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A predictive theory for zero–THz spectroscopy

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Abstract—A simple theory of zero–THz spectroscopy is developed which for the first time is capable of predicting the bandshape from a knowledge of the microwave critical frequency ω_c without the use of adjustable parameters. The limitations of the theory are reached as the separation increases between the microwave and far i.r. peaks in loss and power absorption, respectively.

In this paper we develop a theory of zero–THz absorption [1–3] which may be used to predict quantitatively the far i.r. part of the complete absorption/dispersion profile from a knowledge only of the dielectric critical frequency ω_c, the inverse of the critical time τ_c, which is related through an internal field factor to the Debye relaxation time [4] τ_D. The theory contains no adjustable parameters apart from Debye's τ_D, and provides a quantitative measure of the zero–THz profile in terms of the mean square torque $\langle N_1^2\rangle$, defined below for the symmetric top. The theory is easily related [5] to those of NEE and ZWANZIG [6], FATUZZO and MASON [7], LOBO *et al.* [8], BAROJAS *et al.* [9], KIVELSON and MADDEN [10], QUENTREC and BEZOT [11] and EVANS *et al.* [12]. The essential difference is that these all contain adjustable variables, whilst the method described here does not. At the same time we do not wish to claim anything more for this approach than that it allows us to describe a very complicated N body phenomenon in terms which are very simple yet an improvement on the phenomenological approach and on that based on memoryless equations [13]. A more rigorous treatment is molecular dynamics simulation, a method which has been used recently by BROT *et al.* [14] to corroborate strikingly the dynamic internal field theory of FATUZZO and MASON [7], incorporated into the structure of the present analytical method by NEE and ZWANZIG [6], LOBO *et al.* [8] and KIVELSON and MADDEN [10]. The macro-micro theorem of Kivelson and Madden can be related straightforwardly to the results of this section, which can also be corrected with the Fatuzzo–Mason internal field theory [7] using the results of Lobo *et al.*

Fundamentally in zero–THz spectroscopy of liquid systems we have the general features embodied in

$$[d\epsilon^*(\omega)/d\omega]_{\omega_c} = 0 \qquad (1)$$

$$[d\alpha(\omega)/d\omega]_{\omega_1} = 0 \qquad (2)$$

$$[d\omega^2\alpha(\omega)/d\omega]_{\omega_2} = 0 \qquad (3)$$

and so on for $\omega_1 \ldots, \omega_n, n \to \infty$. In these equations ω_c is the critical frequency mentioned already, ω_1 is the angular frequency ($= 2\pi\bar{\nu}_1 c$, where $\bar{\nu}$ is the wavenumber in cm^{-1}) at which the power absorption coefficient $\alpha(\omega)$ (in neper cm^{-1}) peaks in the far i.r. In equation (3) ω_2 is the angular frequency at which the fourth spectral moment peaks in the mid i.r. and so on. Equation (1) has been used for more than 60 years, (2) for about 10, and equation (3) has not been used experimentally at all; although preliminary analysis of the extensive *high accuracy* $\alpha(\omega)$ data of REID, G. J. EVANS and M. W. EVANS [1, 15, 16] shows that its use is quite feasible [17]. We shall not elaborate this theme further in this paper, but use equations (1) and (2) only.

These are independent of models. They hold for all polar liquids except when the viscosity becomes high enough to resolve α and β processes at ultra-low frequencies in the vitreous state so that there is more than one ω_c in equation (1).

The power absorption coefficient is related to the real $[\epsilon'(\omega)]$ and imaginary $[\epsilon''(\omega)]$ parts of the complex permittivity by the Maxwell equation

$$\alpha(\omega) = \frac{\omega\epsilon''(\omega)}{n(\omega)c} \qquad (4)$$

where $n(\omega)$ is the refractive index, defined by

$$n(\omega) = \{[\epsilon'(\omega)^2 + \epsilon''(\omega)^2]^{1/2} + \epsilon'(\omega)\}^{1/2}/\sqrt{2} \qquad (5)$$

and c the velocity of light. Equation (4) is the key to zero–THz spectroscopy [equations (1)–(3), etc.] as opposed to its historical predecessor, dielectric spectroscopy, embodied in equation (1) alone and therefore a very incomplete description of molecular dynamics and interactions. The real problem in molecular terms is to find a relatively simple method of satisfying equations (1)–(3), etc. and at the same time correctly describe the ω depen-

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dence of $\epsilon''(\omega)$, $\alpha(\omega)$, $\omega^2\alpha(\omega)$, etc. The interpretation is complicated by (a) the internal field problem [14] and (b) by collision induced absorption [1]. In solutions of chloroform for example the former is relatively unimportant but the latter is always present. REID [18] has estimated that collision induced absorption accounts for some 40% of the area (A) beneath $\alpha(\omega)$ in 10% (v/v) $CHCl_3$/decalin. The theory of this section allows us to separate the ω dependence of this contribution for the first time from the purely dipolar part, that which obeys the Gordon/Brot sum rule [3] for A used by Reid.

