The Itinerant Oscillator Treated and Extended in Terms of a Mori Continued Fraction.

by

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Abstract

The angular velocity and orientational auto correlation function of a disk are evaluated using a four-variable Mori formalism. It is pointed out that the equivalent three-variable formalism is formally identical to the inertia-corrected itinerant oscillator model developed recently by Coffey et al[4]. Therefrom a sound physical interpretation can be given to the four-variable model in terms of a disk (in the 2-D case) surrounded by two annuli, the outermost of which undergoes rotational diffusion.

Introduction

The itinerant oscillator as a model for diffractional motion in condensed fluids has been a consistent theme in the literature over the past decade. It was first propounded by Hill[1] and extended by Wyllie[2] and Larkin[3]. Lately, Coffey et al[4] have developed a more realistic, inertia-corrected version in two dimensions. An alternative approach to the same problem is that of generalizing the Langevin equation so that the friction coefficient is replaced by a memory kernel. The auto-correlation function (a.c.f.) may then be expanded in a Mori continued fraction which has been shown[7] to converge under the right conditions. The purpose of this letter is to use such a continued fraction expansion to estimate the angular velocity a.c.f. for a disk, and then to use the recently derived relations of Lewis et al[5] to calculate the orientational a.c.f. therefrom[6]. It transpires that the angular velocity a.c.f. of Coffey et al is formally identical to 'three variable' Mori theory, and therefore a clear physical interpretation of higher order truncations suggests itself.

Theory

Consider the Mori/Kubo generalisation[7] of the Langevin equation for a disk undergoing itinerant torsional oscillation in a plane. Neglecting dipole-dipole coupling[8], we have in the field-free case, for a moment of inertia I:

$$\dot{\underset{\sim}{\omega}}(t) + \int_0^t K_0(t-\tau)\,\underset{\sim}{\omega}(\tau) = \underset{\sim}{\Gamma}(t) \qquad (1)$$

where $I\underset{\sim}{\Gamma}(t)$ is the couple due to extraneous random torques, and the factor:

$$\int_{-\infty}^{t} K_0(t-\tau)\,\omega(\tau)\,d\tau$$

is the frictional couple arising from the medium. We emphasize that $\Gamma(t)$ is Gaussian and non-Markovian. K_0, the memory function, is defined by:

$$K_0(t) = \langle \Gamma(t)\cdot\Gamma(0)\rangle / \langle \omega(t)\cdot\omega(0)\rangle$$

Solving eqn(1) leads to the following in Laplace space (p):

$$\tilde{\omega}(p) = \frac{\omega(0) + \mathcal{L}(\Gamma(t))}{p + \tilde{K}_0(p)} \qquad (2)$$

so that:

$$\langle \omega(t)\cdot\omega(0)\rangle = \langle \omega(0)\cdot\omega(0)\rangle \mathcal{L}^{-1}\left[\left(p + \tilde{K}_0(p)\right)^{-1}\right] \qquad (3)$$

Since $\Gamma(t)$ is a variate that obeys the same type of stochastic differential equation as (1), it follows that:

$$\left[p + \tilde{K}_0(p)\right]^{-1} = \left[p + K_0(0)/(p + \tilde{K}_1(p))\right]^{-1} = \ldots\ldots \qquad (4)$$

where K_1 is the memory function of K_0. It has been shown[4] that the 'three variable truncation' of equations (4), i.e.:

$$K_1(t) = K_1(0)\exp(-\gamma t)$$

yields the final expression for $\alpha(\omega)$, the power adsorption coefficient, formally identical to the inertia-corrected itinerant oscillator model of Coffey et al, although these authors used an entirely different starting proposition. In this letter we propose to extend the Mori theory to the next order of truncation[9], using:

[illegible] (5)

The physical significance of this is discussed below, but first we note that eqn.(2) now reads:

[illegible] (6)

where [illegible], so that in inverting the transform in eqn.(6) we need to solve a quantic in the denominator, viz:

[illegible]

Writing this as:

[illegible]

then it has the discriminant[10]:

[illegible]

where [illegible], and

[illegible] $- 2c^3/27.$

The equation can be reduced by the substitution $p = p_1 - b/4$ to:

[illegible]

Now a quantic with q,r,s real; [illegible] and [illegible] has:

(i) 4 distinct real roots if q and $4s - q^2$ are negative and $\Delta > 0$;

(ii) no real root if q and $4s - q^2$ are not both negative and $\Delta > 0$;

(iii) 2 distinct real and 2 imaginary roots if $\Delta < 0$;

(iv) at least 2 equal real roots if $\Delta = 0$.

