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Macro-micro relations in dipolar orientational relaxation: An exactly solvable model of dielectric relaxation

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The relationship between the microscopic orientational relaxation time (τ_m) and the collective, macroscopic relaxation time (τ_M) of a dipolar liquid has been a subject of considerable interest. We examine this relation for the kinetic Ising model of Glauber, used recently by Skinner to describe dielectric relaxation in glassy polymers. In this model, exact solutions for both the same spin and the collective spin time correlation functions are possible. We find that these two correlation functions are entirely different from each other. The self spin correlation function is highly nonexponential, as pointed out by Glauber and by Skinner. But, the collective spin relaxation is single exponential, and the wave vector and frequency dependent dielectric function is of simple Debye form. The reason for this difference is discussed.

I. INTRODUCTION

The orientational motion of a dipolar molecule in a dense dipolar liquid is rather complicated because of the long range nature of the dipolar interactions. As a result, a quantitative understanding of dipolar orientational relaxation is yet to reach a satisfactory stage. An especially and intriguing question in this area is the relationship between the microscopic, i.e., the single particle, and the macroscopic, i.e., the collective, orientational relaxations in a dipolar liquid.^{1,2} Experimentally, magnetic relaxation experiments provide the most direct information on the single particle motion whereas dielectric relaxation and light scattering experiments measure the collective orientational relaxation. Experimental results available in some systems²⁻⁴ indicate that these two relaxations can be substantially different if only the magnitude of the relaxation times are considered. The functional form of the time dependence of the two orientational correlation functions may not be very different.

Several years ago, Kivelson and Madden⁵ made an interesting study on the interrelationship between the microscopic and the macroscopic orientational relaxation functions. We define the collective dipole moment by

$$\mathbf{M}(t) = \sum_i \mu_i(t), \quad (1)$$

where μ_i is the dipole moment of the i th molecule and the sum is over all the N molecules of the system. Next, define the two time correlation functions $C_M(t)$ and $C_m(t)$ by

$$\begin{aligned} C_M(t) &= \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle M^2(0) \rangle, \\ C_m(t) &= \langle \mu_i(0) \cdot \mu_i(t) \rangle / \langle \mu_i^2(0) \rangle, \end{aligned} \quad (2)$$

where the averages are over an equilibrium ensemble. The final result of macro-micro theorem of Kivelson and Madden⁵ is that if $C_m(t)$ can be expanded as a sum of exponentials, then $C_M(t)$ takes the same form with scaled parameters. Although there are certain approximations that restrict the validity of this theorem, it is clearly an important theorem that deserves further study.

We have recently reported a study of the relationship between the macroscopic and microscopic relaxation times

in a dense dipolar liquid.⁶ We have shown that the macro-micro theorem is satisfied in a Markovian theory based on a generalized Smoluchowski equation⁷ where the intermolecular interactions are taken into account through a mean-field force term derived from the density functional theory of inhomogeneous systems.⁸ In the linearized Markovian theory considered, both $C_M(t)$ and $C_m(t)$ were single exponential. The relationship between the relaxation times τ_m and τ_M was found to be given by.⁶

$$\tau_M = \tau_m \left[1 + \frac{\rho_0}{4\pi} c(111; k=0) \right]^{-1}, \quad (3)$$

where $c(111; k=0)$ is the Fourier transform of the (111) component in the spherical harmonic expansion of the two-particle direct correlation function and ρ_0 is the average number density of the liquid. Equation (3) predicts a *slowing down of the collective orientational relaxation compared to the single particle motion with increase in liquid polarity*. This feature has already been observed in computer simulations.⁹

The derivation of Eq. (3) was based on several approximations which are rather difficult to remove satisfactorily. Thus, it will be of interest to explore the macro-micro relations in an exactly solvable system. In this paper we present such a study. The model we have chosen is the kinetic Ising model with Glauber¹⁰ dynamics. Although this model may not be an ideal one for dipolar liquid dynamics, similar models have been used previously to explain dielectric relaxation in glassy polymers.^{11,12} For example, Skinner¹² has shown that temporal evolution of the spin-spin time correlation function in the Glauber kinetic Ising model is given fairly accurately by the well-known Kohlrausch-Williams-Watts (KWW) empirical relaxation function

$$\phi(t) = \exp[-(t/\tau)^\beta], \quad (4)$$

with $\beta \approx 0.6$ in the intermediate coupling regime. Skinner has further shown that the dynamics in a kinetic Ising model can be interpreted in terms of the dynamics of domain wall defects in which the two fundamental processes are defect migration and defect creation and annihilation. So, Skin-

ner¹² could provide a nice quantitative model for the earlier work of Glarum¹³ and Bordewijk¹⁴ on defect diffusion models of dielectric relaxation.