The core of the theories such as that of KIVELSON and MADDEN [10] we have mentioned already is a Mori approximant which we have fully described in the literature. The spectrum [$\epsilon''(\omega)$ and $\alpha(\omega)$] may be described concisely, in terms of the Fourier/Laplace transform of

$$\bar{C}_u(p) = \frac{p^2 + \gamma p + K_1}{p^3 + \gamma p^2 + (K_0 + K_1)p + \gamma K_0}. \qquad (6)$$

This is the simplest possible equation which can be used to describe equations (1) and (2) only. It is also the basis of the internal field/dielectric friction theory of LOBO *et al.* [8]. The inverse Laplace transform of $\bar{C}_u(p)$ may be related to the dipole-orientation time correlation function, and via the macro–micro theorem to the autocorrelation function $C_u(t)$. Here $\mathbf{u}$ is the dipole unit vector ($\boldsymbol{\mu}/|\boldsymbol{\mu}|$ where $\boldsymbol{\mu}$ is the molecular dipole moment). The Euler equations are linearized in deriving equation (6), i.e. the nonlinearities are projected into the random noise term of the Liouville equation written by NEE and ZWANZIG [6], for example, as a generalized Langevin equation for $\mathbf{u}$ itself. GRIGOLINI, FERRARIO and EVANS [19] have recently shown how this approximation can be removed using a generalization of the continued fraction of SACK [20], GROSS [21] and KUBO [22] using a stochastic Liouville equation. At low enough frequencies equation (6) reduces to the Debye equations for $\epsilon'(\omega)$ and $\epsilon''(\omega)$. For isotropic rotational diffusion K_0 and K_1 are scalar thermodynamic averages. For anisotropic rotational diffusion each is a tensor: in the case of $CHCl_3$ these happen to be diagonalizable in the same frame of reference as the moment of inertia tensor. In the case of rototranslational diffusion (neutron scattering each is a super-tensor [23] (a tensor whose elements are themselves tensors), and for vibration/rotation/translation diffusion also super-tensors. γ in equation (6) is a scalar defined by the fundamental hypothesis on the memory function K_1

$$K_1(t) = K_1(0)\exp(-\gamma t) \qquad (7)$$

when K_0 and K_1 are tensors or super-tensors so is γ. In zero–THz spectroscopy fundamental theorems on time-reversal, parity and reflection imply that we may consider only rotational, as apart from roto-translational diffusion provided the overall specimen is isotropic. If this is not the case (as in the aligned nematic) γ, K_0 and K_1 become tensors with interesting spectral consequences currently being investigated by one of us.

For the symmetric top we have

$$K_1(0) = \langle \ddot{u}^2(0)\rangle / \langle \dot{u}^2(0)\rangle - \langle \dot{u}^2(0)\rangle / \langle u^2(0)\rangle \qquad (8)$$

so that

$$\langle N_\perp^2\rangle = I_B^2\left[K_0(K_0 + K_1) - 2K_0^2\left(1 + \frac{I_A}{4I_B}\right)\right] \qquad (9)$$

where $\langle N_\perp^2\rangle$ is the mean square torque in a direction perpendicular to the dipole axis.

Equations (6) and (7) were first used almost simultaneously by QUENTREC and BEZOT [11], EVANS and EVANS [24] and KIVELSON and MADDEN [10]. However, these early attempts were based on regarding γ and K_1, and in some cases K_0, as adjustable. In consequence the only practical method of comparing theory and experiment was $\alpha(\omega)$ curve fitting. This method ignores any collision induced contribution to the bandshape. This is thought to be much more severe for $\alpha(\omega)$ than for $\epsilon''(\omega)$. It is obviously desirable to develop a method whereby K_1 and γ can be determined using only τ_c and thereby extrapolate the theoretical curve to higher frequencies by converting to $\alpha(\omega)$ [equation (4)], i.e. to predict the far i.r. spectrum of a polar liquid rather than attempt a phenomenological description.

