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A quantum statistical model of a three-dimensional linear rigid rotator in a bath of oscillators: I. Electrical susceptibility derivation

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Abstract. We consider a model Hamiltonian describing a rotor as fixed and weakly interacting with a bath of oscillators. From the basic principles of statistical mechanics, we derive the corresponding master equation for the rotor density matrix operator. Two relevant limit regimes, imposed by the weak-coupling assumptions, are then examined in detail. The first regime, corresponding to the classical Brownian limit, leads to the same electrical susceptibility formulae as deduced from the well known Fokker–Planck–Kramers equation for the rotational Brownian motion. The second regime appears as the Van Hove limit for the master equation in the interaction picture. Based on the application of a mathematical theorem by E B Davies, this limit provides an elegant Van Vleck–Weisskopf lineform for the electrical susceptibility, explicitly expressed for the model considered here.

1. Introduction

The study of the dielectric properties generated by the rotational motion of linear molecules in non-polar media is an active field of work [1–6]. A close analysis of the vast literature [7, 8] concerning theoretical studies on the quantum rotational motion shows that there are fundamental difficulties in the understanding of the problem. The main difficulty is that there are various aspects of the relation between commonly used phenomenological models and microscopic dynamics that are not well understood. Moreover, existing theories based on model Hamiltonians have not been carried far enough to clearly establish their relation to phenomenological models.

In order to clarify the problem, in this work we consider the quantum model Hamiltonians of a rigid fixed rotor interacting with a bath of harmonic oscillators.

From the basic principles of statistical mechanics we establish the weakly-coupled master equation for the density matrix associated with the motion of the rotor. Some authors have tackled this problem using projection operator techniques [9–11]. The rotor possesses a permanent dipole moment along its axis interacting with an external applied electric field. This model has already been treated by Lindenberg and West [2] in the classical case. Instead of using the master equation approach, they have established the Langevin equations for the rotational motion of the rotor. In the limit regime, where the random force created by the bath in the Langevin equations results from a white noise, they have obtained the Fokker–Planck–Kramers (FPK) equation [1, 2, 4, 6, 12–14]. Identical results have been recovered by the master equation approach with the effects of an applied electrical field included [15]. The white noise is a consequence of the fact that the dynamical evolution of the bath is infinitely faster than that of the rotor and so is a characteristic of the Brownian motion.

In the full quantum treatment, the bath creates a quantum noise which no longer generates such an infinitely fast motion [11]. The correlation time of the bath is of the same order of magnitude as the thermal correlation time $\tau_T = \hbar/k_B T$ ($\hbar$ is Planck's constant, k_B the Boltzmann constant and T the absolute temperature). The weak-coupling assumption imposes that this time must be much shorter than the typical relaxation time associated with the evolution of the rotor [11, 16]. This constraint restricts the validity of the master equation to two limit regimes. The first regime corresponds to the classical Brownian limit [17] discussed above. The second regime corresponds to the Van Hove limit [18–21] applied to the master equation, describing the density matrix in the interaction picture. In this case, we can apply a mathematical theorem by Davies which reduces the master equation in an analytically tractable form [17, 21, 22].

The electrical susceptibility of the rotor can be calculated in the two limit regimes. In the classical Brownian limit, this has been done in previous papers [12–14, 23]. In the Van Hove limit, the susceptibility is given by the Van Vleck–Weisskopf lineform expression [8, 16], whose parameters are explicitly calculated from the model.

The paper is organized as follows. Section 2 deals with the theoretical framework from which we establish the weak-coupling master equation. In section 3, we show how to derive the expression for the linear dielectric susceptibility for the two limit regimes. Section 4 ends with the conclusions.

2. Theoretical framework

Let us consider a symmetric rigid rotor, fixed at its centre and free to rotate about this centre. The rotor is in a bath of non-interacting harmonic oscillators that interact harmonically with either end of the rotor. The centres of mass of the bath are spatially fixed. The rotor possesses a permanent dipole moment susceptible to interact with an applied electric field. In the quantum treatment, the Hilbert space associated with this model is the tensorial product of the Hilbert space associated with the rotor system $\mathcal{H}_S$ and that associated with the bath system $\mathcal{H}_B$:

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B. \tag{1}$$

In this Hilbert space, the Hamiltonian operator associated with the model is written as [2]

$$\hat{H}_T = \hat{H} + \hat{H}_E(t) \tag{2}$$

with

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} \tag{3}$$

where the definitions are as follows.

(a) The rotor system Hamiltonian is

$$\hat{H}_S = \frac{1}{2I}\hat{L}^2 = -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\beta}\frac{\partial}{\partial\beta}\sin\beta\frac{\partial}{\partial\beta} + \frac{1}{\sin^2\beta}\frac{\partial^2}{\partial\alpha^2}\right). \tag{4}$$

I is the moment of inertia about the principal axes and $\hat{L}$ are the components of the angular momentum operator. Its components can be expressed in terms of the azimuthal angle α

and the polar angle β of the rotor, respectively referring to the fixed direction of an applied field as polar axis:

$$\hat{L}_x = \frac{\hbar}{\mathrm{i}}\left(-\sin\alpha\frac{\partial}{\partial\beta} - \cos\alpha\cot\beta\frac{\partial}{\partial\alpha}\right)$$
$$\hat{L}_y = \frac{\hbar}{\mathrm{i}}\left(\cos\alpha\frac{\partial}{\partial\beta} - \sin\alpha\cot\beta\frac{\partial}{\partial\alpha}\right)$$
$$\hat{L}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\alpha}. \tag{5}$$

(b) The Hamiltonian of a set of three-dimensional oscillators is

$$\hat{H}_{\mathrm{B}} = \sum_\nu \tfrac{1}{2}(\hat{p}_\nu^2 + \omega_\nu^2\hat{q}_\nu^2) = \sum_\nu \hbar\omega_\nu(\hat{a}_\nu^+ \cdot \hat{a}_\nu + \tfrac{3}{2}). \tag{6}$$

$\hat{q}_\nu$ is the operator associated with the νth oscillator displacement from the equilibrium configuration, $\hat{p}_\nu$ the associated conjugated momentum operator and ω_ν the frequency variable. The mass of the oscillators is taken to equal unity. In terms of the creation and annihilation operators $\hat{a}_\nu^+$, $\hat{a}_\nu$, the operators $\hat{q}_\nu$ and $\hat{p}_\nu$ can be written as

$$\hat{q}_\nu = \left(\frac{\hbar}{2\omega_\nu}\right)^{1/2}(\hat{a}_\nu + \hat{a}_\nu^+) \tag{7}$$

$$\hat{p}_\nu = \mathrm{i}\left(\frac{\hbar\omega_\nu}{2}\right)^{1/2}(\hat{a}_\nu^+ - \hat{a}_\nu) \tag{8}$$

with the commutation relations:

$$[\hat{a}_\nu, \hat{a}_{\nu'}^+] = \mathbf{1}\delta_{\nu,\nu'} \tag{9}$$

where $\mathbf{1}$ is the identity operator.

(c) The Hamiltonian of the coupling between the bath and the rotor is

$$\hat{H}_{\mathrm{SB}} = \sum_\nu c_\nu\hat{q}_\nu \cdot \hat{u}. \tag{10}$$

c_ν is the coupling parameter between the oscillator ν and one of the rotor ends.

$$\hat{u} = (\cos\alpha\sin\beta, \sin\alpha\sin\beta, \cos\beta) \tag{11}$$

is the unit vector oriented along the given end.

(d) The time-dependent Hamiltonian due to the applied electric field $E(t)$ is

$$\hat{H}_{\mathrm{E}}(t) = \hat{V}_{\mathrm{E}}(t) = -\mu\hat{u}_z E(t) = -\mu\cos\beta E(t) \tag{12}$$

where μ is the dipole moment. The applied electric field is assumed to be along the z axis, with the unit vector operator component $\hat{u}_z$ [3, 6, 14, 15].

