in which the angular momentum is related in the simplest way to the angular velocity, $L_i = I_i \omega_i$, where $I_i$ are the principal moments of inertia. Performing some simple transformations, one can show [1] that the motion of a cluster which is assumed to be isotropic in the $xy$ plane, $I_1 = I_2 \equiv I$ and $\chi_1 = \chi_2$, is governed by the differential equation for the nutation angle $\theta$

$$\frac{d^2\theta}{dt^2} + \frac{\beta}{I}\frac{d\theta}{dt} + \frac{\Delta\chi}{2I}\sin(2\theta) = 0 \tag{2}$$

where $\Delta\chi = \chi_3 - \chi_1$. It is clear from eqn. (2) that the undamped motion of the cluster is associated with the anisotropy of the magnetic (electric) susceptibility $\Delta\chi$.

Let $F$ be an alternating field, $F = F_0 \cos \omega t$. Substituting this expression into eqn. (2), one obtains the non-linear differential equation with coefficients periodic in time, which allows only numerical solutions. However, some general properties of solutions of eqn. (2) can be found by making the linear approximation $\sin 2\theta \approx 2\theta$. Then, eqn. (2) takes the form of the damped Mathieu equation [3] (with dimensionless time $\tau = \omega t$)

$$\frac{d^2\theta}{d\tau^2} + \frac{\beta}{I\omega}\frac{d\theta}{d\tau} + [a - 2b\cos(2\tau)]\theta = 0 \tag{3}$$

where

$$a = 2b = \frac{\Delta\chi F_0^2}{I\omega^2} \tag{4}$$

Depending on the values of the parameters $a$, $b$ and $\beta/I\omega$, solutions of the Mathieu equation (3) can be damped, periodic or divergent. Figure 1, which is plotted in coordinates $a$ and $b$, shows all possible solutions of eqn. (3). The solid lines correspond to periodic solutions which separate regions of damped and divergent solutions for the undamped Mathieu equation to which eqn. (3) reduces when $\beta = 0$. When friction is taken into account, the instability regions shrink and shift upward. The instability regions for $\beta \neq 0$ are shown by the shading in Fig. 1. The additional constraint (4) on the Mathieu equation (3) means that the periodic solutions are defined by the intersection of the solid lines in Fig. 1 with the straight line $a = 2b$. The number of intersections is finite since the solid lines shift upward with increasing $a$. Therefore, the linearized eqn. (2) has a finite number of periodic solutions restricted from both sides by $a_{min}$ or $a_{max}$, i.e. for a given substance and a given field, by $I_{min}$ and $I_{max}$. In other words, only clusters

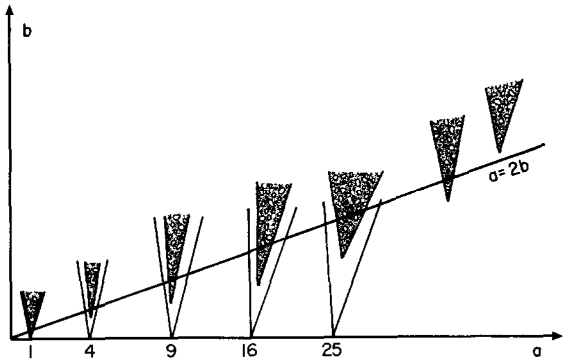


Fig. 1. Different types of solutions of the Mathieu equation plotted in the plane of the parameters $a$ and $b$. The solid lines correspond to periodic solutions dividing the ranges of damped and divergent solutions. The shaded areas show the instability regions when friction is taken into account. The intersections of the line $a = 2b$ with the internal solid lines define the periodic solutions of eqns. (3) and (4).

of intermediate size (which exist only during melting in benzene!) are able to rotate in an external alternating field.

In the general case, the non-linear equation (2) also has a restricted number of clusters with resonant sizes. However, the variety of possible periodic motions appears in the non-linear case. Changing, say, the amplitude of an external field, one passes from the pendulum-like vibrations considered above to the hour-hand rotations with different periods. It is much easier, from the experimental point of view, to change the frequencies rather than the amplitudes of an external field which, however, corresponds to a simultaneous change of all the parameters. Moreover, in some region of the parameters, solutions of eqn. (2) become "chaotic": a cluster sometimes rotates in one direction, suddenly reverses, stops and continues in the same or the reverse direction, and so on.