This may be accomplished using equations (1), (2) and (6) in combination. From equations (1) and (6)

$$\gamma^2 = \frac{[\omega_c^2 - (K_0 + K_1)][5\omega_c^4 - \omega_c^2(K_0 + K_1)]}{(K_0 - \omega_c^2)(K_0 + 3\omega_c^2)} \qquad (10)$$

and from equations (2) and (6)

$$\gamma^2 = \frac{2\omega_1^4[\omega_1^2 - (K_0 + K_1)]}{(K_0 - \omega_1^2)(K_0 + \omega_1^2)}. \qquad (11)$$

Solving equations (10) and (11) for K_1 we have

$$K_1 = -\frac{b}{2} \pm \frac{1}{2}(b^2 - 4c)^{1/2} \qquad (12)$$

with

$$b = \frac{A_1}{\omega_c^2} - (6\omega_c^2 - 2K_0)$$

$$c = (\omega_c^2 - K_0)(5\omega_c^2 - K_0) - \frac{A}{\omega_c^2}(\omega_1^2 - K_0)$$

$$A_1 = \frac{2\omega_1^4(K_0 - \omega_c^2)(K_0 + 3\omega_c^2)}{(K_0 - \omega_1^2)(K_0 + \omega_1^2)}.$$

Now, when $4c > b^2$; K_1 becomes complex and loses its physical significance as a thermodynamic average [equation (9)]. At the same time we know from observation information theory and from general thermodynamic principles that entropy maximization in a liquid will tend to maximize $(\omega_1 - \omega_c)$ for given T, the absolute temperature. Accordingly, when $b^2 = 4c$ in equation (12) this condition is satisfied and the relation between b and c gives us ω_1, the far i.r. peak, knowing only ω_c, the microwave peak frequency.

We emphasize that this is the simplest workable approach to a complicated problem. In the appendix we demonstrate how to elaborate the theory to take into account (a) the internal field and (b) cross-correlations with the macro–micro theorem of Kivelson and Maddon.

However, the results for chloroform at different T and in CCl_4 solution are encouraging. The theory (given ω_c) correctly predicts the observed $\bar{\nu}_1[=\omega_1/(2\pi c)]$ to within about 1 or 2 cm^{-1} without internal field corrections, which we wish to regard at present as a complication (albeit not very severe, see Fig. 1). For the first time Debye's original ideas have been properly extended to deal with the far i.r. in the sense that the whole profile can be estimated from τ_c (or the Debye relaxation time τ_D). The point at which K_1 becomes complex corresponds fairly well to the frequency at which $\alpha(\omega)$ is observed to peak in the far i.r.

Despite this the limitations of the present theory are very easily exposed merely by taking equation (3) into account. Equations (4)–(6) produce a plateau in $\omega^2\alpha(\omega)$ as $\omega \to \infty$, i.e. the fourth moment is not defined, essentially because of the Markov/Doob hypothesis [12] on $K_1(t)$, equation (7). The next step in the theory would be to use the truncation