Let us define $\hat{\rho}(t)$ as the probability density matrix operator defined at time t in the Hilbert space, $\mathcal{H} = \mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{B}}$. The normalization condition imposes the relation

$$\operatorname{tr}\hat{\rho}(t) = \operatorname{tr}_{\mathrm{S}} \otimes \operatorname{tr}_{\mathrm{B}}\hat{\rho}(t) = 1 \tag{13}$$

where $\operatorname{tr}_{\mathrm{B}}$ and $\operatorname{tr}_{\mathrm{S}}$ denote the partial traces over a complete set of orthonormal functions in, respectively, $\mathcal{H}_{\mathrm{B}}$ and $\mathcal{H}_{\mathrm{S}}$.

The Von-Neumann–Liouville equation for the density matrix operator is

$$\frac{\partial}{\partial t}\hat{\rho}(t) + (\mathrm{i}\hat{\mathcal{L}} + \mathrm{i}\hat{\mathcal{L}}_{\mathrm{E}}(t))\hat{\rho}(t) = 0 \tag{14}$$

where we used the Liouville operator's commutation relations

$$\mathrm{i}\hat{\mathcal{L}}\hat{\rho}(t) = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}(t)] \qquad \mathrm{i}\hat{\mathcal{L}}_{\mathrm{E}}(t)\hat{\rho}(t) = \frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{E}}(t), \hat{\rho}(t)]. \tag{15}$$

By analogy, let us define

$$\mathrm{i}\hat{\mathcal{L}}_{\mathrm{S}}\hat{\rho}(t) = \frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{S}}, \hat{\rho}(t)] \tag{16}$$

$$\mathrm{i}\hat{\mathcal{L}}_{\mathrm{B}}\hat{\rho}(t) = \frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{B}}, \hat{\rho}(t)] \tag{17}$$

$$\mathrm{i}\hat{\mathcal{L}}_{\mathrm{SB}}\hat{\rho}(t) = \frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{SB}}, \hat{\rho}(t)]. \tag{18}$$

In the following we will consider the canonical ensemble. In this case, when $E(t) = 0$, the equilibrium solution of the Von-Neumann–Liouville equation is

$$\hat{\rho}(t) \to \hat{\rho}^{\mathrm{eq}} \equiv \frac{\exp[-(\hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{B}} + \hat{H}_{\mathrm{SB}})]/k_{\mathrm{B}}T}{\mathrm{tr}(\exp[-(\hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{B}} + \hat{H}_{\mathrm{SB}})]/k_{\mathrm{B}}T)}. \tag{19}$$

Our aim is to describe the dynamics of the rotor moving under the influence of the bath of oscillators. This is realized by deriving a generalized master equation [2, 11] for the reduced rotator density matrix operator

$$\hat{\rho}_{\mathrm{S}}(t) = \mathrm{tr}_{\mathrm{B}}\, \hat{\rho}(t). \tag{20}$$

Carrying out the trace over the states of the bath in (19), in the weak-coupling limit, we can neglect the term $\hat{H}_{\mathrm{SB}}$ and deduce the corresponding reduced density matrix operator

$$\hat{\rho}_{\mathrm{S}}(t) \to \hat{\rho}_{\mathrm{S}}^{\mathrm{eq}} = \frac{\mathrm{e}^{-\hat{H}_{\mathrm{S}}/k_{\mathrm{B}}T}}{\mathrm{tr}_{\mathrm{S}}(\mathrm{e}^{-\hat{H}_{\mathrm{S}}/k_{\mathrm{B}}T})}. \tag{21}$$

The conditions of validity of this approximation will be established later.

To obtain the master equation, we define the projection operator $\hat{\mathcal{P}}$, the action of which on the density matrix operator can be written as

$$\hat{\mathcal{P}}\hat{\rho}(t) = \mathrm{tr}_{\mathrm{B}}\, \hat{\rho}(t) \otimes \hat{\rho}_{\mathrm{B}}^{\mathrm{eq}} \tag{22}$$

where

$$\hat{\rho}_{\mathrm{B}}^{\mathrm{eq}} = \frac{\mathrm{e}^{-\hat{H}_{\mathrm{B}}/k_{\mathrm{B}}T}}{\mathrm{tr}_{\mathrm{B}}(\mathrm{e}^{-\hat{H}_{\mathrm{B}}/k_{\mathrm{B}}T})}. \tag{23}$$

The corresponding complementary operator reads

$$\hat{\mathcal{Q}} = 1 - \hat{\mathcal{P}}. \tag{24}$$

Such projection operators, not depending on the interaction $\hat{H}_{\mathrm{SB}}$, are used to derive the master equation, when we impose the initial condition

$$\hat{\rho}(t = 0) = \hat{\rho}_{\mathrm{S}}(t = 0) \otimes \hat{\rho}_{\mathrm{B}}^{\mathrm{eq}} \tag{25}$$

which also does not depend on the interaction operator $\hat{H}_{\mathrm{SB}}$. When $\hat{H}_{\mathrm{E}}(t) = 0$, using the assumption (25), the master equation in the weak-coupling limit is found to be in the form [2, 11, 16]:

$$\left(\frac{\partial}{\partial t} + \mathrm{i}\hat{\mathcal{L}}_{\mathrm{S}}\right)\hat{\rho}_{\mathrm{S}}(t) = \hat{\mathcal{K}}\hat{\rho}_{\mathrm{S}}(t) \tag{26}$$

where

$$\hat{\mathcal{K}}\hat{\rho}_{\rm S}(t) = {\rm tr}_{\rm B}\left[\int_0^{+\infty} {\rm d}t'\, {\rm i}\hat{\mathcal{L}}_{\rm SB}{\rm e}^{-({\rm i}\hat{\mathcal{L}}_{\rm S}+{\rm i}\hat{\mathcal{L}}_{\rm B})t'}{\rm i}\hat{\mathcal{L}}_{\rm SB}{\rm e}^{{\rm i}\hat{\mathcal{L}}_{\rm S}t'}\hat{\rho}_{\rm S}(t)\otimes\hat{\rho}_{\rm B}^{\rm eq}\right]. \tag{27}$$

Let us recall here (see appendix A) that this result is identical to the more mathematically complicated form [9]:

$$\left(\frac{\partial}{\partial t} + {\rm i}\hat{\mathcal{L}}_{\rm S}\right)\hat{\rho}_{\rm S}(t) + {\rm tr}_{\rm B}[{\rm i}\hat{\mathcal{L}}_{\rm SB}\hat{\Sigma}^{(1)}\hat{\Sigma}_{\rm S}^{-1}\hat{\rho}_{\rm S}(t)]$$
$$= {\rm tr}_{\rm B}\left[\int_0^{+\infty} {\rm d}t'\, {\rm i}\hat{\mathcal{L}}_{\rm SB}{\rm e}^{-({\rm i}\hat{\mathcal{L}}_{\rm S}+{\rm i}\hat{\mathcal{L}}_{\rm B})t'}\hat{\Sigma}^{(0)}{\rm i}\hat{\mathcal{L}}_{\rm SB}\hat{\Sigma}_{\rm S}^{-1}{\rm e}^{{\rm i}\hat{\mathcal{L}}_{\rm S}t'}\hat{\rho}_{\rm S}(t)\right]. \tag{28}$$

$\hat{\Sigma}^{(0)}$ and $\hat{\Sigma}^{(1)}$ are, respectively, the zeroth- and first-order term of the development in the interaction $\hat{H}_{\rm SB}$ of $\hat{\Sigma}$ which, for any well defined operator $\hat{A}$, is defined as

$$\hat{\Sigma}\hat{A} \equiv \frac{1}{k_{\rm B}T\,{\rm tr}({\rm e}^{-\hat{H}/k_{\rm B}T})}\int_0^1 {\rm d}s\, {\rm e}^{-s\hat{H}/k_{\rm B}T}\hat{A}{\rm e}^{-(1-s)\hat{H}/k_{\rm B}T}. \tag{29}$$

$\hat{\Sigma}_{\rm S}^{-1}$ *is the inverse operator of* $\hat{\Sigma}_{\rm S}$ defined as

$$\hat{\Sigma}_{\rm S}\hat{A} \equiv \frac{1}{k_{\rm B}T\,{\rm tr}_{\rm S}({\rm e}^{-\hat{H}_{\rm S}/k_{\rm B}T})}\int_0^1 {\rm d}s\, {\rm e}^{-s\hat{H}_{\rm S}/k_{\rm B}T}\hat{A}{\rm e}^{-(1-s)\hat{H}_{\rm S}/k_{\rm B}T}. \tag{30}$$

The derivation of (28) assumes the following interaction-dependent initial condition:

$$\hat{\rho}(t=0) = \hat{\Sigma}\,{\rm tr}_{\rm B}(\hat{\Sigma}^{-1}\hat{\rho}_{\rm S}(t=0)) \tag{31}$$

and the use of different projection operators as the quantum analogue to the corresponding interaction-dependent classical projection operators [9, 15].

