On cooperative modes of reorientation in liquid crystals^{a)}

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The role of cooperative modes of reorientation in liquid crystals for the spectral densities of importance in magnetic resonance relaxation is examined from the viewpoint of microscopic models that can be solved analytically. These include linear arrays of rods in an applied external field whose orientations are strongly coupled and whose motion is described by overdamped and coupled diffusion equations. Also considered are Cayley-tree models, which, at least for nearest neighbors, can mimic higher dimensions than one. All these models lead to the result that the qth normal mode of relaxation has a decay rate that depends upon q as $\sin^2(qa/2)$, where a is the lattice spacing. Using simple scaling, it is argued that if a is replaced by $a' \equiv La$, so our model consists of blocks of L rodlike molecules with renormalized parameters, then molecular detail becomes less important and the model arrays become more physically representative. These results are then utilized to extend the standard hydrodynamic theory for long wave vectors q to short wave vectors approaching molecular dimension. The spectral densities obey scaling (i.e., are nearly independent of a') and are nearly identical to the hydrodynamic result for lower frequencies. However, the new results do show small departures at the higher frequencies usually studied by NMR.

I. INTRODUCTION

Cooperative modes of reorientation are now known to play an important role in the NMR relaxation of molecules in liquid crystals.¹⁻⁶ Their role in ESR relaxation is less clear, in part because of the higher frequency terms to be averaged in the ESR spin Hamiltonian.^{5,7} The theory utilized for calculating relaxation rates is based on the hydrodynamic model of director fluctuations^{8,9} as adapted for spin relaxation. $^{1-5,7,10,11}$ This is basically a theory appropriate for low wave vector **q** such that molecular details are unimportant and the liquid crystalline phase may be treated as a continuum. Nevertheless, the theory is typically used for large q with only the restriction of a cutoff $\mathbf{q}_c \equiv 2\pi/a$ where a is of molecular dimension. This is a rather arbitrary and uncertain procedure. Can the low q limit even be extended to moderate values of q, and how do the high q modes go into the localized (but cooperative) modes of reorientation of individual molecules? The latter question was discussed previously⁵ in terms of a generalized Fokker-Planck equation which describes individual molecular reorientation in the field of the instantaneous value of the director, while the director relaxes on a slower time scale according to the hydrodynamic theory.

In this work, we explore a different point of view to examine the first question in an attempt to improve the model of the director fluctuations for obtaining the spectral densities needed for magnetic resonance relaxation. We base our considerations on simple physical models which have the virtue of being amenable to analytical solution.

Our simplest model is based upon the solution to the rotational diffusion of a linear array of rigid rods whose

orientations are strongly coupled to their next nearest neighbors. When this coupling is strong enough, this becomes a system of torsional oscillators engaged in Brownian diffusion, the mathematical solution of which is well known¹² and has appeared in recent work on polymer chain dynamics.^{13,14} We make use of these mathematically related treatments, although we use a somewhat more compact formalism. We also introduce the aligning effects of a constant external field (e.g., a magnetic field) to guarantee long-range order of the chains.

Unrealistic features of this model, if we were to identify the hard rods of the model with actual liquid crystalline molecules are: (1) the actual molecules can reorient by large angles, although our model rods are constrained to small torsional motions; (2) the actual molecules can translate, while the rods are taken as forming a fixed array; (3) the actual molecules are flexible and have many internal modes of motion. Thus, we do not claim any physical value for our model on the actual molecular level. Instead, we introduce simple scaling and renormalization concepts^{15(a)} leading to the point of view that this model is useful for blocks of actual molecules which, if large enough, would remove molecular detail so that features (1)-(3) are no longer problems.

The matter of dimensionality is also important. Analytical solutions are readily achieved for onedimensional arrays, but we were not able to solve regular two and three-dimensional models. Instead, we resort to Cayley tree models, ^{15(b)} which are mathematical constructs that can mimic, at least for nearest neighbors, two- or three-dimensional behavior. The Cayley tree lattice models are more amenable to analytic solution and we discuss our solutions. What does emerge from a consideration of these models is a strong suggestion that features of the one-dimensional solution should carry over to two and three dimensions with only minor changes. On the basis of this we propose an ex-

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pression for three-dimensional spectral densities from director fluctuations.

The main feature which emerges from the models considered is that the free energy as well as the relaxation terms should depend upon \mathbf{q} as $\sin^2(a'/2)q$, where a' is a scaling length, instead of the q^2 dependence predicted by hydrodynamic theory. Since our models are not rigorously three dimensional, but they do reduce to the q^2 dependences of the hydrodynamic theory, we view our approach as suggesting a functional dependence upon \mathbf{q} to extend the well-established hydrodynamic theory for low \mathbf{q} to higher values of \mathbf{q} approaching (but not necessarily equal to) molecular dimensions.

The resulting spectral-densities $J(\omega)$ obtained with the $\sin^2(a'/2)q$ functional form agree quite well with the hydrodynamic result for low frequencies $(\omega/2\pi)$ \lesssim 1 MHz as they should. In the range of 1-100 MHz, which is currently studied by NMR, ¹⁻⁶ differences of nearly a factor of 2 may be observed in the limit of very slowly diffusing molecules. The effect of including finite translational diffusion of the molecules is to reduce differences between the predictions for the lower frequencies, but to enhance somewhat the high-frequency (asymptotic) results by $\sim 50\%$ in the present case. Careful experiments would be needed to distinguish such differences, but it might possibly be that more detailed models could lead to more substantial effects. We point out that some of the analytic methods employed in the analysis of the Cayley tree model could, e.g., be adapted to numerical studies of large regular two- and three-dimensional arrays of coupled Brownian torsional oscillators.