$$K_2(t) = K_2(0) \exp(-\gamma_1 t)$$

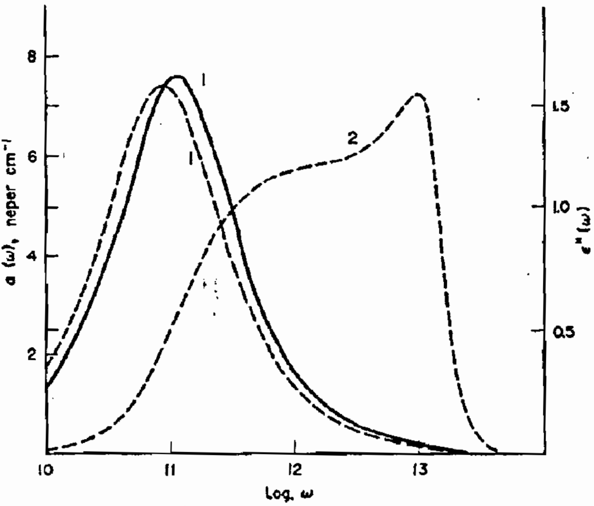
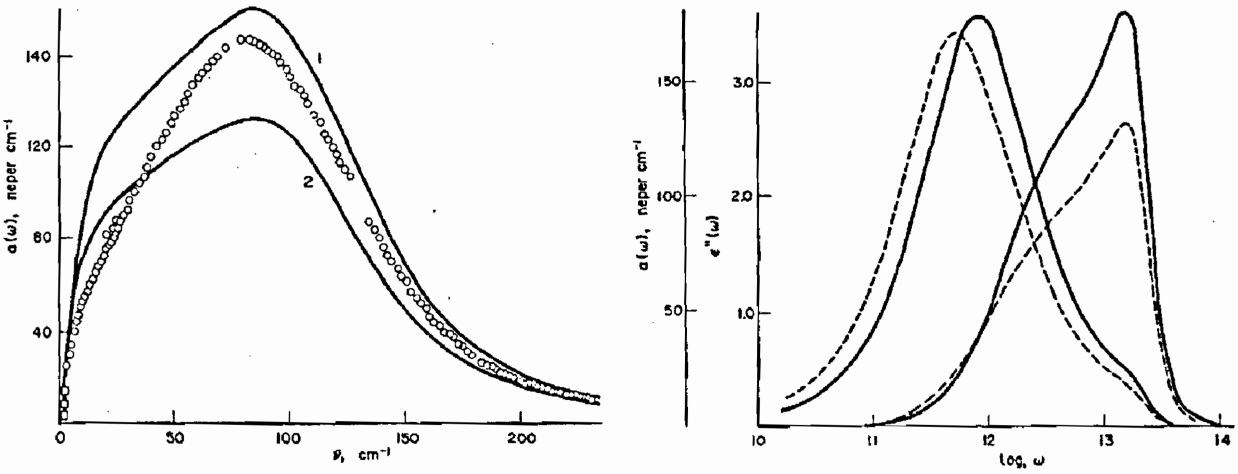


Fig. 1. Loss and power absorption coefficient of chloroform liquid: (1) —— Theoretical curve with parameters of Table 1; (1) – – – curve (1) corrected for the internal field; (2) ---- power absorption coefficient corrected for the intense field with the theory of Lobo *et al.*

and solve equations (1)–(3) simultaneously for γ, K_1, K_2, ω_1 and ω_2. The process could be repeated indefinitely provided that an autocorrelation function can be differentiated to infinite order. According to SCAIFE [25] this is not possible, but the argument is not settled. In any case in practice it is possible (unpublished work) to produce $\omega^2\alpha(\omega)$ experimentally so that the peak frequency ω_2 is well defined, in some cases $\omega^4\alpha(\omega)$ (with great difficulty) but not $\omega^6\alpha(\omega)$ with any certainty.

Figure 1 clearly shows that for chloroform, induced absorption is an important contributor in the far i.r. Even though the microwave intensity [of $\epsilon''(\omega)$] is reproduced exactly (with the usual ϵ_0 and ϵ_∞) the resulting far i.r. intensity is too small by about 50%. This is in approximate accord with the Gordon/Brot sum rule (although HILL [26] has raised some doubts about the applicability of this in liquids).



(a)

(b)

Fig. 2. (a) O Experimental absorption of pure liquid methylene chloride at 298 K. (1) Theoretical curve with $\tau_c = 1.2$ ps (obs. = 1.4 ps). (2) Theoretical curve corrected for internal field with the Fatuzzo/Mason factor as developed by Lobo *et al.* (b) Illustration of (a) on a log scale.

Table 1. Prediction of far i.r. peak frequencies from the microwave frequency τ_c