The last term $\hat{\mathcal{K}}\hat{\rho}_{\rm S}(t)$ in (26) can be handled by means of the following properties.

(i)

$${\rm e}^{-({\rm i}\hat{\mathcal{L}}_{\rm S}+{\rm i}\hat{\mathcal{L}}_{\rm B})t}\hat{A} = {\rm e}^{-\frac{{\rm i}}{\hbar}(\hat{H}_{\rm S}+\hat{H}_{\rm B})t}\hat{A}{\rm e}^{\frac{{\rm i}}{\hbar}(\hat{H}_{\rm S}+\hat{H}_{\rm B})t}. \tag{32}$$

(ii) In the spherical harmonics basis $|l,m\rangle$, we can decompose:

$$\hat{u} = \sum_{l=1}^{+\infty}\hat{u}_l^+ + \hat{u}_l^- \tag{33}$$

where the components of $\hat{u}_l^+$ read

$$\hat{u}_{lx}^+ = \sum_{m=-l}^{l}\frac{1}{2}|l,m\rangle\left\{\left[\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}\right]^{1/2}\langle l-1,m+1| - \left[\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}\right]^{1/2}\langle l-1,m-1|\right\}$$
$$\hat{u}_{ly}^+ = \sum_{m=-l}^{l}-\frac{1}{2{\rm i}}|l,m\rangle\left\{\left[\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}\right]^{1/2}\langle l-1,m+1| + \left[\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}\right]^{1/2}\langle l-1,m-1|\right\}$$
$$\hat{u}_{lz}^+ = \sum_{m=-l}^{l}|l,m\rangle\left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{1/2}\langle l-1,m| \tag{34}$$

and where

$$\hat{u}_l^- = (\hat{u}_l^+)^\dagger. \tag{35}$$

(iii) The evolution of the dynamical operator $\hat{u}$ resulting from the free Hamiltonian $\hat{H}_S$ is periodic and given at time τ by

$$\hat{u}(\tau) = e^{i\hat{\mathcal{L}}_S\tau}\hat{u} = \sum_{l=1}^{+\infty} e^{i\omega_l\tau}\hat{u}_l^+ + e^{-i\omega_l\tau}\hat{u}_l^- \tag{36}$$

where

$$\omega_l = \frac{\hbar l}{I} \tag{37}$$

are the transition frequencies.

(iv) The evolution of the dynamical operator $\hat{q}_\nu$ resulting from the free Hamiltonian $\hat{H}_B$ is given at time τ by

$$\hat{q}_\nu(\tau) = e^{i\hat{\mathcal{L}}_B\tau}\hat{q}_\nu = \cos(\omega_\nu\tau)\hat{q}_\nu + \frac{\sin(\omega_\nu\tau)}{\omega_\nu}\hat{p}_\nu. \tag{38}$$

(v) Using the statistical factor of Bose–Einstein

$$N(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1} \tag{39}$$

for the boson gas, we deduce

$$\begin{aligned} &\mathrm{tr}_B(\hat{a}_\nu^+\hat{a}_{\nu'}\hat{\rho}_B^{eq}) = N(\omega_\nu)\mathbf{1}\delta_{\nu,\nu'} \\ &\mathrm{tr}_B(\hat{a}_\nu\hat{a}_{\nu'}\hat{\rho}_B^{eq}) = \mathrm{tr}_B(\hat{a}_\nu^+\hat{a}_{\nu'}^+\hat{\rho}_B^{eq}) = 0. \end{aligned} \tag{40}$$

Then using (10), we carry out the partial trace over the bath. Furthermore, making an integration by parts over t', equation (27) becomes

$$\begin{aligned} \hat{\mathcal{K}}\hat{\rho}_S(t) &= -\frac{1}{\hbar}\int_0^{+\infty} dt' \sum_\nu \frac{c_\nu^2}{\omega_\nu}\cos(\omega_\nu t')\Bigg[\hat{u}_{\cdot}, (N(\omega_\nu)+\tfrac{1}{2})[\hat{u}(-t'), \hat{\rho}_S(t)] \\ &\quad - \frac{i}{2\omega_\nu}\left[\frac{d\hat{u}(-t')}{dt'}, \hat{\rho}_S(t)\right]_+\Bigg] \end{aligned} \tag{41}$$

$$\begin{aligned} &= -\sum_\nu \frac{c_\nu^2}{2\hbar\omega_\nu}\sum_{l=1}^{+\infty}\Bigg\{\pi\delta(\omega_l-\omega_\nu)[\hat{u}_{\cdot}, (N(\omega_l)+\tfrac{1}{2})[\hat{u}_l^+ + \hat{u}_l^-, \hat{\rho}_S(t)] \\ &\quad -\tfrac{1}{2}[\hat{u}_l^+ - \hat{u}_l^-, \hat{\rho}_S(t)]_+] - i\left[\left(\frac{1}{\omega_l-\omega_\nu}\right)_p + \left(\frac{1}{\omega_l+\omega_\nu}\right)_p\right] \\ &\quad \times\left[\hat{u}_{\cdot}, (N(\omega_\nu)+\tfrac{1}{2})[\hat{u}_l^+ - \hat{u}_l^-, \hat{\rho}_S(t)] - \frac{\omega_l}{2\omega_\nu}[\hat{u}_l^+ + \hat{u}_l^-, \hat{\rho}_S(t)]_+\right]\Bigg\}. \end{aligned} \tag{42}$$

The subscript p denotes the principal value. The last expression can be simplified if the various modes of the oscillators are very close together in frequency. The sum $\sum_\nu$ in the last expression is then replaced by an integral over the continuum:

$$\int_0^{+\infty} d\omega_\nu g(\omega_\nu) \tag{43}$$

where the function $g(\omega_\nu)$ represents the spectral density of the oscillators. c_ν is replaced by the function $c(\omega_\nu)$. With these considerations defined, equation (26) becomes

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) + \frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)] = -\sum_{l=1}^{+\infty}\left\{\frac{g(\omega_l)c^2(\omega_l)}{\hbar\omega_l}\frac{\pi}{2}[\hat{\boldsymbol{u}}_\cdot, (N(\omega_l)+1)(\hat{\boldsymbol{u}}_l^-\hat{\rho}_S(t) - \hat{\rho}_S(t)\hat{\boldsymbol{u}}_l^+) + N(\omega_l)(\hat{\boldsymbol{u}}_l^+\hat{\rho}_S(t) - \hat{\rho}_S(t)\hat{\boldsymbol{u}}_l^-)] + i\int_0^{+\infty} d\omega_\nu \frac{g(\omega_\nu)c^2(\omega_\nu)\omega_l}{\hbar\omega_\nu(\omega_\nu^2-\omega_l^2)_p}\left[\hat{\boldsymbol{u}}_\cdot, (N(\omega_\nu)+\tfrac{1}{2})[\hat{\boldsymbol{u}}_l^+ - \hat{\boldsymbol{u}}_l^-, \hat{\rho}_S(t)] - \frac{\omega_l}{2\omega_\nu}[\hat{\boldsymbol{u}}_l^+ + \hat{\boldsymbol{u}}_l^-, \hat{\rho}_S(t)]_+\right]\right\}. \tag{44}$$