Faber¹⁶ has tried to deal with the present subject from the Debye point of view. He uses a continuum model based upon extending the hydrodynamic limit but with a cutoff in the spectrum of modes determined by the total number of molecules. A fundamental flaw with the Debye approach to distortion modes in liquid crystals and noted by Faber is the presence of large fluctuations, i.e., of finite rotations of the molecules, which preclude a simple independent mode approach. Our approach may instead be thought of as replacing the hydrodynamic continuum with a simple limiting molecular model, and this is the source of the different q dependence of the modes. The difficulties encountered by Faber in dealing with substantial disorder on a molecular level, because he, following Debye, deals with all 2Nmodes by continuum theory, are instead formally dealt with here by the renormalized blocks of molecules whose properties are simpler. Thus, we can still allow for additional degrees of freedom within each block for the more complex motions on a molecular level. We believe our approach clarifies these aspects of the problem.

The matter of localized cooperative modes, for which molecular detail is relevant, is dealt with in another work, ¹⁷ where we introduce the dynamic cluster model for liquid crystals, and we also consider the coupling of the short-range (or localized) and long-range (or hydrodynamic) cooperativity along lines previously discussed. In Sec. II, we introduce and solve the model of coupled torsional diffusion of a linear chain of rods in an applied static field. The angular autocorrelation function and spectral density for this model are obtained in Sec. III, while the Cayley tree model is discussed in Sec. IV. Renormalization and scaling is introduced in Sec. V, and the modified three-dimensional spectral density appears in Sec. VI, where it is compared to the hydrodynamic results. Concluding remarks appear in Sec. VII.

II. COUPLED ROTATIONAL DIFFUSION IN AN APPLIED STATIC FIELD

Consider a fixed, linear array of N+1 identical rigid rods that are equally spaced along the x axis (i.e., a separation distance of a). The rotational motion of each rod has only a single degree of freedom correponding to rotation about an axis parallel to the y axis and passing through the center of the rod. The orientation of the *i*th rod is described by the angle θ_i $(-\pi \le \theta_i \le \pi)$ which is the angle between the major axis of the *i*th rod and a fixed reference axis parallel to the z axis. Assuming that each rod is coupled to a bath of particles which is constantly held at thermal equilibrium, and the coupled rotational motion of the rods is overdamped so we can neglect their angular velocities (for times longer than their relaxation time¹⁸) then we can express the motion of this system through the multidimensional conditional probability $P(\theta^{\circ} | \theta, t)$ which satisfies the Smoluchowski equation. 12-14

$$\frac{\partial P(\boldsymbol{\theta}^{\circ} \mid \boldsymbol{\theta}, t)}{\partial t} = R \nabla_{\boldsymbol{\theta}} \cdot \left[\nabla_{\boldsymbol{\theta}} P(\boldsymbol{\theta}^{\circ} \mid \boldsymbol{\theta}, t) + \beta P(\boldsymbol{\theta}^{\circ} \mid \boldsymbol{\theta}, t) \nabla_{\boldsymbol{\theta}} U(\boldsymbol{\theta}) \right].$$
(1)

Here θ is an N+1 dimensional vector whose components are the $\{\theta_i\}$, while $P(\theta^\circ | \theta, t)$ is the probability that the system of rods will be found in the orientation $\theta = \{\theta_i\}$ at time t if the system is in the orientation θ° at t = 0. Also, R is the rotational diffusion coefficient and $\beta = 1/k_B T$, ∇_{θ} is the divergence operator in the N+1dimensional space spanned all by the θ_i . $U(\theta)$ is an angular dependent potential, which, in this model, can be chosen to have the following form:

$$U(\boldsymbol{\theta}) = U_{int}(\boldsymbol{\theta}) + U_{ext}(\boldsymbol{\theta}) , \qquad (2)$$

where $U_{int}(\theta)$ represents the potential energy due to coupling of the relative orientations of next nearest neighbors, which we write as

$$U_{int}(\theta) = -\epsilon_{int} \sum_{i=1}^{N-1} \cos^2 \theta_{i,i+1} , \qquad (3)$$

where $\theta_{i_i,i+1} \equiv \theta_{i+1} - \theta_i$ and represents the relative angle of rotation between the *i*th and *i* + 1th rod. $U_{ext}(\theta)$ represents the potential energy due to the energy of interaction of the rods with a static electric or magnetic field aligned parallel to the reference *z* axis, and we write it as

$$U_{\text{ext}}(\theta) = -\epsilon_{\text{ext}} \sum_{i=0}^{N} \cos^2 \theta_i .$$
 (4)

Since $\theta_i \approx \theta_{i\pm 1}$ is an energetically favorable orientation, then it follows $\epsilon_{int} > 0$, as in a model employing ferromagnetic interactions. Similarly, we let $\epsilon_{ext} > 0$, so $\theta_i \approx 0$ is preferred. In the limit that rod-rod and rodfield coupling allows only small angular deviations in each θ_i we can approximate $\cos^2 \theta_i \approx 1 - \theta_i^2$ and $\cos^2 \theta_{ij}$ $\approx 1 - \theta_{ij}^2$. The linearized force on the *i*th rod then can be written using Eqs. (3) and (4) as

$$f_{i}(\boldsymbol{\theta}) = \left(-\frac{\partial U(\boldsymbol{\theta})}{\partial \theta_{i}}\right)_{\boldsymbol{\theta}_{j\neq i}} = -2\left[\left(2\epsilon_{\mathrm{int}} + \epsilon_{\mathrm{ext}}\right)\theta_{i} - \epsilon_{\mathrm{int}}\left(\theta_{i+1} + \theta_{i-1}\right)\right].$$
(5)

From Eq. (5) we can define the quantities $\hat{\epsilon} = 2\beta R \epsilon_{int}$ and $\hat{\epsilon}' = 2\beta R \epsilon_{ext}$ each having units s⁻¹. The linearized form of Eq. (1) now becomes

$$\frac{\partial P}{\partial t} = (\partial/\partial \theta)^T \cdot [R(\partial P/\partial \theta) + P\mathbf{A}'\theta], \qquad (6)$$

where $P = P(\theta^{\circ} | \theta, t)$; $(\partial/\partial \theta)$ is an N+1 dimensional column vector with components $(\partial/\partial \theta_i)$; θ is an N+1 dimensional column vector with components θ_i ; and the matrix $\mathbf{A}' = (\hat{\mathbf{c}}\mathbf{A} + \hat{\mathbf{c}}'\mathbf{1})$ where \mathbf{A} is the coupling matrix which has elements $A_{00} = A_{NN} = 1$, $A_{ii} = 2$ (for $2 \le i \le N-1$) and $A_{i,i+1} = -1$, with all other elements equal to zero. **1** is the N+1 dimensional unit matrix.

