

MODIFIED LANGEVIN FUNCTIONS FOR NEW BIREFRINGENCE EFFECTS IN MOLECULAR LIQUIDS

M.W. EVANS

Dept. of Physics, University of Lancaster, Lancaster, U.K.

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ABSTRACT

New types of Langevin function are developed for the analytical description of birefringence and anisotropy effects discovered recently by supercomputer simulation of molecular liquids. These include Langevin and Kielich functions for birefringence induced by a circularly polarised laser field, and for electric field induced anisotropy in the centre of mass diffusion of an asymmetric top in three dimensions.

INTRODUCTION

Recent supercomputer simulation of molecular diffusion, including that of liquid water, has revealed the existence of several new birefringence phenomena which appear as the result of applying various types of external force fields. [1-5] These include first order birefringence due to a circularly polarised laser field [1,2] and anisotropy [3] in the centre of mass linear velocity auto-correlation function (a.c.f.) caused by a static uniaxial electric field \underline{E} . The development of such effects needs supercomputer simulation for an explanation and description because the conventional theory [6-12] of molecular diffusion processes is inadequate for combined molecular rotation and translation. However, it is possible to develop a theory for the new types of Langevin function implied by the simulation results, and this is the subject of this paper.

Langevin functions [13] are developed for the alignment of molecular dipoles, $\underline{\mu}$, caused by a circularly polarised laser field of frequency ω . Expressions are provided for field dependent alignment in the x and y axes of a field whose axis is in the z axis of the laboratory frame (x,y,z). The anisotropy recently observed by supercomputer simulation in the centre of mass linear velocity a.c.f. due to a simple z axis external electric field \underline{E} is treated in terms of a basic assumption that the equilibrium distribution

function at field on equilibrium is a bi-dimensional normal distribution [14] in the rotational energy of the applied field, $\underline{\mu} \cdot \underline{E}$, and the excess kinetic energy induced by the field in axis z of frame (x,y,z). The resulting Langevin function is one of field strength and also of the excess kinetic energy induced in the molecular liquid by the cross correlation between molecular rotational and translation diffusion processes.

THEORY

Birefringence Induced by a Circularly Polarised Laser Field

The birefringence in the supercomputer simulation was induced by a circularly polarised field of the type:

$$\underline{E} = E_0 (\underline{i} \cos(\omega t) + \underline{j} \sin(\omega t)) \quad (1)$$

where \underline{i} is a unit vector in axis x and \underline{j} in axis y of the laboratory frame (x,y,z). Here E_0 is the electric field strength of the electromagnetic field and ω the frequency. This is assumed in the simulation to interact with the molecular dipole moment through the time (t) dependent torque

$$\underline{T}_q = -\underline{\mu} \times \underline{E} \quad (2)$$

generating the interaction potential energy

$$V = -\mu E \cos\theta. \quad (3)$$

The probability of finding a dipole moment in a direction between θ and $\theta+d\theta$ with \underline{E} is given by

$$\exp\left(\frac{\mu E}{kT} \cos \theta\right) d(\cos \theta) / \int_{-1}^1 \exp\left(\frac{\mu E}{kT} \cos \theta\right) d(\cos \theta) \quad (4)$$

and the thermodynamic average $\langle \underline{\mu} \cdot \underline{E} \rangle$ is:

$$\langle \underline{\mu} \cdot \underline{E} \rangle = \frac{\int_{-1}^1 \mu \cdot \underline{E} \exp\left(\frac{\mu E}{kT} \cos \theta\right) d(\cos \theta)}{\int_{-1}^1 \exp\left(\frac{\mu E}{kT} \cos \theta\right) d(\cos \theta)} \quad (5)$$