This expression follows an identical structure as the optical master equation derived in [11]. Let us consider the particular case when

$$\frac{\pi}{2}\frac{g(\omega_\nu)c^2(\omega_\nu)}{\omega_\nu^2} = \zeta\frac{\omega_D^2}{\omega_D^2+\omega_\nu^2}. \tag{45}$$

ζ is a friction constant which does not depend on the frequency ω_ν and ω_D is a Debye frequency giving the upper limit of the oscillators frequencies. The situation of equation (45) takes place when $c(\omega_\nu) = c$ does not depend on ω_ν and if the system of harmonic oscillators is assimilated to a gas of phonons, with wave numbers distributed uniformly inside a three-dimensional sphere whose radius is delimited by ω_D [24]. Therefore, before ω_ν has reached ω_D, the spectral density has the quadratic dependence form

$$g(\omega_\nu) = \frac{V}{2\pi^2}\frac{3}{v_s^3}\omega_\nu^2\frac{\omega_D^2}{\omega_D^2+\omega_\nu^2} \tag{46}$$

where ν_s is the sound velocity and V the volume of the gas. Thus, with (45), we can carry out the integral in (44) by transforming it into a contour integral and by determining that the various poles inside the contour are $\pm\omega_l + i0^+$, $i\omega_D$ and $2\pi i n k_B T/\hbar$, where n is a strictly positive integer. We obtain the weakly-coupled master equation associated with the rotor:

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) + \frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S(t)] = -\frac{\zeta}{I}\sum_{l=1}^{+\infty}\frac{\omega_D^2 l}{\omega_D^2+\omega_l^2}\left[\hat{\boldsymbol{u}}_\cdot, (N(\omega_l)+1)(\hat{\boldsymbol{u}}_l^-\hat{\rho}_S(t) - \hat{\rho}_S(t)\hat{\boldsymbol{u}}_l^+) + N(\omega_l)(\hat{\boldsymbol{u}}_l^+\hat{\rho}_S(t) - \hat{\rho}_S(t)\hat{\boldsymbol{u}}_l^-) + i\left(\kappa(x_l, x_D)[\hat{\boldsymbol{u}}_l^+ - \hat{\boldsymbol{u}}_l^-, \hat{\rho}_S(t)] + \frac{\omega_l}{2\omega_D}[\hat{\boldsymbol{u}}_l^+ + \hat{\boldsymbol{u}}_l^-, \hat{\rho}_S(t)]_+\right)\right] \tag{47}$$

where

$$x_l = \hbar\omega_l/(k_B T) \tag{48}$$

$$x_D = \hbar\omega_D/(k_B T) \tag{49}$$

$$\kappa(x_l, x_D) = -\left(\frac{1}{x_D} + 2\sum_{n=1}^{+\infty}\frac{x_l^2 - 2\pi n x_D}{(x_D+2\pi n)(x_l^2+(2\pi n)^2)}\right). \tag{50}$$

This equation is valid if the characteristic time τ_c from which the integral over t' gives negligible contribution is much smaller than the characteristic relaxation frequency estimated here as ζ/I (see the last term in equation (47)) [11, 16]. With the relation (45), we are able to estimate the time τ_c. Putting this relation in the expression (41) and integrating over the frequency ω_ν, we get

$$\hat{\mathcal{K}}\hat{\rho}_S(t) = -\frac{\zeta}{\hbar}\frac{k_B T}{\hbar}\int_0^{+\infty} dt' \Bigg[\hat{u}_\cdot, \Bigg(\omega_D e^{-\omega_D t'} + 2\sum_{n=1}^{+\infty} \frac{\omega_D^2}{\omega_D^2 - (2\pi n k_B T/\hbar)^2} \times \Bigg(\omega_D e^{-\omega_D t'} - \frac{2\pi n k_B T}{\hbar} e^{-(2\pi n k_B T/\hbar)t'} \Bigg)\Bigg)[\hat{u}(-t'), \hat{\rho}_S(t)] - i\omega_D e^{-\omega_D t'} \frac{\hbar}{2k_B T}\left[\frac{d\hat{u}(-t')}{dt'}, \hat{\rho}_S(t)\right]_+ \Bigg]. \tag{51}$$

The characteristic time τ_c is determined by the frequency parameter ω_D of the bath of oscillators system and by $k_B T/\hbar$. Thus, the validity criteria of the weak-coupling assumption are

$$\zeta/I \ll k_B T/\hbar \qquad \text{and} \qquad \zeta/I \ll \omega_D. \tag{52}$$

It is shown in appendix B that when the first criterion is verified, the coupling effect can be neglected for the equilibrium density matrix operator. Equation (21) is then a good approximation which is moreover a solution of (47) (see [16]).

ω_l attain mainly values around the mean angular velocity $\Omega_{\text{mean}} = (k_B T/I)^{1/2}$ for the equilibrium density matrix operator (21) (for $\hat{H}_S \sim \hbar^2 l^2/I \sim k_B T$, $\omega_l \sim \Omega_{\text{mean}}$). We expect that this does not change very much when we do not have equilibrium. This is true if the deviation from the equilibrium is slight. This must be verified *a posteriori* by an explicit evaluation of the solution of the master equation. According to the value of Ω_{mean}, we have two possible regimes.

In the first regime, Ω_{mean} has a value of the same magnitude as ζ/I. Then, we can take the two limits $k_B T/\hbar \to \infty$ and $\omega_D \to \infty$, which correspond to the classical Brownian motion limit [15] in which the dynamic evolution of the bath is much faster than that of the rotor. The master equation established from the classical Hamiltonian corresponding to (2) has been found to give, when $\omega_D \to \infty$, the FPK equation [1, 2, 4, 6, 12–15]:

$$\left[\frac{\partial}{\partial t} + \frac{\omega_\alpha}{\sin\beta}\frac{\partial}{\partial\alpha} + \omega_\beta\frac{\partial}{\partial\beta} + \cot\beta\left(\omega_\alpha^2\frac{\partial}{\partial\omega_\beta} - \omega_\alpha\omega_\beta\frac{\partial}{\partial\omega_\alpha}\right) - \frac{1}{I}\frac{\partial V_E(t)}{\partial\beta}\frac{\partial}{\partial\omega_\beta}\right]W(t) = B\left[\frac{\partial}{\partial\omega_\alpha}\left(\omega_\alpha + \frac{k_B T}{I}\frac{\partial}{\partial\omega_\alpha}\right) + \frac{\partial}{\partial\omega_\beta}\left(\omega_\beta + \frac{k_B T}{I}\frac{\partial}{\partial\omega_\beta}\right)\right]W(t) \tag{53}$$

where

$$B = \frac{\zeta}{I}. \tag{54}$$

The second limit regime takes place when

$$\Omega_{\text{mean}} \gg \zeta/I. \tag{55}$$

In this case, we can use a theorem by Davies [17, 21, 22] which states that when

(i) the spectrum of $\hat{H}_S$ is discrete; and

(ii) it exists, $\delta > 0$, such that

$$\int_0^{+\infty} dt' \left|\sum_\nu \text{tr}_B(\hat{\rho}_B^{\text{eq}}\hat{q}_\nu \cdot \hat{q}_\nu(-t'))\right|(1+t')^\delta < +\infty \tag{56}$$

then, replacing $\hat{H}_{SB}$ by $\lambda\hat{H}_{SB}$, where λ is a coupling parameter for all τ and for all reduced density matrix operator $\hat{\rho}_S$, one obtains

$$\lim_{\lambda\to 0}\sup_{0\leqslant\lambda^2 t\leqslant\tau} \|\text{tr}_B(e^{-i\hat{\mathcal{L}}t}\hat{\rho}_S\otimes\hat{\rho}_B^{\text{eq}}) - e^{(-i\hat{\mathcal{L}}_S + \lambda^2\hat{\mathcal{K}}^\natural)t}\hat{\rho}_S\| = 0 \tag{57}$$

where $\|\ldots\|$ designates the trace norm and

$$\hat{\mathcal{K}}^{\natural}\hat{\rho}_{\rm S} = \lim_{T\to+\infty}\frac{1}{2T}\int_{-T}^{+T}{\rm d}t\,{\rm e}^{{\rm i}\hat{\mathcal{L}}_{\rm S}t}\hat{\mathcal{K}}{\rm e}^{-{\rm i}\hat{\mathcal{L}}_{\rm S}t}\hat{\rho}_{\rm S}. \tag{58}$$