All these peculiar theoretical predictions [2] might be seen experimentally on systems similar to those described above. So far, we have considered different objects in which magnetic (dielectric) moment appears in an external field. However, similar effects exist also for molecules (clusters) having permanent magnetic (electric) moments which are placed in an alternating external field. The drag torque $M \times F$ in eqn. (1) is now linear in the external field $F$, rather than quadratic as it was for the induced moment. Accordingly, the equation of motion (2) is now replaced by

$$\frac{d^2\theta}{dt^2} + \frac{\beta}{I}\frac{d\theta}{dt} + \frac{MF_0 \cos \omega t}{2I} \sin \theta = 0 \tag{5}$$

For $\beta = 0$, eqn. (5) describes a conservative (Hamiltonian) system with two resonant terms, as can be seen by rewriting the oscillating field in eqn. (5) as being composed of two counter-rotating fields

$$\frac{d^2\theta}{dt^2} = \frac{MF_0}{4I}[\sin(\omega t - \theta) - \sin(\omega t + \theta)] \tag{6}$$

A comprehensive numerical analysis of eqns. (5) and (6) has been performed [4] showing the large variety of different types of motion for different values of two dimensionless parameters $\beta/I\omega$ and $MF_0/2I\omega^2$. The simplest experimental set-up for this problem is a magnetic needle in an alternating magnetic field produced by two Helmholtz coils. The chaotic motion of the needle was the main goal of the experiments [5]. In fact, this simple experiment should be an indispensible part of the undergraduate university course which contains explanations of the transition from order to chaos.

The foregoing is related to mechanical systems or, one can say, to zero temperature. As is well known [6], the influence on the cluster of the molecules of a medium, of other clusters as well as of the thermal fluctuations, can be represented by a random force in equations of mechanics. We start here with the simplest case of the linearized undamped equation (3)

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\tau^2} + [a - 2b\cos(2\tau)]\,\theta = \mathrm{f}(\tau) \tag{7}$$

where the random function $\mathrm{f}(\tau)$ is assumed to be Gaussian, zero-mean white noise, i.e. its properties are determined by the second moment

$$\begin{aligned} \langle \mathrm{f}(\tau)\rangle &= 0 \\ \langle \mathrm{f}(\tau)\mathrm{f}(\tau')\rangle &= D\delta(\tau-\tau') \end{aligned} \tag{8}$$

One can easily include damping in our analysis. However, the transition from the linear equations (7) and (3) to the non-linear equation (2) is considerably more complicated, and such an analysis is now in progress.

The following two questions arise in connection with eqn. (7): (a) What drastic changes in kinetic behaviour of a mechanical system described by the noise-free Mathieu equation (3) (with $\beta = 0$) are necessarily reflected in the behaviour of the statistical variables $\theta(t)$ of eqn. (7) that describe such systems in the presence of additive noise? (b) The noise-free undamped Mathieu equation has two characteristic frequencies. The first is that arising when $b$ in eqn. (3) is equal to zero and is $\omega = a^{1/2}$, and the second is $\omega = 2$ which arises from the cosine term. The question is whether these two characteristic mechanical frequencies will also manifest themselves in the statistical description of this system.

A positive answer to the first question with all attendant analysis has been given elsewhere [6]; here, we answer the second question [7].

Using standard techniques [8], one can pass from the second-order differential equation (7) with a random force (the so-called Langevin equation) to the correspondent Fokker–Planck equation for the joint density for the random variables $P(\theta, \dot{\theta}, \tau)$ (where $\dot{\theta} = \mathrm{d}\theta/\mathrm{d}t$)

$$\frac{\partial P}{\partial \tau} = D\frac{\partial^2 P}{\partial \dot{\theta}^2} - \dot{\theta}\frac{\partial P}{\partial \theta} + [a - 2b\cos(2\tau)]\,\theta\frac{\partial P}{\partial \dot{\theta}} \tag{9}$$

with the initial conditions

$$P(\theta, \dot{\theta}, 0) = \delta(\theta - \theta_0)\ \delta(\dot{\theta} - \dot{\theta}_0) \tag{10}$$

We are only interested in the probability density for $\Theta(\tau)$ which is found by integrating over $\dot{\theta}$

$$p(\theta, \tau) \equiv \int_{-\infty}^{\infty} p(\theta, \dot{\theta}, \tau)\, \mathrm{d}\dot{\theta} \tag{11}$$

We record here the final results of these calculations. As one would expect, the distribution function $p(\theta, \tau)$ has a Gaussian form

$$p(\theta, \tau) = (2\pi\sigma_{\theta\theta})^{-1/2} \exp\left[-(\theta - \bar{\theta})^2/2\sigma_{\theta\theta}\right] \tag{12}$$

where the mean value $\bar{\theta}$ satisfies the original noise-free Mathieu equation $\ddot{\bar{\theta}} + [(a - 2b\cos(2\tau)]\bar{\theta} = 0$ and the variance of $\theta(\tau)$, $\sigma_{\theta\theta}(\tau) \equiv \overline{\theta^2} - \bar{\theta}^2$, is the solution of the equation

$$\frac{\mathrm{d}^3\sigma_{\theta\theta}}{\mathrm{d}\tau^3} + 4[a - 2b\cos(2\tau)]\frac{\mathrm{d}\sigma_{\theta\theta}}{\mathrm{d}\tau} + [8b\sin(2\tau)]\,\sigma_{\theta\theta} = 4D \tag{13}$$

We use the standard initial condition $\sigma_{\theta\theta}(\tau = 0) = 0$. Then, the diffusion constant $D$ can be scaled out of the problem, allowing us to set $D = 1$ in all of the calculations that follow.