The matrix A' is a tridiagonal matrix (nearly in a Toeplitz form) which can be diagonalized by the orthogonal transformation Q whose elements are¹⁴

$$Q_{jk} = \sqrt{2/(N+1)} \begin{cases} 1/\sqrt{2}, & k=0, \\ \cos[k\pi(j+\frac{1}{2})/(N+1)], & 1 \le k \le N. \end{cases}$$
(7)

The columns of \mathbf{Q} constitute the eigenvectors of \mathbf{A}' . In this model, both ends of the linear array of rods are free, i.e., there are no external constraints on them. This seems reasonable for modeling effects in the bulk. However, an alternate model can be developed by using periodic boundary conditions, i.e., by requiring the (N+1)th rod to exhibit the same motion as the first, and the results for this model are included in Appendix A. Of course, as we let $N \rightarrow \infty$, differences due to different boundary conditions should become unimportant. Then Eq. (6) can be written in terms of the N+1 normal coordinates $\boldsymbol{\xi} = \mathbf{Q}^{-1}\boldsymbol{\theta}$ as¹²⁻¹⁴

$$\frac{\partial P}{\partial t} = \sum_{k=0}^{n} \left[R \; \frac{\partial^2 P}{\partial \xi_k^2} + \mu_k \; \frac{\partial(\xi_k P)}{\partial \xi_k} \right] \quad , \tag{8}$$

where now $P = P(\xi^{\circ} | \xi, t)$ and $\xi = \{\xi_k\}$. That is, $P(\xi^{\circ} | \xi, t)$ is the probability that the system of rods will be found in the orientation ξ at time t if it is in the orientation ξ° at t = 0. The N+1 eigenvalues of A' are

$$\mu_k = 4\hat{\epsilon} \sin^2[k\pi/2(N+1)] + \hat{\epsilon}', \quad 0 \le k \le N$$
(9)

for the free boundary conditions. The solution to Eq. (8) is separable in the normal mode coordinates and is

$$P(\boldsymbol{\xi}^{\circ} | \boldsymbol{\xi}, t) = \prod_{k=0}^{n} \phi_{k}(\boldsymbol{\xi}_{k}^{\circ} | \boldsymbol{\xi}_{k}, t) , \qquad (10)$$

where¹²⁻¹⁴

$$\phi_{k}(\xi_{k}^{\circ}|\xi_{k},t) = [(\mu_{k}/2\pi R)/(1 - \exp(-2\mu_{k}t))]^{1/2} \\ \times \exp[-(\mu_{k}/2R)(\xi_{k} - \overline{\xi}_{k})^{2}/(1 - \exp(-\mu_{k}t))]$$
(11)

and $\overline{\xi}_k = \xi_k^{\circ} \exp(-\mu_k t)$. The equilibrium limit, $t \to \infty$ on Eq. (11) is

$$\phi_{k}^{eq}(\xi_{k}) = \phi_{k}(\xi_{k}^{o} | \xi_{k}^{o}) = (\mu_{k}/2\pi R)^{1/2} \exp[-(\mu_{k}/2R)\xi_{k}^{2}].$$
(12)

Thus, each normal mode behaves as an independent Gaussian random process, that is characteristic of the overdamped Brownian harmonic oscillator. In constructing this solution, we have allowed the θ_i to vary from $-\infty$ to $+\infty$ instead of just $-\pi$ to $+\pi$, which is permissible since the probability of large deviations from $\theta_i = 0$ is negligible. The complete equilibrium solution to Eq. (8) is

$$P_{eq}(\boldsymbol{\xi}^{\circ}) \equiv P(\boldsymbol{\xi}^{\circ} | \boldsymbol{\xi}, \infty) = Z \exp\left[-\left(\frac{1}{2}R\right) \sum_{k=0}^{N} \mu_{k} \boldsymbol{\xi}_{k}^{2}\right]$$
(13)

with the normalization factor $Z = \prod_{k=0}^{N} (\mu_k/2\pi R)^{1/2}$. Finally, we note that we can obtain $P(\theta^\circ | \theta, t)$ from $P(\xi^\circ | \xi, t)$ according to

$$P(\boldsymbol{\xi}^{\circ} | \boldsymbol{\xi}, t) = P(\mathbf{Q}^{-1}\boldsymbol{\theta}^{\circ} | \mathbf{Q}^{-1}\boldsymbol{\theta}, t) = P(\boldsymbol{\theta}^{\circ} | \boldsymbol{\theta}, t) , \qquad (14)$$

where the first equality follows from the linear transformation from the ξ to the Q, and the second equality states simply that the conditional probability is now expressed as a function of the independent variables θ° and θ .

It has been shown^{5,7} that Eq. (8) may be solved for each $\phi_k(\xi_k^\circ|\xi_k,t)$ in terms of its eigenfunctions which are the Hermite functions. This is obtained by writing the differential equation obeyed by each $\phi_k(\xi_k^\circ|\xi_k,t)$ as

$$\dot{\phi}_k = L_k \phi_k , \qquad (15a)$$

where

$$L_{k} \equiv R \frac{\partial^{2}}{\partial \xi_{k}^{2}} + \mu_{k} \frac{\partial}{\partial \xi_{k}} \xi_{k} .$$
 (15b)

and "symmetrizing" the operator L_k by the following transformation:

$$\tilde{L}_{k} = (\phi_{k_{*} \text{ eq}})^{-1/2} L_{k} (\phi_{k_{*} \text{ eq}})^{1/2} = R \frac{\partial^{2}}{\partial \xi_{k}^{2}} + \frac{\mu_{k}}{2} \left(1 - \frac{\mu_{k}}{2R} \xi_{k}^{2} \right),$$
(16)