In this paper we present, we believe for the first time, the analytic expression for the wave vector (k) and frequency dependent dielectric function, $\epsilon(k, \omega)$, of the Glauber kinetic Ising model. We find that although the spin-spin correlation function is highly nonexponential, the relaxation of the collective dipole moment is exponential and $\epsilon(k, \omega)$ is of simple Debye form. The macroscopic dielectric relaxation time, τ_M is obtained from $\epsilon(k=0, \omega)$. Thus, in this model system, the macroscopic and microscopic correlation functions are of quite different forms. In this context, it is of interest to recollect an earlier analysis of Oxtoby¹⁵ who also considered relations between the macroscopic and the microscopic correlation functions and showed that because of cross correlations, a macroscopic correlation function may decay faster than a microscopic correlation function.

The organization of the rest of the paper is as follows. In Sec. II we describe the kinetic Ising model and define the correlation functions. In Sec. III, we calculate the wave vector and frequency dependent dielectric function. In Sec. IV we present the numerical results comparing $C_m(t)$ and $C_M(t)$, Sec. V concludes with a brief discussion.

II. KINETIC ISING MODEL

Glauber's kinetic Ising model consists of a one-dimensional array of spins, each having two possible orientations identified by the spin variable $\sigma = \pm 1$. The energy of the system is given by the Ising Hamiltonian

$$H = -J \sum_{(ij)}' \sigma_i \sigma_j, \quad (5)$$

where the prime denotes a sum over the nearest neighbors. The coupling constant J is taken to be positive, indicating that the lowest energy state is the one of perfect alignment. Note that the relevant dimensionless parameter is $K = J/k_B T$. As pointed out by Budimir and Skinner,¹² the Hamiltonian in Eq. (5) is to be regarded as a free energy when applying to real systems because all other degrees of freedom have been integrated out. The parameter K is a measure of the static correlation length ξ through $\xi = 1/\ln [\coth(K)]$.

The probability of a given spin state $(\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N)$ at time t is denoted by $p(\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N)$ where N is the number of spins in the system. The time rate of change of these probabilities is assumed to be given by the Glauber "master equation"¹⁰

$$\begin{aligned} \frac{d}{dt} p(\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N, t) \\ = - \sum_j W_j(\sigma_j) p(\sigma_1, \sigma_2, \dots, \sigma_N, t) \\ + \sum_j W_j(-\sigma_j) p(\sigma_1, \sigma_2, \dots, -\sigma_j, \dots, \sigma_N, t), \end{aligned} \quad (6)$$

where the sums go over all the spins. The transition probability $W_i(\sigma_i)$ is the probability per unit time of flipping the i th spin; W obviously depends on the spin state of the chain. The

most general form of a nearest neighbor dependent transition probability for such a model is given by¹⁰

$$W_i(\sigma_i) = \frac{\alpha}{2} \left[1 + \delta \sigma_{i-1} \sigma_{i+1} - \frac{\gamma}{2} (1 + \delta) \sigma_i \{ \sigma_{i-1} + \sigma_{i+1} \} \right], \quad (7)$$

where $\gamma = \tanh(2K)$. As discussed by Budimir and Skinner,¹² this transition probability allows for the following processes:

$$\begin{aligned} & \begin{matrix} k_1 \\ \uparrow \downarrow \uparrow \rightleftharpoons \uparrow \uparrow \uparrow, \\ k_3 \end{matrix} \\ & \begin{matrix} k_2 \\ \uparrow \uparrow \downarrow \rightleftharpoons \uparrow \downarrow \downarrow, \\ k_2 \end{matrix} \end{aligned} \quad (8)$$

where $k_3 = k_1 \exp(-4K)$ to satisfy detailed balance. Note that rates k_1 , k_2 and k_3 are functions of the variable α , γ and δ . k_1 and k_2 are not determined *a priori*. Glauber¹⁰ chose $k_1/k_2 = 1 + \tanh(2K)$. It appears that it is the only choice that leads to an analytic solution of the problem. Skinner¹² pointed out that if we make the choice $k_1 = 0$ (which corresponds to $\delta = 0$) then the relaxation can be interpreted as a random walk of domain walls and one recovers an interactive Glarum model⁸ of defect diffusion. Both Glauber and Skinner considered the dynamics at constant temperature. However, α and γ are obviously functions of temperature. Reiss¹⁶ has recently studied nonequilibrium dynamics by making these constants some simple functions of time dependent temperature. This approach is meaningful if the other degrees of freedom that give the temperature change in such a way that a time dependent temperature can be defined. We are primarily interested in the spin-spin correlation function, defined by

$$C_{ij}(t) = \langle \sigma_i(0) \sigma_j(t) \rangle = \sum_{\sigma} \sum_{\sigma'} \sigma_i p(\sigma_1, \sigma_2, \dots, \sigma_N, 0) \times \sigma_j' p(\sigma_1', \sigma_2', \dots, \sigma_N', t). \quad (9)$$