Equation (13) with $D = 1$ has been solved numerically. Let us consider several cases of results found for $\sigma_{\theta\theta}(\tau)$ to illustrate the qualitative behaviour possible for different values of the parameters $a$ and $b$.

*(1) $a > 0$, $b = 0$*

Since the time dependence disappears from the Mathieu equation, the resulting equation (13) is readily solved and $\sigma_{\theta\theta}(\tau)$ is found to be

$$\sigma_{\theta\theta}(\tau) = \frac{\left[2a^{1/2}\tau - \sin(2a^{1/2}\tau)\right]}{2a^{3/2}} \tag{14}$$

Thus, the variance increases monotonically as a function of $\tau$ with a modulating ripple.

*(2) $a = 0$, $b > 0$*

When $a = 0$ only oscillations with $\omega = 2$ or with the period $\pi$ exist in the original mechanical equation. One therefore expects that these oscillations will appear in some guise in a graph of $\sigma_{\theta\theta}(\tau)$ plotted as a function of $\tau$. This behaviour is evident from the curve in Fig. 2 which has been calculated for the case $b = 1$. The period $\pi$ is indicated by the + signs in the figure, and the variance of $\theta(\tau)$ has oscillatory behaviour with this periodicity. Notice that $\sigma_{\theta\theta}(\tau)$ decreases as a function of time for certain ranges of $\tau$ corresponding to a sharpening of the Gaussian peak. This is somewhat counter-intuitive in that the variance should increase monotonically with time. As

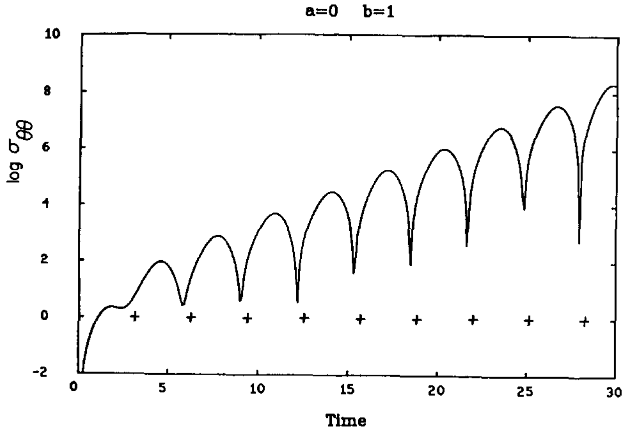


Fig. 2. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for the parameters $a = 0$, $b = 1$. The + symbols in this and the following figures correspond to multiples of $\pi$.

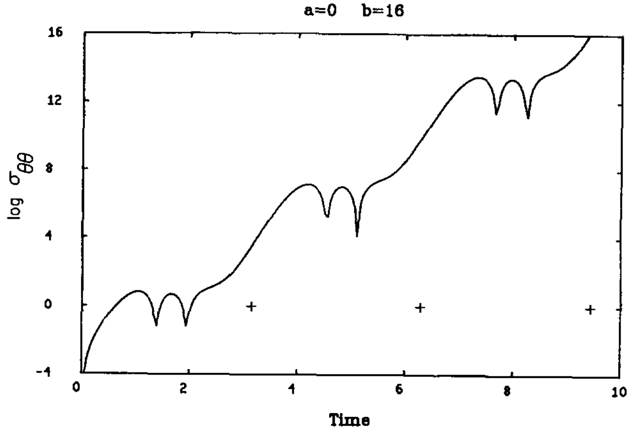


Fig. 3. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for $a = 0$, $b = 16$. Additional fine structure appears compared with Fig. 2.

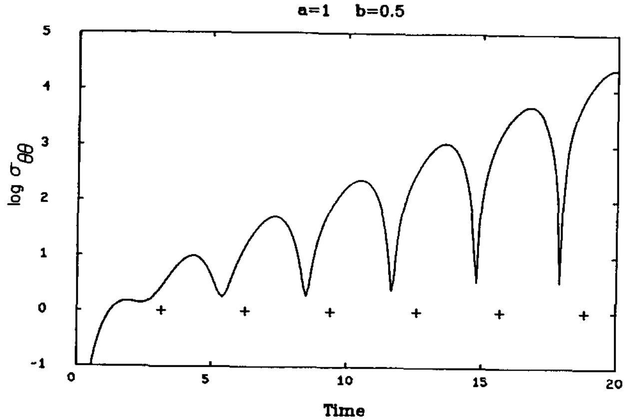


Fig. 4. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for $a = 1$, $b = 0.5$.