where $\tilde{L}_{k}\phi_{k,eq}^{1/2} = 0$. Then the solutions of the eigenvalue problem

$$\tilde{L}_{k}\psi_{n_{k}} = E_{n_{k}}\psi_{nk} \tag{17}$$

are given by the Hermite functions

$$\psi_{n_k}(\xi_k) = N_{n_k} \exp(-\mu_k \, \xi_k^2 / 4R) \, H_{n_k} \left(\frac{\mu_k}{2R} \Big|^{1/2} \xi_k \right) \,, \qquad (18)$$

where $H_n(x)$ are the Hermite polynomials and

$$N_{n_k} = ([\mu_k/2R]^{1/2}/\sqrt{\pi}2^n k n_k!)^{1/2}$$

and $E_{n_k} = n_k \mu_k$. The conditional probability for the ξ_k th mode is then written as the Green's function,

$$\phi_{k}(\xi_{k}^{\circ}|\xi_{k},t) = \exp\left[-\tilde{L}_{k}t\right]\delta(\xi_{k}-\xi_{k}^{\circ})$$
(19)

or, by use of the eigenfunction representation of the Dirac delta function and from the above results,

$$\phi_{k}^{\circ}(\xi_{k}^{\circ}|\xi_{k},t) = \sum_{n_{k}=0}^{\infty} \exp[-n_{k}\mu_{k}t]|n_{k}\rangle\langle n_{k}^{\circ}| \qquad (20)$$

using

$$|n_{k}\rangle = \left|\phi_{k}^{\text{eq }1/2}\psi_{n_{k}}(\xi_{k})\right\rangle$$
(21a)

and

$$\langle n_k | = \langle \phi_k^{eq-1/2} \psi_{n_k}(\xi_k) |$$
(21b)

and noting $\langle n_j | L_k | n_l \rangle = E_{n_k} \delta_{k,l} \delta_{k,j}$. From Eqs. (10) and (20) we have the solution to the complete conditional probability in the form

$$P(\xi^{\circ} | \xi, t) = \sum_{n_0=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} c_{n_0\cdots n_N} | n_0 \cdots n_N \rangle \langle n_0^{\circ} \cdots n_N^{\circ} |$$
$$= \sum c_n | n \rangle \langle n^{\circ} | , \qquad (22)$$

where we have used the product states of the normal modes, denoted by

$$|\mathbf{n}\rangle = |n_0 \cdots n_N\rangle = |n_0\rangle |n_1\rangle \cdots |n_N\rangle$$

and

$$c_{\mathbf{n}} = c_{n_0 \cdots n_N}(t) \equiv \exp\left[-\sum_{k=0}^N n_k \mu_k t\right] \,.$$

The equivalence of Eq. (20) with Eq. (11) is shown in Appendix B.

III. THE ANGULAR AUTOCORRELATION FUNCTION

We now calculate the correlation function:

$$G_{ii}(t) = \langle \theta'_i(\tau)\theta'_i(t+\tau)\rangle = \langle \theta_i(\tau)\theta_i(t+\tau)\rangle - \langle \theta_i^2\rangle , \qquad (23)$$

where $\theta'_i(t) \equiv \theta_i(t) - \langle \theta_i \rangle$ and the angular brackets indicate ensemble averages. The explicit form of the averages is given by

$$G_{ii}(t) = \int d\theta_i \int d\theta_i^{\circ} \theta_i^{\prime} W(\theta_i^{\circ}, \theta_i, t) \theta_i^{\circ \prime} . \qquad (24)$$

The reduced distribution function $W(\theta_i^\circ, \theta_i, t)$ is given by

$$W(\theta_i^{\circ}, \theta_i, t) = \int' d\theta \int' d\theta^{\circ} P(\theta^{\circ} | \theta, t) P_{eq}(\theta^{\circ}) , \qquad (25)$$

where the prime on the multiple integrals excludes integrating over θ_i and θ_i° . It is easier to use the equivalent expressions in terms of the normal mode coordinates ξ° and ξ [cf., Eq. (14)]. Thus we have

$$G(t) = \int d\boldsymbol{\xi} \int d\boldsymbol{\xi}^{\circ} P(\boldsymbol{\xi}^{\circ} | \boldsymbol{\xi}, t) \, \theta^{\circ} \, \theta P_{eq}(\boldsymbol{\xi}^{\circ}) - \left[\int d\boldsymbol{\xi}^{\circ} \, \theta^{\circ} \, P_{eq}(\boldsymbol{\xi}^{\circ}) \right]^{2} ,$$
(26)

which may alternatively be written in terms of the bra-ket notation of Eq. (22) as

$$G(t) = \sum_{\mathbf{n}}' \exp(-E_n t) \left| \left\langle \mathbf{0} \right| \theta \left| \mathbf{n} \right\rangle \right|^2$$
(27)

with

$$\sum_{\mathbf{n}}' \equiv \sum_{n_0} \sum_{n_1} \cdots \sum_{n_N}$$

while

$$E_n = \sum_{k=0}^N E_{n_k}$$

The prime on the multiple summation carries the restriction $|\mathbf{n}\rangle \neq |\mathbf{0}\rangle$, where $|\mathbf{0}\rangle$ designates the product of the ground state eigenfunctions of each rod, i.e., n_0 = 0, n_1 = 0..., n_N = 0. We now write θ_i in terms of the ξ_k as

$$\theta_i = \sum_k Q_{ik} \xi_k \tag{28}$$

and we use Eq. (7) for the Q_{ik} . For a rod in the bulk, we can, without loss of generality let i = N/2 with N even for the free boundary conditions, so Eq. (7) becomes

$$\theta_{N/2} \equiv \theta = \xi_0 / \sqrt{N+1} + \sqrt{2/(N+1)} \sum_{\substack{k=2\\ \text{even}}}^{N} (-1)^{k/2} \xi_k \qquad (29)$$

