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New Fluctuation-Dissipation Theorems.

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Abstract

New fluctuation-dissipation theorems are derived for the linear and non-linear theories of dielectric relaxation and the dynamic Kerr effect caused by an applied static electric field E_Z in the Z axis of the laboratory frame (X, Y, Z). These are based on the set of non-vanishing cross correlation functions now known to exist in all molecular and atomic liquids, and are examples of the set of fluctuation-dissipation relations provided by the Theorem of G. P. Morriss and D. J. Evans.

Introduction

In the past few years, the conventional theory of dielectric relaxation and the dynamic Kerr effect has been criticised {1} on the basis of computer simulations {2-10} which have shown the neglect of the set of non-vanishing cross-correlation functions (c.c.f.'s). The latter are numerically discernible in the laboratory frame (X, Y, Z) and in the molecule fixed frame (x, y, z) of the point group character tables. The set becomes much larger in the presence of an applied external force field of arbitrary strength and symmetry, which induces new ensemble averages with the same symmetry as that of the field. This affects the validity of the customary linear response fluctuation dissipation theorem {11-13}, which is qualitatively obvious from the fact that an applied electric field, for example, allows the existence of cross correlation functions such as {2}

$$< v_X(t)\omega_Y(0) > = - < v_Y(t)\omega_X(0) > \qquad (1)$$

which exist in the field-on steady state and vanish at field-free thermodynamic equilibrium. In fluctuation-dissipation theory, the response of the system is an average over some variable B, a function of positions and momenta of the N particle ensemble. It is frequently overlooked, however, that this is an average in the **non-equilibrium state of the system** {11}. This is clear from the fact that the applied field, however small in magnitude, puts the system out of true thermodynamic equilibrium. Furthermore, the observable in dielectric and Kerr effect theory is the response function, a measure of departure from equilibrium. Customary dielectric and Kerr effect theory neglects time cross correlation functions, and in particular those induced by the applied field, an electric field in this context. The response is equated with the **equilibrium** correlation function by customary linear response theory and its fluctuation dissipation theorem. This leads to a very incomplete appreciation of the ensemble dynamics, in that the existence of time cross correlation fucntions shows that the phase function, Λ, which couples the field induced hamiltonian H_{ext} to the external force F_e

$$H_{ext}(t) = - AF_e(t) \qquad (2)$$

can be correlated with more than just one variable B measuring the response of the system. Furthermore the **transient** average $< \Lambda(0)\dot{B}(0) >_{\text{non-equlibrium}}$ may exist while its equilibrium counterpart $< \Lambda(0)\dot{B}(0) >_{\text{equilibrium}}$ vanishes. The latter is the customary response function of linear response theory.

This fundamental point is not addressed in the customary theory of dielectric and Kerr effect relaxation {14,15}.

In this letter we use the Theorem of G. P. Morriss and D. J. Evans {16} to remedy the problem by providing several new fluctuation dissipation relations valid for all electric field strengths and therefore in non-linear as well as linear response. These explicitly account for cross correlation functions and the symmetry effect of the applied field.

The Theorem of G. P. Morriss and D. J. Evans

This Theorem {16} is an important development which provides numerous new insights to the way in which molecular and atomic ensembles respond to applied force fields of arbitrary strength and symmetry. It was derived by Morriss and D. J. Evans {16} from first principles, and examples of the Theorem at work have recently been reviewed by Heyes {17}. It can be stated through the equation {16,17}

$$< B(t) > = < B(0) > - \frac{F_e}{kT}\int_0^t < B(s)J(0) > ds \tag{3}$$

where B(t) is an arbitrary time dependent phase variable of the molecular (or atomic) ensemble, and where F_e and J are respectively the applied force field and dissipative flux, defined by eqn (2). Here H is the hamiltonian. The integrand on the r.h.s. of eqn (3) is a **transient time correlation function**, which plays a major role for non-linear, non-equilibrium statistical mechanics analogous to the partition function {16} in thermodynamics and equilibrium statistical mechanics. The Theorem, eqn. (3), generalises the Green Kubo relations {18} and links the non-equilibrium value of a phase variable (the l.h.s.) to the integral over a time correlation function between the dissipative flux J(0) in the equilibrium state and B at a time s after the external field F_e has been turned on. One example of the Theorem at work is the relation {17}