providing the Langevin functions

$$L(a) = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \quad (6)$$

in direction x of frame (x,y,z) and

$$L_1(b) = \frac{e^b + e^{-b}}{e^b - e^{-b}} - \frac{1}{b} \quad (7)$$

in direction y. Here

$$a = \frac{\mu E_0}{kT} \cos \omega t \quad (8)$$

and

$$b = \frac{\mu E_0}{kT} \sin \omega t \quad (9)$$

It is clear from the structures of eqns (6) and (7) that the degree of alignment depends on the usual Langevin argument $\mu E/kT$ and on the field frequency, ω and periodicity. Equivalent results for first order alignment by the magnetic component of the electromagnetic field are also obtainable, as well as for higher order alignment effects proportional to $\langle \cos^n \theta \rangle$, where n is a positive integer. The results for Langevin functions [15,16] of order 2 to 6 are

$$\begin{aligned} L_2(a) &= 1 - \frac{2 L_1(a)}{a} \quad ; \\ L_3(a) &= \coth(a) - \frac{3}{2} L_2(a) \quad ; \\ L_4(a) &= 1 - \frac{4}{a} L_3(a) \quad ; \\ L_5(a) &= \coth(a) - \frac{5}{a} L_4(a) \quad ; \\ L_6(a) &= 1 - \frac{6}{a} L_5(a) \quad ; \end{aligned} \quad (10)$$

with equivalent expressions for functions in the y axis involving a substituted by b.

More generally the electromagnetic field interacts with the diffusing molecule through the torque

$$\underline{T}_q^{(m)} = - \underline{\mu} \times \underline{m} \quad , \quad (11)$$

where \underline{m} is expanded as the series

$$\underline{m} = \underline{\mu} + \underline{\alpha} \cdot \underline{E} + \frac{1}{2} \underline{\beta} : \underline{EE} + \frac{1}{6} \underline{\gamma} : \underline{EEE} \quad (12)$$

where $\underline{\alpha}$ is the molecular polarisability, $\underline{\beta}$ the hyper-polarisability and so on. Each of the terms in this expansion generates its equivalent Langevin function. For the torque

$$T_{-q}^{(\alpha)} = \underline{\alpha} \cdot \underline{E} \times \underline{E} \quad (13)$$

for example the equivalent energy is

$$q_i = (\alpha E_0^2) \cos^2 \omega t / (2kT) \quad (14)$$

For this type of torque, the odd order Langevin functions disappear for all field strengths E, i.e.

$$L_1^{(\alpha)} = L_3^{(\alpha)} = L_5^{(\alpha)} = \dots = 0 \quad (15)$$

but the even order Langevin functions exist and are given [13,15,16] in axis x by

$$L_2^{(\alpha)}(\pm q_i) = \frac{1}{2q_i} \pm \frac{1}{2q_i^{1/2} I(\pm q_i)} \quad (16)$$

(to second order). Here

$$I(\pm q_i) = e^{\mp q_i} \int_0^{q_i^{1/2} \pm x^2} e^{-x^2} dx \quad (17)$$

with an equivalent expression in axis y with energy

$$q_j = (\alpha E_0^2) \sin^2 \omega t / (2kT) \quad (18)$$

These analytical results fully confirm the effects found in the computer simulation, [3] i.e. birefringence in axes x and y for a z axis circularly polarised applied field of type (1). These effects could be observed experimentally in principle with strong laser fields and optical Kerr effect apparatus adapted for this purpose. Further computer simulations should aim at a detailed numerical evaluation of the experimental and analytical results, as a function of field strength and frequency.

ANISOTROPY IN THE LINEAR CENTRE OF MASS VELOCITY A.C.F. INDUCED BY A STATIC ELECTRIC FIELD

This is a more subtle effect which relies for its existence on the statistical cross correlation between molecular rotational and translational diffusion. It was recently discovered [3] by supercomputer simulation and is

numerical evidence for the existence of these cross correlations. The existence of the anisotropy implies that the fundamental theory of the Langevin function for the application of a static electric field to a molecular liquid should be extended to involve these new cross correlations.