since the N/2th rod will be a node in the standing wave modes of k odd. Then (irrespective of boundary conditions and noting $\mu_k > 0$) we rewrite ξ_k in terms of the raising and lowering operators $R_{k,k}$:

$$\xi_{k} = \left(\frac{R}{\mu_{k}}\right)^{1/2} (R_{k^{*}} + R_{k^{*}}) , \qquad (30)$$

with

$$R_{k^*} | n_k \rangle = \sqrt{n_k + 1} | n_k + 1 \rangle , \qquad (31a)$$

and

$$R_{k-} | n_{k} \rangle = \sqrt{n_{k}} | n_{k} - 1 \rangle . \tag{31b}$$

Thus, from Eq. (29) we have

$$\langle \mathbf{0} \mid \boldsymbol{\theta} \mid \mathbf{n} \rangle = \sum_{k=0}^{N} T_{k} \langle \mathbf{0} \mid (\boldsymbol{R}_{k^{*}} + \boldsymbol{R}_{k^{*}}) \mid \mathbf{n} \rangle$$
(32)

with

$$T_{k} = (-1)^{k/2} \left[(R/\mu_{k})(2 - \delta_{k_{0}}) / (N+1) \right]^{1/2} .$$
(33)

Now

$$\langle \mathbf{0}_{k} | (\mathbf{R}_{k^{\bullet}} + \mathbf{R}_{k^{\bullet}}) | \mathbf{n}_{k} \rangle = \langle \mathbf{0}_{k} | \mathbf{R}_{k^{\bullet}} | \mathbf{1}_{k} \rangle \delta_{\mathbf{n}_{k^{\bullet}} \mathbf{1}_{k}} = \delta_{\mathbf{n}_{k^{\bullet}} \mathbf{1}_{k}} .$$
(34)

This shows that only singly excited states of $|n\rangle$ such as $|0, 0, \ldots, 1, \ldots, 0\rangle$ contribute, so

$$|\langle \mathbf{0} | \boldsymbol{\theta} | \mathbf{n} \rangle|^2 = T_k^2 \,\delta_{n_0,0} \delta_{n_1,0} \cdots \delta_{n_k,1} \cdots \delta_{n_N,0} \,.$$

Thus, we obtain

$$G(t) = R \exp(-\hat{\epsilon}' t) / \hat{\epsilon}' (N+1) + [2R/(N+1)] \sum_{\substack{k=2\\ \text{even}}}^{N} \exp(-\mu_k t) / \mu_k$$
(35)

It also follows from Eq. (32) that $\langle \theta \rangle = \langle \mathbf{0} | \theta | \mathbf{0} \rangle = \mathbf{0}$. The mean-square fluctuation $\langle \theta^2 \rangle$ is given by

$$\langle \theta^2 \rangle = \sum_{\mathbf{n}} \langle \mathbf{0} | \theta | \mathbf{n} \rangle \langle \mathbf{n} | \theta | \mathbf{0} \rangle$$
$$= G(\mathbf{0}) = \left[R / (N+1) \hat{\mathbf{\epsilon}}' \right] \left[1 + 2 \hat{\mathbf{\epsilon}}' \sum_{\substack{k=2\\ k \neq n}}^{N} \mu_k^{-1} \right] \quad . \tag{36}$$

In the limit of $\hat{\epsilon}' \rightarrow 0$, i.e., no external field, then $\mu_0 = 0$ [cf. Eq. (9)], and the ξ_0 mode follows simple rotational diffusion [cf. Eq. (8)] with eigenvectors $(1/\sqrt{2\pi}) \exp(i\epsilon_0 n_0/\sqrt{N+1})$ which are orthonormal over the range

$$0 \le \xi_0 \le \xi_{0, \max} = (1/\sqrt{N+1}) \sum_j \theta_{j, \max} = 2\pi \sqrt{N+1} .$$

The eigenvalues are immediately found to be $E_{n_0} = n_0^2 R/(N+1)$. (The ξ_k for $k \neq 0$ still represent torsional modes.) Thus, we consider the correlation function

 $g_m(t) = \langle \exp(-im\theta(\tau)) \exp(+im\theta(t+\tau)) \rangle$

$$\cong \langle \exp(-im\xi_0(\tau)/\sqrt{N+1}) \exp[im\xi_0(t+\tau)/\sqrt{N+1}] \rangle \\ \times \left(1 + \frac{2m^2}{N+1}\right) \sum_{\substack{k=2\\ k \neq n}}^{N} \langle \xi_k(\tau)\xi_k(t+\tau) \rangle$$
(37)

and we obtain for $N \gg 1$,

$$g_{m}(t) = \exp(-m^{2}Rt/N) \left\{ 1 + \left[2m^{2}R/(N+1) \right] \sum_{k=2}^{N} \exp(-\mu_{k}'t)/\mu_{k}' \right\}$$
(38)

with $\mu'_k = \mu_k(\hat{\epsilon}' = 0)$. Comparing Eq. (38) with Eq. (35) we see that the two cases lead to correlation functions with somewhat similar structures.

Taking now the limit $N \rightarrow \infty$, we approximate the summation over k in Eq. (35) by an integral using the trapezoidal rule. [We also use the identity $\int_{t}^{t} \exp(-\mu_{k}t') dt' = \exp(-\mu_{k}t)/\mu_{k}$ in Eq. (35).] We

 $f_t \exp(-\mu_k t) a t \approx \exp(-\mu_k t)/\mu_k \ln Eq. (35).$ we obtain¹⁹

$$\lim_{N\to\infty} G(t) = R \int_t^{\infty} \exp\left[-\left(2\hat{\boldsymbol{\epsilon}} + \hat{\boldsymbol{\epsilon}}'\right)t'\right] I_0(2\hat{\boldsymbol{\epsilon}}t') dt', \quad (39)$$

where $I_0(z)$ is the zero order modified Bessel function.