Solute	ϵ_0	τ_c(ps)	$\bar{\nu}_{max}$ (obs.)/cm^{-1}	$\bar{\nu}_{max}$ (calc)/cm^{-1}	$10^{-24}K_0(s^{-2})$	$10^{-24}K_1(s^{-2})$	$10^{-12}\gamma(s^{-1})$	I_A	I_B	I_C
10% Solute solutions in decalin at 293 K								Moments of inertia (10^{-40} g cm^2)		
CH_2Cl_2	2.59	1.0	52	52	17.1	498	24.1	26	256	277
Tetrahydrofuran	2.59	1.8	46							
Furan	2.25	2.0	51	52	6.75	224	16.6	88	90	179
Pyridine	2.92	3.1	45	49	4.21	215	16.4	140	145	285
t-Butyl chloride	2.62	3.4	24	54	0.91	272.5	18.4	191	286	286
Fluorobenzene	2.47	3.9	39	31	2.11	86.9	10.5	147	324	471
Chloroform	2.36	4.2	30	30	1.45	199.9	15.0	252	252	500
2-Methylpyridine	2.66	8.5								
Toluene	2.2	9.0	60	70	2.09	420.4	22.3	152	325	477
Pentafluorobenzene	2.4	9.8	30	27	0.76	75.0	10.0	629	832	1460
Chlorobenzene	2.46	10.7	34	54	1.36	254.4	17.5	147	530	677
Oxylene	2.27	12.0	65	78	1.76	529.3	25.1	256	367	619
Bromobenzene	2.50	16.2	24	54	0.91	272.5	18.4	147	820	967
Nitrobenzene	4.18	20	39	80	1.04	440.4	21.2	208	690	898
Benzonitrile	3.00	27	47	94	1.32	2140.0	60.3	147	550	697
1-Chloronaphthalene	2.43	29	47	82	0.76	582.3	26.2	550	850	1400

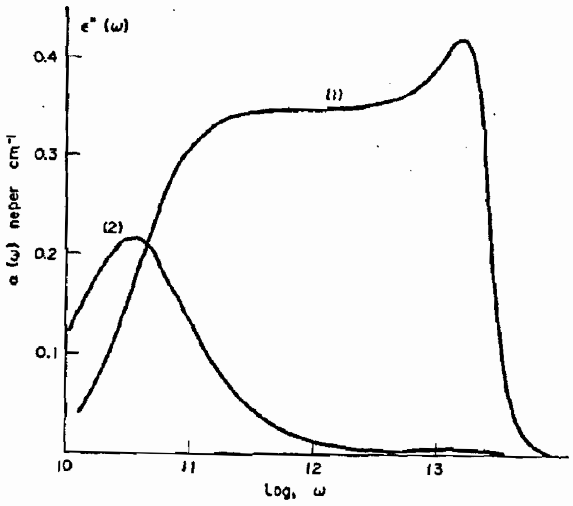


Fig. 3. Limitations of the theory for 10% v/v nitrobenzene in decalin. (1) Power absorption; (2) loss.

The result for CH_2Cl_2 (Fig. 2) indicates that in this molecule induced absorption is not such an important factor. The theoretical far i.r. peak position, predicted from the microwave critical frequency (ω_c), is satisfactory when we consider that this is very sensitive to the exact position of ω_c because of the small moment of inertia (I_A) in CH_2Cl_2.

Finally Table 1 lists the results for 15 solutes [15,16] in decalin at 293 K. The agreement between the observed and calculated peak frequencies is good in general especially for the smaller molecules, but becomes less so as the asymmetry increases. The theoretical bandshapes in the latter cases becomes progressively flatter and broader than the corresponding experimental curves. Nitrobenzene (Fig. 3) is a good example.

This exposes the limitations of the particular Mori approximant used in that as the ω_c frequency decreases (τ_c becomes longer) the far i.r. region of the spectrum theoretically begins to look more like the Debye plateau [1,2] of classical diffusion theory.

This result illustrates the extreme sensitivity of zero-THz spectroscopy to the detailed behaviour of a predictive analytical theory.

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APPENDIX

The internal field correction

Lobo *et al.* have treated this problem using the concept of dielectric friction. They have shown that

$$
\begin{aligned}
1 &- i\omega\mathscr{L}_a C_s(t)\\
&= \left[1-\frac{I^*\omega^2}{2kT}-\frac{i\omega\langle N_T^2\rangle\tau}{(1-i\omega\tau)2(kT)^2} - \left(1-\frac{n^2}{\epsilon(0)}\right)\left(\frac{\epsilon^*(\omega)-\epsilon(0)}{2\epsilon^*(\omega)+\epsilon_\infty}\right)\right]^{-1} \qquad \text{(A1)}
\end{aligned}
$$

where $I^* = I_B$ for a symmetric top.