$$\eta(t) = -\frac{< P_{xy}(t) >}{\dot{\gamma}} = \frac{V}{kT}\int_0^t < P_{xy}(s)P_{xy}(0) > ds \tag{4}$$

for the viscosity, which reduces {17} to the well known Green-Kubo relation {18} in the limit $\dot{\gamma} \rightarrow 0$. Here $\dot{\gamma}$ is the strain rate and P_{xy} is the off-diagonal component of the pressure tensor. Eqn. (4) involves a time correlation function between $P_{xy}(0)$ from the equilibrium system and $P_{xy}(s)$ from the **perturbed system**, and is valid for arbitrary strain rate $\dot{\gamma}$. The Morriss / Evans Theorem thus deals indiscriminately and consistently with linear and non-linear response, thus removing the need for linear response approximation {12-15}.

Application of the Theorem to Dielectric Relaxation and the Dynamic Kerr Effect

We consider a static electric force field E_Z applied to a dipolar molecular ensemble. It is well known {12-15} that the field interacts with each molecule through the latter's multipole moments, i.e. the dipole, quadrupole, octopole, and so on. Without loss of generality we can consider that part of the interaction between field and molecular dipole moment. This is characterised by the torque $-\mu \times E$ where μ is the molecular dipole moment. The energy $\mu \cdot$ E supplements the system hamiltonian. Thus, eqn. (3) reads

$$< B(t) > = < B(0) > - \frac{E_Z}{kT}\int_0^t < B(s)\dot{\mu}_Z(0) > ds \tag{5}$$

where $\dot{\mu}_Z$ is the time derivative of μ_Z, and is known as the "rotational velocity" {12-15}. The Theorem (3) thus reads, for example

$$< \dot{\mu}_Z(t) > = - \frac{E_Z}{kT} \int_0^t < \dot{\mu}_Z(s) \dot{\mu}_Z(0) > ds \tag{6}$$

In eqn (5), B(t) is in general any phase variable of the N molecule ensemble, and this equation allows us to take account of the set of non-vanishing c.c.f.'s induced by E_Z of arbitrary strength, $E_Z \neq 0$. The following are examples of the new fluctuation-dissipation theorems governing dielectric relaxation and the dynamic Kerr effect.

Setting B(t) to μ_Z, we recover a generalisation of the fluctuation dissipation of linear response theory as customarily applied to dielectric relaxation

$$< \mu_Z(t) > = - \frac{E_Z}{kT} \int_0^t < \mu_Z(s) \dot{\mu}_Z(0) > ds \tag{7}$$

relating the orientational transient $< \mu_Z(t) >$ to the non-equlibrium time correlation function which is the integrand on the right hand side. Traditional experimental methods {12-15} use $\mu E_Z << kT$, but eqn (7) show clearly that even for any applied electric field strength the orientational fall transient is dependent on the field strength {1}. Linear response theory equates the time dependence of the fall transient and the equilibrium orientational auto-correlation function.