In the limit of short times we can write the integral of Eq. (39) as $\int_0^{\infty} -\int_0^{t}$ and expand the Bessel function in the range of $2\hat{\epsilon}t \ll 1$. For longer times Eq. (39) can be used directly. In summary,

$$R\left\{ \begin{bmatrix} \hat{\epsilon}'(4\hat{\epsilon} + \hat{\epsilon}') \end{bmatrix}^{-1/2} - t \right\}, \quad \hat{\epsilon}t \ll 1$$
$$\hat{\epsilon}'t \ll 1$$
$$\lim_{N \to \infty} G(t) = \frac{R}{2\sqrt{\hat{\epsilon}\hat{\epsilon}'}} \operatorname{erfc}(\sqrt{\hat{\epsilon}'t}), \quad \hat{\epsilon}t > 1,$$
$$\hat{\epsilon}'t > 1 \qquad (40)$$
$$\frac{R}{2\sqrt{\hat{\epsilon}\hat{\epsilon}'}} \frac{\exp(-\hat{\epsilon}'t)}{\sqrt{\pi\hat{\epsilon}'t}}, \quad \hat{\epsilon}t \gg 1$$

From Eq. (40) we have for $\lim_{N\to\infty} \langle \theta^2 \rangle$,

$$\left\langle \theta^2 \right\rangle = G(0) = R[\hat{\epsilon}'(4\hat{\epsilon} + \hat{\epsilon}')]^{-1/2} \tag{41}$$

and from Eqs. (39) and (40) we find the relative correlation function for $\epsilon' t$, $\epsilon t > 1$,

$$\lim_{N\to\infty} G(t)/G(0) \cong \frac{1}{2} \left[(4\hat{\epsilon} + \hat{\epsilon}')/\hat{\epsilon} \right]^{1/2} \operatorname{erfc}(\sqrt{\hat{\epsilon}' t}) , \qquad (42)$$

which yields for $4\hat{\boldsymbol{\epsilon}} \gg \hat{\boldsymbol{\epsilon}}'$ the simple form,

$$\lim_{N\to\infty} G(t)/G(0) = \operatorname{erfc}(\sqrt{\epsilon' t}), \quad \epsilon' t > 1.$$
(43)

The spectral density follows easily using Eq. (35). By definition

$$J(\omega) = 2 \operatorname{Re} \int_0^\infty \exp(-i\omega t) \langle \theta(t)\theta(0) \rangle dt .$$
 (44)

Thus

$$J(\omega) = 2 \operatorname{Re} \left\{ \frac{R}{[N+1]} \hat{\epsilon}'(\hat{\epsilon}' + i\omega)^{-1} \right] \\ + \left[\frac{2R}{N+1} \right] \sum_{\substack{k=2\\k \text{ or } n}}^{N} \left[\mu_{k}^{-1}(\mu_{k} + i\omega)^{-1} \right] \right\} .$$
(45)

In the $N \rightarrow \infty$ limit we have from Eq. (39),

$$J(\omega) = 2 \operatorname{Re} \int_{0}^{\infty} \exp(-i\omega t) \left[A - R \int_{0}^{t} \exp[-(2\hat{\epsilon} + \hat{\epsilon}')t'] \times I_{0}(2\hat{\epsilon}t') dt' \right] dt$$
(46)

with the real constant $A = R[\hat{\epsilon}'(4\hat{\epsilon} + \hat{\epsilon}')]^{-1/2}$.

Equation (46) simplifies by using the properties of the Laplace transform, and recognizing that the integral of the constant term A is pure imaginary. This leaves

$$J(\omega) = 2\operatorname{Re}\left\{\frac{iR}{\omega[(i\omega+2\hat{\epsilon}+\hat{\epsilon}')^2-4\hat{\epsilon}^2]^{1/2}}\right\} \quad \text{for } \hat{\epsilon}' > 0.$$
(47)

The apparent divergence as $\omega \rightarrow 0$ in Eq. (47) vanishes by rewriting $J(\omega)$ in the form

$$J(\omega) = 2R \operatorname{Re}\left\{\frac{i}{\omega} \left[\frac{(\hat{\epsilon}'B - \omega^2) - i\omega(B + \hat{\epsilon}')}{(\hat{\epsilon}'^2 + \omega^2)(B^2 + \omega^2)}\right]^{1/2}\right\}$$
(48)

with $B = 4\hat{\epsilon} + \hat{\epsilon}'$. This expression is simplified by taking the complex square root of the numerator. This can be evaluated approximately at low frequencies, for $|\omega(B + \hat{\epsilon}')/(\hat{\epsilon}'B - \omega^2)| \ll 1$,

$$J(\omega) \cong R \left[\frac{(B+\hat{\epsilon}')}{(\hat{\epsilon}'B-\omega^2)^{1/2}} \right] \left[\frac{1}{(\hat{\epsilon}'^2+\omega^2)(B^2+\omega^2)} \right]^{1/2}$$
(49)

and thus:

$$J(0) = R(B + \hat{\epsilon}')(\hat{\epsilon}'B)^{-3/2} .$$
 (50)

In the range $\hat{\epsilon}' \ll \omega \ll \hat{\epsilon}$ one obtains from Eq. (48) that

$$J(\omega) \approx \frac{R}{\omega} \left(\frac{2}{\omega\hat{\epsilon}}\right)^{1/2} , \qquad (51)$$

while for $\omega \gg \hat{\epsilon}$, $\hat{\epsilon}'$ one has

$$J(\omega) \approx 2R/\omega^2 . \tag{52}$$

When we come to two and three dimensional cases, we find realistic models already pose significant difficulties in obtaining an analytic solution. Instead, we discuss Cayley tree versions in the next section.