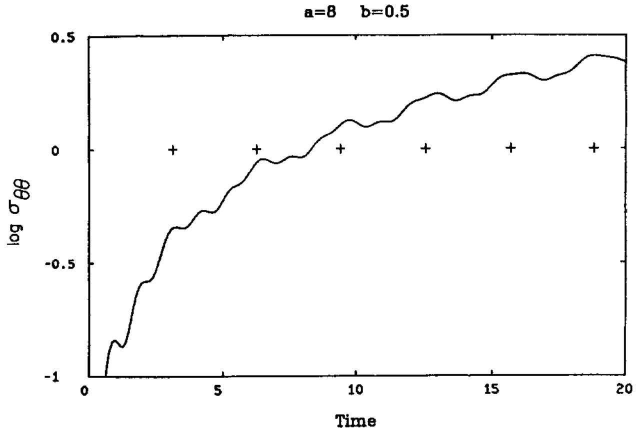


Fig. 5. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for $a = 8$, $b = 0.5$. The more monotonic behaviour can be seen in comparison with Fig. 4 since an increase of $a$ corresponds to the approach to the case $a \gg b$ described by eqn. (14).

the parameter $b$ is increased, more fine structure appears in $\sigma_{\theta\theta}(\tau)$ as shown in Fig. 3 for $b = 16$.

*(3) $a > 0$, $b$ fixed ( = 0.5)*

Figure 4 shows the oscillatory behaviour for $a = 1$ while Fig. 5 for $a = 8$ shows a decrease in the observed oscillations. This latter result might have been expected because in the limit $a \to \infty$, the solution of $\sigma_{\theta\theta}(\tau)$ approaches the prediction of eqn. (14).

*(4) $b > 0$, $a$ positive and fixed ( = 0.5)*

Clearly an increase in $b$ ($b = 0.5$ in Fig. 6 and $b = 5$ in Fig. 7) leads to more pronounced oscillations.

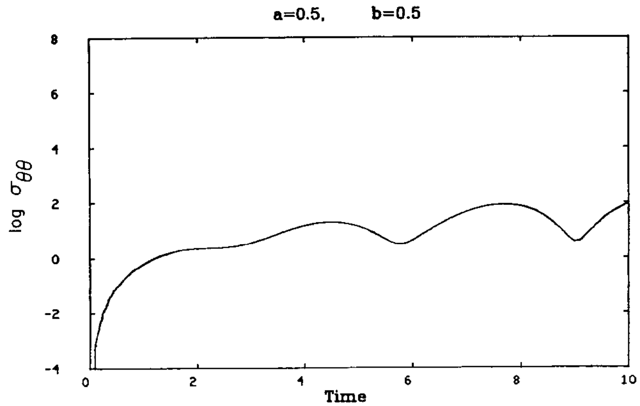


Fig. 6. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for $a = 0.5$, $b = 0.5$.

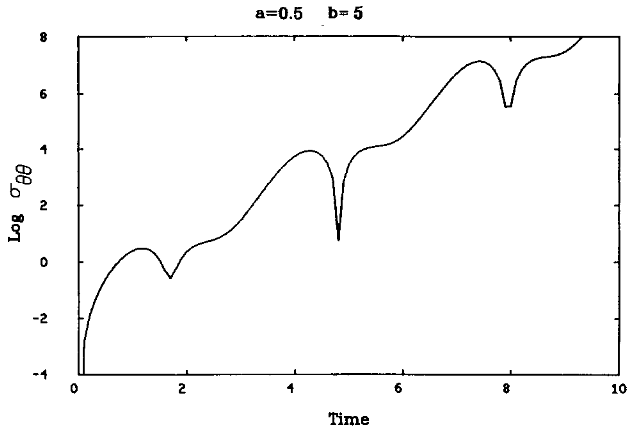


Fig. 7. The function $\sigma_{\theta\theta}(\tau)$ plotted on a semi-logarithmic scale for $a = 0.5$, $b = 5$. A comparative increase in $b$ similar to the decrease in $a$ in Figs. 4 and 5 results in more pronounced oscillations of $\sigma_{\theta\theta}(\tau)$.

One concludes, therefore, that the period for time changes in the deterministic behaviour of a dynamic system is reflected in the behaviour of the statistical variables that describe such a system in the presence of additive noise. It will be recalled that these results have been obtained from the linearized equation, although in the non-linear equations the statistical properties will be similar to the mechanical ones.

We are looking forward to experimental verification of the suggested resonance phenomena.

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