The equilibrium correlation function is defined as

$$\begin{aligned} \gamma_{ij} &= \langle \sigma_i(0) \sigma_j(0) \rangle \\ &= \sum_{\sigma} \sigma_i \sigma_j p(\sigma_1, \sigma_2, \dots, \sigma_N, 0). \end{aligned}$$

For one-dimensional Ising model,

$$\gamma_{ij} = \eta^{|i-j|}, \quad (10)$$

where η is the short-range order parameter, equal to $\tanh(K)$.

III. DIELECTRIC RELAXATION

In the present problem, the wave vector and frequency dependent dielectric function is given by the following linear response theory expression:⁹

$$\epsilon(k, \omega) = 1 + \frac{4\pi\beta}{L} \mathcal{L} \left[- \frac{dC_p(k, t)}{dt} \right], \quad (11)$$

where $\beta = (k_B T)^{-1}$, k_B is Boltzmann constant, T is the temperature, and L is the length of the system. $C_p(k, t)$ is the polarization-polarization correlation function and \mathcal{L} de-

notes a Laplace transformation with the frequency ω as the variable conjugate to time t . In the one-dimensional Ising model, $C_p(k, t)$ is given by

$$\begin{aligned} C_p(k, t) &= \langle P(-\mathbf{k})P(\mathbf{k}) \rangle \\ &= \mu^2 \sum_{(j,l)} e^{ika(j-l)} \langle \sigma_j(0) \sigma_l(t) \rangle \\ &= \mu^2 \sum_{(j,l)} e^{ika(j-l)} C_{jl}(t), \end{aligned} \quad (12)$$

where μ is the magnitude of electric dipole of each spin. Let us define the dynamic structure factor by the following expression

$$S(k, t) = \sum_m e^{ikam} \langle \sigma_j(0) \sigma_{j+m}(t) \rangle \quad (13)$$

Equation (11) is now written in the form

$$\epsilon(k, \omega) = 1 + 4\pi\beta\mu^2\rho \mathcal{L} \left[-\frac{dS(k, t)}{dt} \right], \quad (14)$$

where $\rho = N/L$, N is the total number of spins. In the following, we shall take the simultaneous limits $N \rightarrow \infty$, $L \rightarrow \infty$ with $N/L = \rho$ fixed. We next proceed to evaluate $S(k, t)$. It was shown by Glauber¹⁰ that for the particular choice $k_1/k_2 = 1 + \tanh(2K)$ of the transition probabilities, the correlation function $C_{jj+m}(t)$ is given by

$$C_{jj+m}(t) = e^{-\alpha t} \sum_{n=-\infty}^{\infty} \eta^{|n|} I_{n-m}(\alpha\gamma t), \quad (15)$$

where $I_k(Z)$ is the modified Bessel function of order k and argument Z . The dynamic structure factor is evaluated as follows. We start with

$$\begin{aligned} S(k, t) &= e^{-\alpha t} \sum_{m=-\infty}^{\infty} e^{ikam} \sum_{n=-\infty}^{\infty} \eta^{|n|} I_{n-m}(\alpha\gamma t) \\ &= e^{-\alpha t} \sum_{n=-\infty}^{\infty} \eta^{|n|} e^{ikan} \sum_{q=-\infty}^{\infty} e^{-ikaq} I_q(\alpha\gamma t) \end{aligned} \quad (16a)$$

$$= e^{-\alpha t} \sum_{n=-\infty}^{\infty} \eta^{|n|} e^{ikan} e^{\alpha\gamma t \cos ka} \quad (16b)$$

$$= e^{-(1-\gamma \cos ka)\alpha t} S(k), \quad (17)$$

where the static equilibrium structure factor $S(k)$ is defined by the last equation. In going from Eq. (16a) to (16b), we have used the generating functional of the modified Bessel function. The sum in $S(k)$ can be evaluated to obtain

$$S(k) = (1 - \eta^2)(1 - 2\eta \cos ka + \eta^2)^{-1}. \quad (18)$$

Equation (15) is rewritten in the following form:

$$S(k, t) = S(k) e^{-\Gamma(k)t}, \quad (19)$$

where the wave vector dependent relaxation time $\Gamma(k)$ is given by

$$\Gamma(k) = \alpha(1 - \gamma \cos ka). \quad (20)$$

We next substitute Eq. (17) in Eq. (12) to obtain the following expression for the dielectric function

$$\epsilon(k, \omega) = 1 + \frac{Y_1 S(k)}{1 + i\omega \Gamma(k)^{-1}}, \quad (21)$$

where $Y_1 = 4\pi\beta\mu^2\rho$ and $S(k)$ is given by Eq. (18). Since $\epsilon(k) = 1 + Y_1 S(k)$, we may write Eq. (19) in the more conventional form

$$\epsilon(k, \omega) = 1 + \frac{\epsilon(k) - 1}{1 + i\omega \tau(k)} \quad (22)$$

with $\tau(k) = \Gamma(k)^{-1}$. In the long wavelength limit, the Debye form of $\epsilon(\omega)$ [$\epsilon(k=0, \omega)$] is given by

$$\epsilon(\omega) = 1 + \frac{\epsilon_0 - 1}{1 + i\omega \tau_0} \quad (23)$$

with

$$\epsilon_0 = (1 + \eta)/(1 - \eta), \quad (24)$$

$$\tau_0 = \{\alpha(1 - \gamma)\}^{-1}. \quad (25)$$

IV. NUMERICAL RESULTS AND DISCUSSION

The microscopic correlation function $C_m(t)$ is the self spin time correlation function. The self spin time correlation function is given by.¹⁰

$$C_m(t) = e^{-\alpha t} \sum_{j=-\infty}^{\infty} \eta^{|j|} I_j(\alpha\gamma t). \quad (26)$$

The collective spin correlation function is

$$C_M(t) = S(k=0, t)/S(k=0) = e^{-\Gamma(k=0)t}. \quad (27)$$

In Fig. 1 we have compared these two correlation functions. It can be seen that the two functions are vastly different at all times. The microscopic correlation function is highly nonexponential and it decays faster than the macroscopic correlation function.

Skinner and Budimir¹² has earlier pointed out that the correlation function $C_m(t)$ can be fitted to a stretched exponential KWW form with exponents significantly less than unity for nonzero values of the interaction parameter K . For example, $C_m(t)$ can be fitted well to KWW form with $\beta = 0.675$ for $K = 1$. On the other hand, the macroscopic correlation function $C_M(t)$ is single exponential for all val-

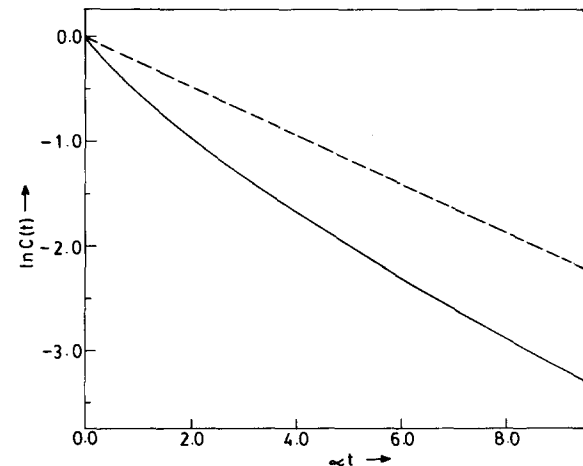


FIG. 1. The time dependence of the microscopic and the macroscopic correlation functions. The microscopic correlation function $C_m(t)$ is shown by the solid line and the macroscopic correlation function $C_M(t)$ is shown by the dashed line. The value of the coupling parameter K is 0.5.

ues of K . As expected, in the limit of $K \rightarrow 0$ (no interaction between spins, the Debye limit), $C_m(t)$ and $C_M(t)$ become equal to each other. The above results clearly show that in the present problem, the macro-micro theorem of Kivelson and Madden⁵ is not applicable.

It is now natural to ask: what happens in higher dimensions which have not been possible to solve exactly? The computer simulation studies suggest that in the two-dimensional Ising model with Glauber dynamics, $S(k=0, t)$ is single exponential at temperatures above the critical temperature T_c . Below T_c , there is considerable nonexponentiality in the relaxation which is partly because of the difference in the dynamical behavior between the spins in large clusters and in small and isolated clusters. Thus, the dielectric relaxation is exponential above T_c , but nonexponential below T_c .