Both conditions (i) and (ii) are satisfied by our model. This theorem can be interpreted as follows. When λ is very small or equivalently, in terms of the physical parameters, when (55) is satisfied, we can replace $\hat{\mathcal{K}}$ by $\hat{\mathcal{K}}^{\natural}$ in the weak-coupling master equation (26). In the applications, $\hat{\mathcal{K}}^{\natural}$ is simpler to use than $\hat{\mathcal{K}}$ because of the commutation relation

$$\mathrm{i}\hat{\mathcal{L}}_{\rm S}\hat{\mathcal{K}}^{\natural} = \hat{\mathcal{K}}^{\natural}\mathrm{i}\hat{\mathcal{L}}_{\rm S} \tag{59}$$

which greatly simplifies the resolution of the newly-obtained master equation. In addition, it is shown [17] that every initial state $\hat{\rho}_{\rm S}$ preserves its positivity during its evolution and approaches the canonical equilibrium distribution as $t\to\infty$. This replacement can also be obtained by rewriting (26) in the interaction picture where $\hat{\rho}_{\rm S}(t)$ is changed into

$$\hat{\rho}_{\rm S}^{I}(t) = {\rm e}^{-{\rm i}\hat{\mathcal{L}}_{\rm S}t}\hat{\rho}_{\rm S}(t) \tag{60}$$

and by applying the Van Hove limit [18–21] to the resulting equation, that consists of tending the coupling parameter λ to zero keeping the product $\lambda^2 t$ as a constant. This limit is the mathematical analogue of the rotating wave approximation [11], used by physicists.

Let us notice that in the form (44) the imaginary part of $\hat{\mathcal{K}}$ diverges in the limit $\omega_{\rm D}\to\infty$. In the calculation of the electrical susceptibility we will see that the divergence will disappear in the two limit regimes.

3. Dielectric susceptibility derivation

The experimental dielectric behaviour of a system is often analysed by measuring the polarization $P(t)$. The steady-state response $P(t) = P(\omega){\rm e}^{{\rm i}\omega t}$ to an alternating field $E(t) = E_0{\rm e}^{{\rm i}\omega t}$ with amplitude E_0 is related to the susceptibility $\chi(\omega)$ by

$$P(\omega) = \chi(\omega)E_0. \tag{61}$$

In our model Hamiltonian, the polarization may be determined by calculating [9]

$$P(\omega) = \int_0^{+\infty}{\rm d}t'\,{\rm e}^{-{\rm i}\omega t'}\,{\rm tr}(\mu^2\hat{u}_z{\rm e}^{-{\rm i}\hat{\mathcal{L}}t'}{\rm i}\hat{\mathcal{L}}\hat{\Sigma}\hat{u}_z)E_0. \tag{62}$$

This quantity is related to the polarization $P_{\rm a}(t)$ resulting from the removal of the DC field E_0 ($E = E_0$ for $t<0$ and $E = 0$ for $t>0$):

$$P(\omega) = P(0) - {\rm i}\omega\int_0^{+\infty}{\rm d}t\,{\rm e}^{-{\rm i}\omega t}P_{\rm a}(t). \tag{63}$$

The after-effect function $P_{\rm a}(t)$ is the ensemble average value of $\cos\beta$:

$$P_{\rm a}(t) = {\rm tr}(\mu\hat{u}_z\hat{\rho}(t)) = {\rm tr}_{\rm S}(\mu\cos\beta\,\hat{\rho}_{\rm S}(t)) \tag{64}$$

where $\hat{\rho}_{\rm S}(t)$ is the solution of the master equation subject to the initial condition:

$$\hat{\rho}_{\rm S}(t=0) = \hat{\rho}_{\rm S}^{\rm eq} + {\rm tr}_{\rm B}(\hat{\Sigma}\hat{u}_z)\mu E_0. \tag{65}$$

Our aim is to calculate the dielectric susceptibility in the weak-coupling limit. For this purpose, we rewrite the susceptibility in terms of the following functions:

$$\sigma_{l,l+1}(t) = \sum_{m=-l}^{l}\langle l,m|\hat{\rho}_{\rm S}(t)\hat{u}^{+}_{l+1z}|l,m\rangle$$

$$= \sum_{m=-l}^{l} \left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} \langle l,m|\hat{\rho}_S(t)|l+1,m\rangle$$

$$\sigma_{l+1,l}(t) = \sum_{m=-l}^{l} \langle l,m|\hat{u}^-_{l+1z}\hat{\rho}_S(t)|l,m\rangle$$
$$= \sigma^*_{l,l+1}(t) \tag{66}$$

to get

$$P_a(t) = \mu \sum_{l=0}^{+\infty} (\sigma_{l+1,l}(t) + \sigma_{l,l+1}(t)). \tag{67}$$

In the weak-coupling limit, the $\sigma_{l,l+1}(t)$ are determined from the master equation. Indeed, taking the product on the right of each side of the master equation (47) with $\hat{u}^+_{l+1z}$ and taking the trace over the product, with the help of the identities

$$\hat{u}^+_l \cdot \hat{u}^-_{l'} = \delta_{l,l'} \sum_{m=-l}^{l} \frac{l}{2l+1} |l,m\rangle\langle l,m| \tag{68}$$

$$\hat{u}^-_l \cdot \hat{u}^+_{l'} = \delta_{l,l'} \sum_{m=-l+1}^{l-1} \frac{l}{2l-1} |l-1,m\rangle\langle l-1,m| \tag{69}$$

$$\hat{u}^+_l \cdot \hat{u}^+_{l'} = 0 \tag{70}$$

$$\hat{u}^-_l \cdot \hat{u}^-_{l'} = 0 \tag{71}$$

$$\sum_{m=-l}^{l} \langle l,m|\hat{u}^-_{l+1} \cdot \hat{\rho}_S(t)\hat{u}^+_{l+2}\hat{u}^+_{l+1z}|l,m\rangle = \frac{l+1}{2l+3}\sigma_{l+1,l+2}(t) \tag{72}$$

$$\sum_{m=-l}^{l} \langle l,m|\hat{u}^-_{l+1} \cdot \hat{\rho}_S(t)\hat{u}^-_{l+1}\hat{u}^+_{l+1z}|l,m\rangle = \frac{1}{(2l+1)(2l+3)}\sigma_{l+1,l}(t) \tag{73}$$

$$\sum_{m=-l}^{l} \langle l,m|\hat{u}^+_l \cdot \hat{\rho}_S(t)\hat{u}^+_{l+2}\hat{u}^+_{l+1z}|l,m\rangle = 0 \tag{74}$$

$$\sum_{m=-l}^{l} \langle l,m|\hat{u}^+_l \cdot \hat{\rho}_S(t)\hat{u}^-_{l+1}\hat{u}^+_{l+1z}|l,m\rangle = \frac{l+1}{2l+1}\sigma_{l-1,l}(t) \tag{75}$$

we get the closed system of equations for the $\sigma_{l,l+1}(t)$ and $\sigma_{l+1,l}(t)$:

$$\begin{aligned}\left[\frac{\partial}{\partial t} - i\omega_{l+1}\right]\sigma_{l,l+1}(t) = -\frac{\zeta}{I}\Bigg\{\Bigg[l^2\frac{A^*_l}{2l+1} + (l+1)^2\left(\frac{A_{l+1}}{2l+3} + \frac{B_{l+1}}{2l+1}\right)\\ +(l+2)^2\frac{B^*_{l+2}}{2l+3}\Bigg]\sigma_{l,l+1}(t) - \frac{(l+1)(A^*_{l+1}+B^*_{l+1})}{(2l+1)(2l+3)}\sigma_{l+1,l}(t)\\ -[(l+1)A^*_{l+1} + (l+2)A_{l+2}]\frac{l+1}{2l+3}\sigma_{l+1,l+2}(t)\\ -(1-\delta_{l,0})[lB_l + (l+1)B^*_{l+1}]\frac{l+1}{2l+1}\sigma_{l-1,l}(t)\Bigg\}\end{aligned} \tag{76}$$