At field on equilibrium, the supercomputer simulations show that the z component of the centre of mass velocity a.c.f. has a different time dependence from those of the x and y components, which are identical. The applied electric field therefore imparts through the torque the additional kinetic energy

$$K_{\text{trans}} = \frac{1}{2} m (v_z - \langle v_z^2 \rangle_{E=0}^{\frac{1}{2}})^2 \quad (19)$$

where $\frac{1}{2} m \langle v_z^2 \rangle_{E=0}^{\frac{1}{2}}$ is the root mean square kinetic energy in axis z at field off equilibrium ($E = 0$). There is therefore a finite statistical cross correlation function at equilibrium in the presence of the electric field between the rotational potential energy $-\mu \cdot E$ imparted by the field and the additional translational kinetic energy. At field on equilibrium there therefore exists a binormal Gaussian distribution function [14] of the form

$$f(X, Y) = \frac{1}{\{2\pi(1-\tau^2)\sigma_x\sigma_y\}^{\frac{1}{2}}} \exp \left[-\frac{1}{2(1-\tau^2)} \left(\frac{X^2}{\sigma_x^2} - \frac{2\tau XY}{\sigma_x\sigma_y} + \frac{Y^2}{\sigma_y^2} \right) \right] \quad (20)$$

with

$$\frac{X^2}{\sigma_x^2} \equiv -\frac{\mu E}{kT} \cos \theta \quad (21)$$

and

$$\frac{Y^2}{\sigma_y^2} \equiv \frac{1}{2} m (v_z - \langle v_z^2 \rangle_{E=0}^{\frac{1}{2}})^2 \quad (22)$$

Here τ is the correlation function between the square root of the field induced rotational energy, $-\mu \cdot E$, and the square root of the excess z axis kinetic energy:

$$\tau \equiv \frac{1}{\sqrt{2}} - (\mu \cdot E)^{\frac{1}{2}} m^{\frac{1}{2}} (\langle v_z^2 \rangle_{E=0}^{\frac{1}{2}}) \Big|_{E \neq 0} \quad (23)$$

which results in the anisotropy induced by the electric field.

Denoting:

$$A \equiv \frac{\mu E}{2kT} / (1 - \tau^2) \quad ; \quad y \equiv v_z - \langle v_z^2 \rangle_{E=0}^{\frac{1}{2}}$$

$$B \equiv \frac{m}{4kT} / (1 - \tau^2) \quad ; \quad x \equiv \cos \theta, \quad (24)$$

$$D \equiv \frac{(\mu E)^{\frac{1}{2}} m^{\frac{1}{2}} \tau}{2^{\frac{1}{2}} kT (1 - \tau^2)} \quad ;$$

we have the averages at field - on equilibrium

$$\langle \underline{\mu} \cdot \underline{E} \rangle = \mu E \frac{\int_0^1 \int_0^\infty x \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx}{\int_0^1 \int_0^\infty \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx} \quad (25)$$

$$\langle \frac{1}{2} m y^2 \rangle = \frac{1}{2} m \frac{\int_0^1 \int_0^\infty y^2 \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx}{\int_0^1 \int_0^\infty \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx} \quad (26)$$

and the mixed average

$$\frac{1}{2} m \langle \underline{\mu} \cdot \underline{E} y^2 \rangle = \frac{1}{2} m \mu \cdot \underline{E} \frac{\int_0^1 \int_0^\infty xy^2 \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx}{\int_0^1 \int_0^\infty \exp(Ax - By - Dx^{\frac{1}{2}} y^{\frac{1}{2}}) dy dx} \quad (27)$$

The "classical" Langevin function, $\langle \underline{\mu} \cdot \underline{E} \rangle$ is therefore modified by the supercomputer observation of electric field induced translational anisotropy. Working out the integrals in this new expression for the Langevin function gives the ratio of series

$$\langle \underline{\mu} \cdot \underline{E} \rangle = \mu E \frac{\int_0^1 e^{Ax} \left(\frac{x^{\frac{1}{2}}}{D} - \frac{2!B}{D^3 x^{\frac{1}{2}}} + \frac{4!}{2!} \frac{B^2}{D^5 x^{3/2}} - \dots \right) dx}{\int_0^1 e^{Ax} \left(\frac{1}{x^{\frac{1}{2}} D} - \frac{2!B}{D^3 x^{3/2}} + \frac{4!}{2!} \frac{B^2}{D^5 x^{5/2}} - \dots \right) dx} \quad (28)$$