It is quite easy to solve the quartic numerically to any degree of accuracy (using the N.A.G. library available on most computers) given the above rules, whence it is possible to discuss the analytical forms the auto-correlation function of angular velocity will take. In case (i) we have:

$$C_\omega(t) = \sum_{n=1}^{4} D_n \exp(-\alpha_n t) \tag{7}$$

where D_n are soluble in terms of the distinct roots α_n by taking partial fractions. In case (ii):

$$C_\omega(t) = {}^1x_1 e^{-\alpha_1 t}\cos\beta_1 t + {}^2x_1 e^{-\alpha_1 t}\sin\beta_1 t + {}^1x_2 e^{-\alpha_2 t}\cos\beta_2 t + {}^2x_2 e^{-\alpha_2 t}\sin\beta_2 t \tag{8}$$

where the roots are $(\alpha_1 + i\beta_1)(\alpha_1 - i\beta_1)(\alpha_2 + i\beta_2)(\alpha_2 - i\beta_2)$, and the x factors are all expressible in terms of α_1, β_1, α_2 and β_2. Similarly in case (iii):

$$C_\omega(t) = {}^1x_1 e^{-\alpha_1 t} + {}^1x_2 e^{-\alpha_2 t} + {}^1x_3 e^{-\alpha_3 t}\cos\beta t + {}^1x_4 e^{-\alpha_3 t}\sin\beta t; \tag{9}$$

and finally, in the fourth case, $\alpha_1 = \alpha_2$, at least, in eqn.(9).

It is possible now to calculate the orientational autocorrelation function $C_u(t)$ of the dipole unit vector u (and thus the i.-r./micro-wave spectrum) by use of the relation:

$$[\text{illegible}] \qquad (10)$$

derived recently by Lewis et al[5] for the disk. Thus in case (i):

$$[\text{illegible}] \qquad (11)$$

In case (ii):

$$[\text{illegible}] \qquad (12)$$

In case (iii):

$$[\text{illegible}] \qquad (13)$$

with a simple charge for the fourth case. In each of eqns.(11) - (13) there is no linear or term in the Maclaurie expansion of the exponent, and at very short times, each reduces to exp ( ), the autocorrelation function for free rotation in 2 - D. At long times the form in each case is exp ( ) where is the equivalent of the Debye relaxation time.

Discussion

The three variable formalism represented by the exponential truncation at $K_1(t)$ may be given physical significance by reference[4] to the Coffey/Calderwood model. Here it is assumed that the mechanical system consisting of the vibrating central molecule and its cage of neighbours may be represented by an annulus which is free to rotate about a central axis perpendicular to itself. Concentric and co-planar with the annulus is a disk (of diameter less than the annulus) which is free to rotate about the same central axis. The disk carries a dipole μ lying along one of its diametes whose orientation is specified by an angle (t) relative to a fixed axis determined by the applied field direction, while the position of a point on the rim of the annulus is specified by an angle (t) relative to the same fixed axis. The mechanical interaction between the central molecule and its neighbours is represented by a restoring torque acting on the dipole and proportional to the displacement (t) - (t). In our notation, , the angular frequency of the disk when the annulus is held stationary; , where I_1 = moment of inertia of the annulus, I_2 = that of the disk, = ; where τ_D is the Debye relaxation time.

In extending the Mori series to the four variable level by truncati

exponentially at $K_2(t)$ we have created the following equations linking (t) to a Wiener process $_2(t)$.

(14)

(15)

(16)

Now $_1(t)$ is Gaussian and Markovian whereas (t) and (t) are non-Markovian, although still Gaussian by the central limit theorem. Thus any fluctuations ( ) and ( ) induce in the surrounding molecules flcutuations which after a time cause <u>further</u> ones in and . So (t) or (t) each remains partly stationary in space[11]. On the other hand ( ) flows through the ensemble, since being Markovian it must not affect again, and thus (t) is propagated, as would be (t) for the Debye sphere, where C (t) is a single exponential with a characteristic time . Further, is a characteristic operator of one or a small number of molecules - typically the nearest neighbour cage, so that (t) depends on the next-nearest neighbours etc. To say that (t) propagates through the fluid is to assert rotational diffusion for the nearest neighbour cage (the annulus of the model above) and thus if (t) propagates, the next-nearest shell must be undergoing this type of motion. So we have in the four-variable theory a disk surrounded by two annuli (in two dimensions), so that $K_2(t)$ is a function of all three moments of inertia and of the disk proper frequency ω_3. Obviously the formalism can be extended although one cannot (by a theorem of groups) solve analytically higher order polynomials than the quantic denominator of eqn.(6).

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