with

$$A_{l+1} = \frac{\omega_D^2}{\omega_D^2 + \omega_{l+1}^2}\left[1 + N(\omega_{l+1}) + i\left(\kappa(x_{l+1}, x_D) - \frac{\omega_{l+1}}{2\omega_D}\right)\right]$$

$$B_{l+1} = \frac{\omega_D^2}{\omega_D^2 + \omega_{l+1}^2} \left[N(\omega_{l+1}) + \mathrm{i} \left(\kappa(x_{l+1}, x_D) + \frac{\omega_{l+1}}{2\omega_D} \right) \right] \tag{77}$$

and the initial conditions

$$\sigma_{l,l+1}(t=0) = \frac{I\mu E_0}{3\hbar^2} \frac{\exp[-l(l+1)\hbar^2/(2Ik_BT)] - \exp[-(l+1)(l+2)\hbar^2/(2Ik_BT)]}{\sum_{l'=0}^{+\infty}(2l'+1)\exp[-l'(l'+1)\hbar^2/(2Ik_BT)]}. \tag{78}$$

These initial conditions allow the computation of the static polarization:

$$P(0) = \mu \sum_{l=0}^{+\infty} (\sigma_{l,l+1}(t=0) + \sigma_{l+1,l}(t=0)). \tag{79}$$

Two limit regimes are of particular interest in this model: the classical Brownian limit and the rotating wave approximation limit.

3.1. The classical Brownian limit

In the classical Brownian limit [15, 17], $\hbar \to 0$ and the dynamics of the bath is much faster than the dynamics of the rotator. The frequency $\hbar/I$ is much smaller than the average angular velocity Ω_{mean} which in turn is much smaller than the typical oscillator frequency oscillators ω_D. Mathematically, this amounts to taking the ratio limits

$$\frac{\hbar}{I\Omega_{\text{mean}}} \to 0 \qquad \frac{\Omega_{\text{mean}}}{\omega_D} \to 0. \tag{80}$$

Classically, the angular velocity is set as the continued variable

$$\omega_l \to \Omega \tag{81}$$

or written in dimensionless form:

$$x = \frac{I\Omega^2}{2k_BT}. \tag{82}$$

In order to have a non-zero Ω we must also impose the limit $l \to \infty$. Moreover, setting as the new classical function

$$\sigma_{l-1,l}(t) \to \hbar\mathcal{U}(x,t) \tag{83}$$

and taking into account that in the classical Brownian regime finite difference becomes a derivative as

$$\frac{Ik_BT(\sigma_{l,l+1}(t) - \sigma_{l-1,l}(t))}{\hbar^2 l} \to \hbar \frac{\partial\mathcal{U}(x,t)}{\partial x} \tag{84}$$

the evolution equation (76) becomes in this limit

$$\left[\frac{\partial}{\partial t} - \mathrm{i}\Omega_{\text{mean}}\sqrt{2x}\right]\mathcal{U}(x,t) = B\left\{\left[2x\frac{\partial^2}{\partial x^2} + 2x\frac{\partial}{\partial x} + 1\right]\mathcal{U}(x,t) + \frac{1}{4x}(\mathcal{U}^*(x,t) + \mathcal{U}(x,t))\right\}. \tag{85}$$

If we make the substitution

$$\mathcal{U}(x,t) = \tfrac{1}{3}\sqrt{\frac{x}{2Ik_BT}}\mathrm{e}^{-x}(\chi_1(x,t) + \mathrm{i}\Omega_{\text{mean}}\sqrt{2x}\chi_2(x,t)) \tag{86}$$

we recover the system (24) and (25) deduced by Kalmykov *et al* [12] and by the authors [6, 13, 14]. The polarization is given by the Sack's continued fraction [23]:

$$P(\omega) = \frac{\mu^2 E_0}{3k_B T}(1 - \cfrac{i\omega'}{i\omega' + \cfrac{2\gamma}{1 + i\omega' + \cfrac{2\gamma}{2 + i\omega' + \cfrac{4\gamma}{3 + i\omega' + \cfrac{4\gamma}{4 + i\omega' + \cfrac{6\gamma}{5 + i\omega' + \cdots)}}}}}} \tag{87}$$

where

$$\gamma = \frac{I k_B T}{\zeta^2} \tag{88}$$

and

$$\omega' = \frac{I\omega}{\zeta}. \tag{89}$$

3.2. Rotating wave approximation limit

In this case, the off-diagonal terms in (76) are neglected and the master equation becomes

$$\left[\frac{\partial}{\partial t} - i(\omega_{l+1} + \Delta\omega_{l+1}) + \Gamma_{l+1}\right]\sigma_{l,l+1}(t) = 0 \tag{90}$$

where we define the frequency shifts:

$$\begin{aligned}\Delta\omega_{l+1} = -\frac{\zeta}{I}\bigg[&\frac{\omega_D^2}{\omega_D^2+\omega_{l+1}^2}(l+1)^2\bigg(\frac{\kappa(x_{l+1},x_D)+(\omega_{l+1}/2\omega_D)}{2l+1}\\ &+\frac{\kappa(x_{l+1},x_D)-(\omega_{l+1}/2\omega_D)}{2l+3}\bigg) - \frac{\omega_D^2}{\omega_D^2+\omega_l^2}(\kappa(x_l,x_D)-(\omega_l/2\omega_D))\frac{l^2}{2l+1}\\ &-\frac{\omega_D^2}{\omega_D^2+\omega_{l+2}^2}(\kappa(x_{l+2},x_D)+(\omega_{l+2}/2\omega_D))\frac{(l+2)^2}{2l+3}\bigg]\end{aligned} \tag{91}$$

and the positive half-widths:

$$\begin{aligned}\Gamma_{l+1} = \frac{\zeta}{I}\bigg[&\frac{\omega_D^2}{\omega_D^2+\omega_l^2}l^2\frac{1+N(\omega_l)}{2l+1} + \frac{\omega_D^2}{\omega_D^2+\omega_{l+1}^2}(l+1)^2\left(\frac{1+N(\omega_{l+1})}{2l+3}+\frac{N(\omega_{l+1})}{2l+1}\right)\\ &+\frac{\omega_D^2}{\omega_D^2+\omega_{l+2}^2}(l+2)^2\frac{N(\omega_{l+2})}{2l+3}\bigg] \geqslant 0.\end{aligned} \tag{92}$$

For very high ω_D, we can take the limit

$$\frac{\omega_D}{\omega_l} \to \infty \qquad \frac{\hbar\omega_D}{k_B T} \to \infty \tag{93}$$

in the previous expressions to obtain

$$\begin{aligned}\Delta\omega_{l+1} &= -2\frac{\zeta}{I}\sum_{n=1}^{+\infty}\frac{(2\pi n)^3(x_{l+2}^2 - x_l^2)}{(x_l^2+(2\pi n)^2)(x_{l+1}^2+(2\pi n)^2)(x_{l+2}^2+(2\pi n)^2)}\\ &= \frac{\zeta}{I}\frac{2(l+1)}{\pi}\bigg\{-\frac{l^2}{(2l+1)(4l+4)}[\Psi(1+ix_l/(2\pi))+\Psi(1-ix_l/(2\pi))]\end{aligned}$$

$$+\frac{(l+1)^2}{(2l+1)(2l+3)}[\Psi(1+\mathrm{i}x_{l+1}/(2\pi))+\Psi(1-\mathrm{i}x_{l+1}l/(2\pi))]$$

$$-\frac{(l+2)^2}{(2l+3)(4l+4)}[\Psi(1+\mathrm{i}x_{l+2}/(2\pi))+\Psi(1-\mathrm{i}x_{l+2}/(2\pi))]\Bigg\} \quad (94)$$

$$\Gamma_{l+1}=\frac{\zeta}{I}\left[l^2\frac{1+N(\omega_l)}{2l+1}+(l+1)^2\left(\frac{1+N(\omega_{l+1})}{2l+3}+\frac{N(\omega_{l+1})}{2l+1}\right)+(l+2)^2\frac{N(\omega_{l+2})}{2l+3}\right] \quad (95)$$