There have been two other interesting studies which need to be addressed here. The first one is the well-known lattice model calculation by Zwanzig¹⁷ of $\epsilon(\omega)$. In this model, point dipoles, fixed at lattice sites, are allowed to undergo rotational Brownian motion and at the same time interact with each other via dipolar interaction. Zwanzig calculated the first terms of a density expansion of $\epsilon(\omega)$ and demonstrated that the long range dipole-dipole interactions introduces a range of time scales all smaller than the rotational time.

In the second study, Shore and Zwanzig, calculated $C_M(t)$ for a model of electric dipoles perpendicular to the chain. Each dipole is free to rotate in the plane perpendicular to the chain and undergoes harmonic interactions with each other. The decay was found to be nonexponential, except at very short and very long times when the decay was exponential.

The result obtained in the present study differs from the previous ones in the exact exponential behavior of $C_M(t)$. We have several comments on this difference. Firstly, the difference may be a consequence of Glauber dynamics. Secondly, our solution of $\epsilon(k, \omega)$ is exact. Thirdly, the long-range nature of dipolar interactions are absent here. As discussed by Nee and Zwanzig,¹⁸ this long-range interaction give rise to a time varying reaction field which is responsible for nonexponential decay of $C_M(t)$. We have shown elsewhere¹⁹ that the translational modes of the liquid, if important, can reduce the impact of the reaction field and give back a single exponential decay.

As discussed earlier, even in higher dimensional Ising models with Glauber dynamics, we expect a simple Debye-like behavior for $\epsilon(\omega)$ and very different behavior for the single particle and the collective orientational correlation functions. In this connection we note that some progress with the two-dimensional Ising model with Glauber dynamics have been made by Montroll and Reiss.^{20,21} It might be interesting to use the results obtained there to gain a quantitative understanding of the dynamics of the orientational correlation functions. However, it seems that the exact analytical solution of the type presented here is not possible in the absence of a closed form expression for the spin-spin correlation function. Nevertheless, it is an interesting problem for future study.

It is important to realize that most of the previous calculations of various models of dielectric relaxation were approximate. The exact calculation presented here is, therefore, important. The breakdown of the macro-micro theorem, may be an artifact of the present model, is interesting on its own right.

¹ P. Madden and D. Kivelson, *Adv. Chem. Phys.* **56**, 467 (1984).

² B. Berne and Pecora, in *Dynamic Light Scattering* (Wiley, New York, 1976).

³ M. Evans, G. J. Evans, W. T. Coffey, and P. Grigolini, *Molecular Dynamics and Theory of Broad Band Spectroscopy* (Wiley, New York, 1982).

⁴ E. Pollock and B. Alder, *Phys. Rev. Lett.* **46**, 950 (1981).

⁵ D. Kivelson and P. Madden, *Mol. Phys.* **30**, 1749 (1975).

⁶ A. Chandra and B. Bagchi, *J. Phys. Chem.* **94**, 3152 (1990).

⁷ B. Bagchi, *Annu. Rev. Phys. Chem.* **40**, 115 (1989); A. Chandra and B. Bagchi, *J. Chem. Phys.* **91**, 1829 (1989).

⁸ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 116 (1963).

⁹ E. Pollock and B. Alder, *Annu. Rev. Phys. Chem.* **32**, 311 (1981).

¹⁰ R. Glauber, *J. Math. Phys.* **4**, 294 (1963).

¹¹ J. E. Shore and R. Zwanzig, *J. Chem. Phys.* **63**, 5445 (1975).

¹² J. L. Skinner, *J. Chem. Phys.* **79**, 1955 (1983); J. Budimir and J. L. Skinner, *ibid.* **82**, 5232 (1985).

¹³ S. H. Glarum, *J. Chem. Phys.* **33**, 639 (1960).

¹⁴ P. Bordewijk, *Chem. Phys. Lett.* **32**, 592 (1975).

¹⁵ D. W. Oxtoby, *Mol. Phys.* **34**, 987 (1977).

¹⁶ H. Reiss, *Chem. Phys.* **47**, 15 (1980).

¹⁷ R. Zwanzig, *J. Chem. Phys.* **38**, 2766 (1963).

¹⁸ T. W. Nee and R. Zwanzig, *J. Chem. Phys.* **52**, 6353 (1970).

¹⁹ B. Bagchi and A. Chandra, *Phys. Rev. Lett.* **64**, 455 (1990).

²⁰ E. W. Montroll, *Proc. Natl. Acad. Sci. USA* **78**, 36 (1981).

²¹ E. W. Montroll and H. Reiss, *Proc. Natl. Acad. Sci. USA* **78**, 2659 (1981).