The right-hand side of (A1) may be rewritten as

$$
\frac{p^2+p(1/\tau)+(2kT/I_B)\langle N_T^2\rangle/2(kT)^2}{p^3+p^2(1/\tau)+(2kT/I_B)\left(1+\dfrac{\langle N_T^2\rangle}{2(kT)^2}\right)p+\dfrac{1}{\tau}\dfrac{2kT}{I_B}} \qquad \text{(A2)}
$$

when the internal field correction is removed. This is exactly the same as equation (2.6) with the identities

$$
\gamma \equiv 1/\tau; \quad K_0 \equiv 2kT/I_B; \quad K_1 \equiv \frac{\langle N_T^2\rangle}{I_B kT}.
$$

The mean square torque $\langle N_T^2\rangle$ of Lobo *et al.* is defined in a slightly different way from $\langle N_\perp^2\rangle$, otherwise the two theories are the same. With the definition $\tau_0 = (\langle N_T^2\rangle\tau/2(kT)^2)$ we can correct the theory for the Fatuzzo/Mason internal field with

$$
\frac{\epsilon^*(\omega)}{\epsilon_\infty} = \frac{1}{4}\left[\frac{z_p^2-z^2(\omega)}{z_i^2-z^2(\omega)}\right]+\frac{3}{4}\left[\frac{[z_1^2-z^2(\omega)][z_p^2-z^2(\omega)]}{[z_i^2-z^2(\omega)][z_i^2-z^2(\omega)]}\right]^{1/2}
$$

$$
z_1^2 = 1+\frac{\epsilon_\infty}{\epsilon_0}-\frac{\epsilon_0}{\epsilon_\infty}; \quad z_i^2 = \frac{1}{2}\left(1+\frac{\epsilon_\infty}{\epsilon_0}\right); \quad z_p^2 = \frac{\epsilon_0}{\epsilon_\infty};
$$

$$
z^2(\omega) = \frac{\omega^2 I_B}{2kT}+\frac{i\omega\tau_0}{1-i\omega\tau}; \quad \epsilon^*(\omega) \equiv \epsilon'(\omega)+i\epsilon''(\omega)
$$

(note the plus sign).

In Fig. 2 we illustrate the effect of the internal field correction for chloroform.

The macro–micro relations

The equivalent of equation (A2) has been derived by Kivelson and Madden in their three variable macro–micro correlation theorem linking the single particle autocorrelation function $C_s(t)$ to the multiparticle cross-correlation function $C_M(t)$. In their notation

$$
\begin{aligned}
\bar{C}_s(p) = \tau_{S\theta}\Bigg[1 &+ \left(\frac{\omega^*}{\omega_\theta^*}\right)^2[(\omega_\theta^*+\omega_T^*)^2-2]\\
&+\left(\frac{\omega^*}{\omega_\theta^*}\right)^4[1-2\omega_T^*(\omega_\theta^*+\omega_T^*)]+\left(\frac{\omega^*}{\omega_\theta^*}\right)^6\omega_T^{*2}\Bigg]^{-1}.
\end{aligned} \qquad \text{(A3)}
$$

This is exactly the same as equation (6) with the identities

$$
\gamma^{-1} \equiv \tau_{ST}; \quad \frac{K_1}{K_0} \equiv \left[\frac{\langle(\mathrm{d}^2\cos\theta_1/\mathrm{d}t^2)\rangle}{(kT/I)^2}-1\right].
$$

Here τ_{ST} is the single particle correlation time associated with intermolecular torques. It is related to a single particle orientational correlation time $\tau_{S\theta}$ by

$$
\tau_{S\theta} = \left[\frac{\langle\mathrm{d}^2\cos\theta_1/\mathrm{d}t^2\rangle}{(kT/I)^2}-1\right]\tau_{ST}. \qquad \text{(A4)}
$$

These relations can be used to calculate the dynamic correlation factors of Kivelson *et al.* The method used here is set out more fully in Ref. [2]. To apply the three variable macro–micro correlation theorem we substitute Γ for γ, Φ_0 for K_0 and Φ_1 for K_1 in equation (6) defined by

$$
\Gamma = \gamma(1+\dot{f}N)(1+\ddot{f}N) \qquad \text{(A5)}
$$

$$
\Phi_0 = K_0/(1+Nf) \equiv K_0/g \qquad \text{(A6)}
$$

$$
\begin{aligned}
\Phi_1 &= \frac{kT}{I}(1+\ddot{f}N)\left[\frac{\langle(\mathrm{d}^2\cos\theta_1/\mathrm{d}t^2)^2\rangle}{(kT/I)^2}-1\right] \qquad \text{(A7)}\\
&= \frac{(1+\ddot{f}N)}{2kTI}\langle N_T^2\rangle.
\end{aligned}
$$

From (A5) to (A7) we can obtain f, $\dot{f}$ and $\ddot{f}$, the dynamic correlation factors.