where

$$\Psi(u)=\frac{\mathrm{d}\ln\Gamma(u)}{\mathrm{d}u} \quad (96)$$

is the derivative of the logarithm of the factorial gamma function $\Gamma(u)$. Solving the differential equation (90), the susceptibility becomes

$$\chi(\omega)=\sum_{l=0}^{+\infty}\left[\frac{\mathrm{i}(\omega_{l+1}+\Delta\omega_{l+1})+\Gamma_{l+1}}{\mathrm{i}\omega+\mathrm{i}(\omega_{l+1}+\Delta\omega_{l+1})+\Gamma_{l+1}}+\frac{-\mathrm{i}(\omega_{l+1}+\Delta\omega_{l+1})+\Gamma_{l+1}}{\mathrm{i}\omega-\mathrm{i}(\omega_{l+1}+\Delta\omega_{l+1})+\Gamma_{l+1}}\right]$$
$$\times\frac{I\mu^2}{3\hbar^2}\frac{\exp[-l(l+1)\hbar^2/(2Ik_BT)]-\exp[-(l+1)(l+2)\hbar^2/(2Ik_BT)]}{\sum_{l'=0}^{+\infty}(2l'+1)\exp[-l'(l'+1)\hbar^2/(2Ik_BT)]}. \quad (97)$$

Figure 1 shows the real and imaginary parts of the reduced susceptibility

$$\chi_{\mathrm{r,st}}(\tilde{\omega})=\frac{\chi(\omega)}{\chi(0)}=\chi'_{\mathrm{r,st}}(\tilde{\omega})-\mathrm{i}\chi''_{\mathrm{r,st}}(\tilde{\omega}) \quad (98)$$

against the dimensionless frequency

$$\tilde{\omega}=\frac{I\omega}{\hbar} \quad (99)$$

for the values of dimensionless parameters $\zeta/(I\Omega_{\mathrm{mean}})=0.001$ and $\hbar^2/(Ik_BT)=0.05$ and $x_D\to\infty$. The curves show the rotational lines caused by the important absorption near the resonance frequencies ω_l. In figures 2 and 3, we have represented the evolution of the reduced half-widths Γ_l and the frequency shifts $\Delta\omega_l$ divided by B against the quantum number l for $\hbar^2/(Ik_BT)=0.05$. The half-widths do not change appreciably with l, while the frequency shifts are negligible compared to the corresponding resonance frequencies. The loss factor corresponding to the imaginary part is positive as a consequence of the positivity of the Γ_l in (97).

4. Conclusions

From a pure quantum Hamiltonian model, we analytically calculated the electrical susceptibility. The effect of the interaction of the bath on the rotor has not been obtained phenomenologically but as a logical deduction of the weak-coupling limit. Although this model is a very simplified scheme, it provides a method for calculating the relaxation frequency ζ/I, the half-widths Γ_l and the frequency shifts $\Delta\omega_l$ in terms of the physical characteristics of the bath and of the interaction form between the bath and the rotor.

The quantum result (97) for the susceptibility is rigorous as it is based on the application of a pure mathematical theorem by Davies. This theorem provides a method for obtaining a well established master equation that corresponds in physics to the so-called rotating wave approximation (RWA).

The assumptions (52) on the values of the parameters of the model are strong constraints for the model. Indeed, in the first regime the time evolution of the rotor must be slow

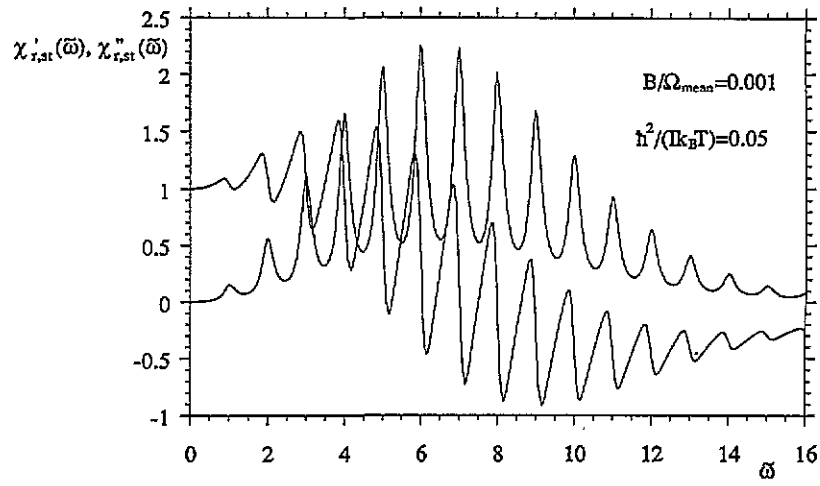

Figure 1. Normalized dispersion plots of the real and imaginary components, $\chi'_{r,st}(\bar{\omega})$ and $\chi''_{r,st}(\bar{\omega})$ of the complex susceptibility against the reduced frequency $\bar{\omega}$ for $\hbar^2/(Ik_BT) = 0.05$ and $B/\Omega_{mean} = 0.001$.

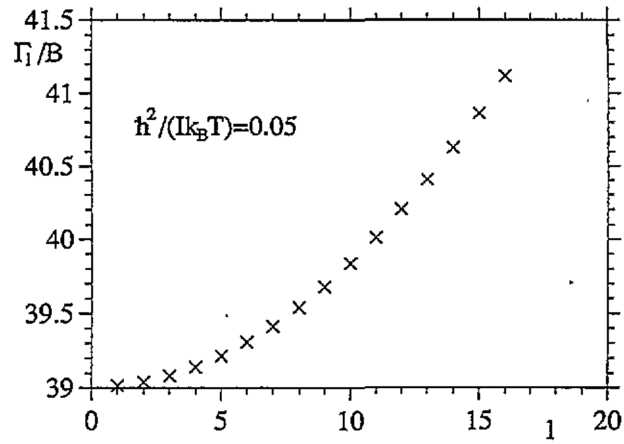

Figure 2. Plot of the half-widths Γ_l/B against the quantum number l for $\hbar^2/(Ik_BT) = 0.05$.

enough compared to the time evolution of the thermal bath, while in the second regime the half-widths and the frequency shifts must be much shorter than the transition frequencies. Furthermore, it must be noted that the classical limit $\hbar \to 0$ is valid in (92) only when the friction coefficient is zero, otherwise the half-widths would diverge. Thus, the Van Hove limit is well adapted only in the quantum formulation of the model.

In a model, such as the 'shish-kebab' model [3, 6, 15], we expect that a similar weakly-coupled master equation can be deduced, even if we have to deal with more complicated forms of interaction coupling and thermal bath.

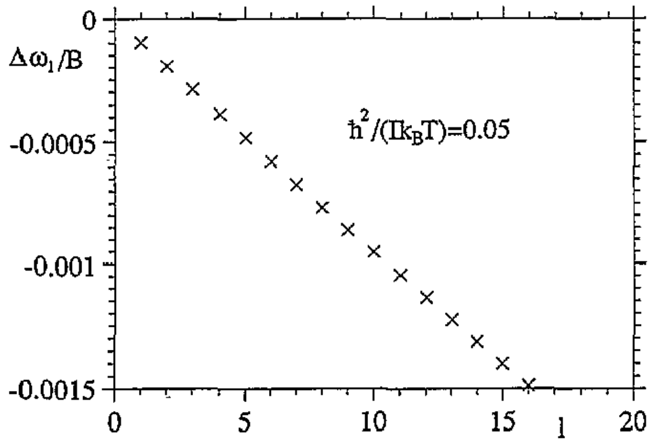

Figure 3. Plot of the frequency shifts $\Delta\omega_l/B$ against the quantum number l for $\hbar^2/(Ik_\mathrm{B}T) = 0.05$.