IV. CAYLEY TREE ARRAYS

We now generalize the one-dimensional case by means of a Cayley tree model, ¹⁶ also known as a Bethe lattice. We start with a particular rod labeled 0.²¹ Rods $1, 2, \ldots, K+1$ are the K+1 nearest neighbors of rod zero and they form the first shell S_1 consisting of first nearest neighbors of rod 0. Each rod in S_1 also has K+1 nearest neighbors: rod 0, and K rods in S_2 , the second-nearest neighbors of rod 0. Each rod in S_2 is a nearest neighbor of only one site in S_1 . This structure continues to branch K times for each rod in S_n and never turns back on itself, so that rods in S_n couple only to rods in S_{n-1} and S_{n+1} (and no rods in S_n are nearest neighbors of other rods in S_{n}). This lattice is homogeneous because each rod could act as the original rod with K+1 nearest neighbors. In this sense the model is like some multidimensional array which is locally like some real geometric array of rods. For this model we may rewrite Eq. (3) as

$$U_{\text{int}}(\hat{\theta}) = -\epsilon_{\text{int}} \sum_{i < j}^{N-1} \cos^2 \theta_{i,j} \Delta(i,j) , \qquad (53)$$

where $\Delta(i,j) = 1$ if *i* and *j* are nearest neighbors and $\Delta(i,j) = 0$ if they are not. The linearized force on rod *i* becomes [cf. Eq. (5)]

$$F_{i}(\hat{\theta}) = -2\left\{ \left[(K+1)\epsilon_{int} + \epsilon_{ext} \right] \theta_{i} - \epsilon_{int} \sum_{j} \theta_{j} \Delta(i,j) \right\} .$$
 (54)

A one-dimensional linear array corresponds to K=1 [cf. Eq. (5)]. For K>1, the coupling matrix **A** is no longer tri-diagonal but it may be transformed to tri-diagonal form by an orthogonal transformation based on the Lanczos algorithm.²⁰ The new vectors (or modes) can be written in terms of the original θ_i according to

$$u_{0} = \theta_{0} ,$$

$$u_{1} = (K+1)^{-1/2} \sum_{i \text{ in } S_{1}} \theta_{i} ,$$

$$u_{n} = [(K+1)K^{n-1}]^{-1/2} \sum_{i \text{ in } S_{n}} \theta_{j} .$$
(55)

Thus, in this basis only the single completely symmetric linear combination of the θ_i in the S_n th shell couples to θ_0 . The tri-diagonal matrix in this basis has diagonal elements $A_{ii} = K + 1$ for all *i* and off-diagonal elements $A_{0,1} = A_{1,0} = -\sqrt{K+1}$ and all other $A_{i,i\pm 1} = -\sqrt{K}$. This particular form of **A** corresponds to a fixed boundary condition instead of the free boundary condition used in the one-dimensional case (cf. Sec. II).²¹ The modes u which couple to $u_0 = \theta_0$ will then obey a diffusion equation very similar to Eq. (6), in particular,

$$\frac{\partial P}{\partial t} = (\partial/\partial \mathbf{u})^T \cdot [R(\partial P/\partial \mathbf{u}) + P\mathbf{A'}\mathbf{u}] , \qquad (56)$$

where $P = P(\mathbf{u}^{\circ} | \mathbf{u}, t)$ and $\mathbf{A}' = (\hat{\boldsymbol{\epsilon}} \mathbf{A} + \hat{\boldsymbol{\epsilon}}' \mathbf{1})$ with \mathbf{A} as given here.

No simple analytic method²¹ was found to diagonalize the $(N+1) \times (N+1)$ matrix **A** for arbitrary K when treating an N shell (i.e., S_1, \ldots, S_N) Cayley tree model. However, rigorous bounds on the eigenvalues $\lambda = (\lambda_0, \lambda_1, \ldots, \lambda_N)$ of **A** can be derived by the use of the "escalator" method of Morris²² and Fox.²³ First, consider the $N \times N$ Toeplitz matrix **W** having elements $W_{ii} = K + 1$ and $W_{i,i\pm 1} = -\sqrt{K}$ with all other $W_{i,j} = 0$. The distinct eigenvalues of **W** are (cf. Rutherford²¹)

$$\mu_{k} = (K+1-2\sqrt{K}) + 4\sqrt{K}\sin^{2}\frac{k\pi}{2(N+1)} \qquad \text{for } k=1,\ldots,N ,$$
(57)

where $\mu_N > \cdots > \mu_1$ and the N components of the eigenvectors $Z^{(k)}$ corresponding to the kth eigenvalue and expressed in terms of the basis vectors of Eq. (55) are¹³

$$Z_m^{(k)} = Z_{mk} = \sqrt{2/N} \sin\left(\frac{\pi km}{N+1}\right) \qquad \text{for } m = 1, \dots, N.$$
 (58)

so Z is the diagonalizing transformation. Secondly, write the eigenvalue problem $A\mathbf{x} = \lambda \mathbf{x}$ in partitioned form as

$$\begin{bmatrix} K+1 & -\sqrt{K+1} \\ -\sqrt{K+1} & \mathbf{W} \end{bmatrix} \begin{bmatrix} \eta \\ \boldsymbol{\xi} \end{bmatrix} = \lambda \begin{bmatrix} \eta \\ \boldsymbol{\xi} \end{bmatrix}$$

which upon inspection yields the characteristic value equation for $\boldsymbol{\lambda}$

$$f(\lambda) = (K+1) \sum_{k} \frac{\mathbf{Z}^{(k)}(\mathbf{Z}^{(k)})^{T}}{\mu_{k} - \lambda} - (K+1-\lambda) = 0 ,$$

where the known solution to the simpler $N \times N$ problem WZ = μ Z is employed. Evaluating this expression for different values of λ one forms a Sturm sequence. The observed changes in sign of the terms in this Sturm sequence reveal that the value of a particular eigenvalue of A "separates" or is bounded by two consecutive roots of W. That is,

$$\mu_{k-1} \leq \lambda_k \leq \mu_k \quad \text{for} \quad k = 2, \dots, N$$

and also one can determine that (for $\lambda_{N+1} > \lambda_N > \cdots > \lambda_1$)

$$0 \leq \lambda_1 \leq \mu_1$$

and

$$\mu_N \leq \lambda_{N+1} \leq K+1 + \sqrt{K+1}$$

by the application of the Gershgorin theorem.²⁴ (This interlacing of eigenvalues is applicable here since $W_{i,i+1} W_{i+1,i} > 0.^{25}$)

In this way it is shown that the eigenvalue distribution of **A** is well approximated by the distribution of the N values of μ_k vs k. The error in this approximation is negligible as N becomes large [i.e., order (100)], as revealed by actual numerical determination of the (N+1) λ_k using the method of bisection.²⁶ If necessary, employing Eq. (57) and the computed μ_k and $\mathbf{Z}^{(k)}$, the exact eigenvectors of **A** $(\eta^{(k)}, \zeta_1^{(k)}, \ldots, \zeta_N^{(k)})$ can be determined.²⁶

Employing an argument identical to that used above to obtain the bounds on the λ_k , we claim in the limit of $N \gg 1$ the eigenvalue spectrum of **A** is well approximated by that of an $(N+1) \times (N+1)$ matrix **W**, with the corresponding similar eigenvectors.