The traditional approach also has no method of explaining why time c.c.f.'s such as those of eqn (3) exist for $\mathbf{E} \neq 0$ and vanish **if and only if** $\mathbf{E} = 0$. However, this is easily accommodated by the new Theorem using, for example, $B(t) = v(t)|\omega(t)$, giving the type (1) and (2) relations

$$< v(t) > = - \frac{E_Z}{kT} \int_0^t < v(s) \cdot \dot{\mu}(0) > ds \tag{8}$$

and

$$< \omega(t) > = - \frac{E_Z}{kT} \int_0^t < \omega(s) \cdot \dot{\mu}(0) > ds \tag{9}$$

The fluctuation-dissipation theorem of type (1), i.e. eqn. (8), shows the presence of a non-vanishing velocity transient due to the fact that the time c.c.f. $< v(t) \cdot \dot{\mu}(0) >$ exists {19} in frame (X, Y, Z), both for $\mathbf{E} \neq 0$ *and* $\mathbf{E} = 0$ from the first principle {11} of group theoretical statistical mechanics. The fluctuation dissipation theorem of type (2), i.e. eqn (9), shows the existence of a non-vanishing angular velocity transient due to the fact that the time c.c.f. $<\omega(t) \cdot \dot{\mu}(0)>$ exists in frame (X, Y, Z) for $\mathbf{E} \neq 0$ (third principle of group theoretical statistical mechanics {11}) but vanishes in this frame when $\mathbf{E} = 0$ (first principle {11}). The transient c.c.f.'s exist for $0 < s < t$ in both cases. We can obtain a third expression merely by multiplying (8) and (9), i.e.

$$<\mathbf{v}(t)><\omega(t)> = \left(\frac{E_Z}{kT}\right)^2 \int_0^t <\mathbf{v}(s)\cdot\dot{\mu}(0)> ds \int_0^t <\omega(s)\cdot\dot{\mu}(0)> ds \qquad (10)$$

which involves the product of translational and rotational transients.

Experimental Observations

The new fluctuation - dissipation theorems (8) - (10) can be investigated by computer simulation for all E_Z, but also provide an opportunity for the experimental observation of transient averages caused by cross correlation functions. An interesting example is $<\mathbf{v}(t)>$ in eqn (8). This vanishes both at field-off thermodynamic equilibrium and field-on equilibrium and field-on equilibrium (the steady state) because of time reversal symmetry. However, it may exist as a transient, and should be observable using conventional apparatus to pulse the molecular ensemble with an applied E_Z. A small net translation should be transiently observable, akin to the well known phenomenon of dielectrophoresis {1}, usually attributed to non-uniformities in the applied electric field, i.e. to field gradients. Similarly, eqn (9) shows the existence of a non-vanishing transient angular velocity, which may be observable by techniques sensitive to molecular angular motion, such as far infra red absorption {12} or nuclear magnetic resonance relaxation. The transient angular velocity is intuitively understandable in terms of a removal of external torque.

Generalisation to Higher Multipoles

In general, the interaction of **E** with the diffusing molecule involves higher multipole moments {12}. The quadrupole interacts with E^2, the octopole with E^3, and so on. Also, each equilibrium (field-off) multipole is distorted by field induced terms. The dissipative flux J is represented in general by $\dot{\mu}$, the time derivative of

$$\mu = \mu_0\mathbf{E} + \mathbf{E}\alpha\mathbf{E} + \gamma\mathbf{EEE} + \ldots\ldots\ldots\ldots \qquad (11)$$

where α is the molecular polarisability, γ the hyperpolarisability and so on. The dissipative flux is related to the time derivative of polaraisability when dealing with α to E^2 interactions, and so on. Each type of field-multipole interaction brings with it its characterisitic set of non-vanishing c.c.f.'s, determined by the symmetry arguments of group theoretical statistical mechanics {11}, thus generating many new types of fluctuation-dissipation theorem from the basic Theorem (2). None of these is considered in the conventional theory {12-15}, which is therefore open to criticism at the fundamental level. There is no longer a need to separate linear from non-linear response, following upon the introduction by Morriss and D. J. Evans of the non-equilibrium time correlation function basic to their Theorem (3). The indications for these remarks have been available for some time {1} and the development of Theorem (3) has provided a simple but profound mathematical statement of the consequencies to the theory of dielectric relaxation and the Kerr effect. These can only be understood by computer simulation.