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Appendix A

The expression in equation (27) can be computed with the aid of the notation (29) and (30) as follows:

$$\begin{aligned}\hat{\mathcal{K}}\hat{\rho}_\mathrm{S}(t) &= \mathrm{tr}_\mathrm{B}\left[\int_0^{+\infty} \mathrm{d}t'\, \mathrm{i}\hat{\mathcal{L}}_\mathrm{SB}\mathrm{e}^{-(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\mathrm{i}\hat{\mathcal{L}}_\mathrm{SB}\hat{\Sigma}^{(0)}\mathrm{e}^{(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\hat{\Sigma}_\mathrm{S}^{-1}\hat{\rho}_\mathrm{S}(t)\right]\\
&= \mathrm{tr}_\mathrm{B}\left\{\int_0^{+\infty} \mathrm{d}t'\, \mathrm{i}\hat{\mathcal{L}}_\mathrm{SB}\mathrm{e}^{-(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\frac{\mathrm{i}}{\hbar}\frac{1}{k_\mathrm{B}T\,\mathrm{tr}(\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})/(k_\mathrm{B}T)})}\right.\\
&\quad\times\int_0^1 \mathrm{d}s\Big[[\hat{H}_\mathrm{SB},\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})s/(k_\mathrm{B}T)}](\mathrm{e}^{(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\hat{\Sigma}_\mathrm{S}^{-1}\hat{\rho}_\mathrm{S}(t))\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})(1-s)/(k_\mathrm{B}T)}\\
&\quad+\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})s/(k_\mathrm{B}T)}(\mathrm{e}^{(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\hat{\Sigma}_\mathrm{S}^{-1}\hat{\rho}_\mathrm{S}(t))[\hat{H}_\mathrm{SB},\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})(1-s)/(k_\mathrm{B}T)}]\\
&\quad\left.+\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})s/(k_\mathrm{B}T)}[\hat{H}_\mathrm{SB},(\mathrm{e}^{(\mathrm{i}\hat{\mathcal{L}}_\mathrm{S}+\mathrm{i}\hat{\mathcal{L}}_\mathrm{B})t'}\hat{\Sigma}_\mathrm{S}^{-1}\hat{\rho}_\mathrm{S}(t))]\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})(1-s)/(k_\mathrm{B}T)}\Big]\right\}. \qquad (100)\end{aligned}$$

Using the property

$$\begin{aligned}[\hat{H}_\mathrm{SB},\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})s/(k_\mathrm{B}T)}] &= -\frac{s}{k_\mathrm{B}T}\int_0^1 \mathrm{d}s'\,\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})ss'/(k_\mathrm{B}T)}[\hat{H}_\mathrm{SB},\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B}]\\
&\quad\times\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})s(1-s')/(k_\mathrm{B}T)} \qquad (101)\end{aligned}$$

we get after handling

$$\hat{\mathcal{K}}\hat{\rho}_\mathrm{S}(t) = -\,\mathrm{tr}_\mathrm{B}\left\{\int_0^{+\infty}\mathrm{d}t'\,\mathrm{i}\hat{\mathcal{L}}_\mathrm{SB}\frac{1}{k_\mathrm{B}T\,\mathrm{tr}(\mathrm{e}^{-(\hat{H}_\mathrm{S}+\hat{H}_\mathrm{B})/(k_\mathrm{B}T)})}\int_0^1\mathrm{d}s\,s\right.$$

$$\times\left[\int_0^1 \mathrm{d}s'\,\mathrm{e}^{-(\hat H_S+\hat H_B)s's/(k_BT)}\frac{1}{k_BT}\frac{\mathrm{d}}{\mathrm{d}t'}(\mathrm{e}^{-(\mathrm{i}\hat{\mathcal{L}}_S+\mathrm{i}\hat{\mathcal{L}}_B)t'}\hat H_{SB})\right.$$
$$\times\mathrm{e}^{-(\hat H_S+\hat H_B)(1-s')s/(k_BT)}\hat\Sigma_S^{-1}\hat\rho_S(t)\mathrm{e}^{-(\hat H_S+\hat H_B)(1-s)/(k_BT)}$$
$$+\mathrm{e}^{-(\hat H_S+\hat H_B)s/(k_BT)}\hat\Sigma_S^{-1}\hat\rho_S(t)\int_0^1 \mathrm{d}s'\,\mathrm{e}^{-(\hat H_S+\hat H_B)s'(1-s)/(k_BT)}$$
$$\left.\left.\times\frac{1}{k_BT}\frac{\mathrm{d}}{\mathrm{d}t'}(\mathrm{e}^{-(\mathrm{i}\hat{\mathcal{L}}_S+\mathrm{i}\hat{\mathcal{L}}_B)t'}\hat H_{SB})\mathrm{e}^{-(\hat H_S+\hat H_B)(1-s')(1-s)/(k_BT)}\right]\right\}$$
$$+\,\mathrm{tr}_B\left[\int_0^{+\infty}\mathrm{d}t'\,\mathrm{i}\hat{\mathcal{L}}_{SB}\mathrm{e}^{-(\mathrm{i}\hat{\mathcal{L}}_S+\mathrm{i}\hat{\mathcal{L}}_B)t'}\hat\Sigma^{(0)}(\mathrm{i}\hat{\mathcal{L}}_{SB}\hat\Sigma_S^{-1}\mathrm{e}^{\mathrm{i}\hat{\mathcal{L}}_St'}\hat\rho_S(t))\right] \qquad (102)$$

which allows the recovery of (28) after integrating the first term over t'.

Appendix B

To estimate the effect of the interaction on the equilibrium density matrix operator, we compute $\mathrm{tr}_B[\exp(-\hat H/(k_BT))]$ until the second order in the interaction. For that, we first develop the exponential operator to get

$$\mathrm{e}^{-(\hat H_S+\hat H_B+\hat H_{SB})/(k_BT)} \cong \mathrm{e}^{-(\hat H_S+\hat H_B)/(k_BT)} - \int_0^1 \mathrm{d}s\,\mathrm{e}^{-(\hat H_S+\hat H_B)(1-s)/(k_BT)}\frac{\hat H_{SB}}{k_BT}\mathrm{e}^{-(\hat H_S+\hat H_B)s/(k_BT)}$$
$$+\int_0^1\mathrm{d}s\int_0^1\mathrm{d}s'\,s\,\mathrm{e}^{-(\hat H_S+\hat H_B)(1-s)/(k_BT)}\frac{\hat H_{SB}}{k_BT}\mathrm{e}^{-(\hat H_S+\hat H_B)ss'/(k_BT)}$$
$$\times\frac{\hat H_{SB}}{k_BT}\mathrm{e}^{-(\hat H_S+\hat H_B)s(1-s')/(k_BT)}+\mathrm{O}\left(\frac{\hat H_{SB}}{k_BT}\right)^3. \qquad (103)$$

After calculations similar to those performed to obtain (44), and after using the formulae (38)–(40) and (68)–(71), the trace over the bath gives

$$\mathrm{tr}_B[\mathrm{e}^{-\hat H/(k_BT)}] \cong \mathrm{e}^{-\hat H_S/(k_BT)}\,\mathrm{tr}_B[\mathrm{e}^{-\hat H_B/(k_BT)}]$$
$$\times\left\{1+\frac{\zeta}{\pi\hbar}\int_0^1\mathrm{d}s\int_0^1\mathrm{d}s'\,s\int_{-\infty}^{+\infty}\mathrm{d}x\,x\frac{x_D^2}{x_D^2+x^2}\frac{\mathrm{e}^{xss'}}{\mathrm{e}^x-1}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}|l,m\rangle\right.$$
$$\left.\times\left[\frac{l\mathrm{e}^{x_lss'}+(l+1)\mathrm{e}^{-x_{l+1}ss'}}{2l+1}\right]\langle l,m|+\mathrm{O}\left(\frac{\hat H_{SB}}{k_BT}\right)^3\right\}. \qquad (104)$$

This last expression allows the verification that the second-order term in $\hat\rho_S^{eq}$ is of order $\zeta x_l/\hbar \sim \zeta\hbar/(Ik_BT)$ and shows that in the limit where $\zeta/I \ll k_BT/\hbar$ the effect of the interaction can be neglected.

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