which shows that when the electrical field \underline{E} vanishes, the Langevin function vanishes, and as the applied electric field \underline{E} goes to infinity the Langevin function approaches a value dominated by the exponential term e^{Ax} in the numerator and denominator of eqn (28), i.e. a value at saturation identical with the classical result. In the intermediate field strength

region, however, the dependence of the classical Langevin function on \underline{E} is different from that in the absence of statistical cross correlation defined by the finite value of τ in eqn (23). This result is independent of field strength and shows that the accepted theory of birefringence phenomena such as the Kerr effect must be modified to take into account the statistically finite value of τ . Clearly, the accepted theory of the Kerr effect [6] prior to the discovery [3] of electric field induced translational anisotropy was implicitly based on the assumption $\tau = 0$.

DISCUSSION

The results in eqns (25) to (28) show clearly that the accepted Langevin function of traditional dielectric theory [6-12] is a simplification of the overall rise transient process, the field-on equilibrium level of which is determined by a result such as eqn (28). This shows that the final level of the rise transient induced by an external electric field is dependent not only on the electric field strength \underline{E} and molecular dipole moment, $\underline{\mu}$, but also on the molecular mass, m , and the field-on equilibrium correlation function, τ , of the assumed bidimensional Gaussian distribution. This result, suggested by the observation of translational anisotropy in a recent supercomputer simulation [3], is a direct consequence of the assumption that the applied field-induced potential energy, $-\underline{\mu} \cdot \underline{E}$, and the excess translational kinetic energy (eqn. (19)) induced by the field-on equilibrium molecular dynamical process, are correlated statistically. Note that the result of eqn (28) can be extended straightforwardly to a circularly polarised applied laser field by replacing \underline{E} by $E_0 \cos(\omega t)$ or by $E_0 \sin(\omega t)$.

This seems to be the first study of the consequences of electric (or laser) field induced anisotropy-of molecular linear centre of mass diffusion processes.

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APPENDIX

The result of the text, eqn (28), shows that the classical Langevin function is also dependent on the molecular mass provided that there is field-on statistical correlation between the quantities $|\langle \underline{\mu} \cdot \underline{E} \rangle|^{\frac{1}{2}}$ and $|K_{\text{trans}}^{\frac{1}{2}}|$. The value of this correlation can be determined numerically by computer

simulation. The Langevin function is affected more strongly by the molecular mass for light molecules. For very heavy molecules, in the limit $D \rightarrow \infty$, the expression for the Langevin function given in terms of integrals in eqn (28) reduces to

$$\langle \underline{\mu} \cdot \underline{E} \rangle = \mu E \left(\alpha - 2\beta \frac{kT}{E} \right) / \left(\beta - 2\gamma \frac{kT}{\mu E} \right) \quad (A1)$$

where

$$\alpha = \left(\frac{1}{3} + \frac{A}{5} + \frac{A^2}{7 \cdot 2!} + \frac{A^3}{9 \cdot 3!} + \dots \right) ,$$

$$\beta = \left(1 + \frac{A}{3} + \frac{A^2}{5 \cdot 2!} + \frac{A^3}{7 \cdot 3!} + \dots \right) ,$$

$$\gamma = \left(-1 + A + \frac{A^2}{3 \cdot 2!} + \frac{A^3}{5 \cdot 3!} + \dots \right) ,$$

and is independent of m to $1/D^3$ in the series expansion of numerator and denominator. In the opposite limit, $D \rightarrow 0$, the individual terms of the series expansion all become significant and the Langevin function is no longer independent of m .

This type of bi-dimensional normal distribution is significant in situations where two variables are statistically correlated in a molecular liquid. For example, there should be such correlation in the theory of flow induced birefringence, in the theory of flow and birefringence induced by applied field gradients, and in the theory of aligned liquid crystals.