Thus, using this large N approximation $\mu_k \cong \lambda_k$ (where the μ_k are now appropriate for an N+1 dimensional W) allows the calculation of angular reorientation correlation functions, such as Eq. (26), for the Cayley tree model of cooperative dynamics. We will briefly outline two methods of calculation of the correlation function below. First, we follow the approach used earlier. Our discussion of the A matrix reveals that the eigenvalues $\mu_{k,cT}^{(N+1)}$ of the N+1 dimensional (Cayley tree model) matrix A' are approximated as

$$\mu_{k_{\bullet}}^{(\mathcal{U})} \mathcal{I} \cong \hat{\epsilon} (\sqrt{K} - 1)^2 + 4 \hat{\epsilon} \sqrt{K} \sin^2 \frac{k\pi}{2(M+1)} + \hat{\epsilon}' = \hat{\epsilon} \mu_k + \hat{\epsilon}' \quad \text{for } k = 1, \dots, M$$
(59)

and here M = N + 1. For K = 1 these eigenvalues are virtually identical to Eq. (9) for the linear chain. Also, from Eqs. (58) and (55) we have in matrix notation $\mathbf{Z}\mathbf{u} = \boldsymbol{\xi}$, where $\boldsymbol{\xi}$ are the normal modes. Then we can form the conditional probability $P(\xi^{\circ}|\xi,t)$ $= P(\mathbf{Z}\mathbf{u}^{\circ}|\mathbf{Z}\mathbf{u}, t) = P(\mathbf{u}^{\circ}|\mathbf{u}, t)$ similar to the method used in Sec. II. Thus, in this case $P(\xi^{\circ}|\xi,t)$ can be expressed via Eqs. (10)-(22) employing products of normal mode eigenfunctions i.e., the Hermite functions, [Eqs. (18) and (21)] with the eigenvalues $E_{\mathbf{z}}$ $=\sum_{k=1}^{N+1} n_k \mu_{k,CT}^{(N+1)}$. The transformation matrix Z, obtained from Eq. (58), would now be substituted in the analysis in place of Q^{-1} which was employed in the previous cases [cf. Eq. (7)]. Therefore, for the Cayley tree model the multiparticle conditional probability can be obtained in the form of Eq. (22), and G(t) may then be calculated.

Because the transformation matrix Z converts the u of Eq. (55) rather than the original θ , we found an

3083

alternative method more convenient. It is suggested by comparing the u of Eq. (55) for K=1 with the methods of Sec. II for the one-dimensional case. Consider an N shell Cayley tree model with a perturbed force matrix $\hat{\mathbf{A}}' = (\hat{\boldsymbol{\epsilon}}\mathbf{A} + \hat{\boldsymbol{\epsilon}}'\mathbf{1})$, where $\hat{\mathbf{A}}_{0,1} = \hat{\mathbf{A}}_{1,0} = -\sqrt{2K}$. We shall again approximate the N+1 eigenvalues of $\hat{\mathbf{A}}$ as the above $\mu_{k_{k}CT}^{(N+1)}$, and thus the eigenvectors $Z_{m}^{(k)}$ are appropriate, within a small error, for $\hat{\mathbf{A}}$. Consider an independent adjoint Cayley tree lattice system with N-1 shells for interacting rods having the same interaction parameters and diffusive properties as our original rod system, and also having K+1 neighbors found only among the members of the newly constructed system. For this system we approximate $\hat{A}' \cong (\hat{\epsilon} W + \hat{\epsilon}' 1)$, and we require the diffusive motion of the two systems to be uncoupled.²⁷ The new basis vectors become $u'' = \{u_N, u_{N-1} \dots u_1, \hat{u}_0, \hat{u}_1 \dots \hat{u}_{N-1}\}$ and the 2N+1 dimensional matrix A'' is approximated as



Now we introduce an orthogonal transformation matrix **S** which yields the new basis vectors $\mathbf{v} = \mathbf{Su''}$. Its function is to construct symmetric and antisymmetric pairs from the original and adjoint Cayley tree basis vectors in such a manner that the central rod (i.e., θ_0) appears as the N+1th (or central rod) of the combined system. Thus the structure of the calculation is rendered virtually identical to that for the case in Sec. II and the solution follows almost immediately. The nonzero matrix elements of **S** are

$$S_{i,i} = 1/\sqrt{2} = S_{i,2N+2-i} \text{ for } i = 1, \dots, N;$$

$$S_{N+1,N+1} = 1;$$

and

$$S_{i,i} = -S_{i,2N+2-i} = -1/\sqrt{2}$$
 for $i = N+2, \dots, 2N+1$.

Thus $SA''\mathbf{S}^{-1} = \mathbf{W}$ written for the 2N + 1 dimensional space, and $v_{N+1} = u_0 = \theta_0$. This yields

$$\theta \equiv \theta_0 = \sqrt{2/2N+1} \sum_{\substack{k=1 \\ \text{odd}}}^{2N+1} (-1)^{(k+1)/2} \xi_k .$$

Using the raising and lowering operator form of ξ_k and

$$T_{k,CT} = (-1)^{(k+1)/2} \left[\frac{2R}{\mu_{k,CT}^{(2N+1)}} (2N+1) \right]^{1/2}$$

[cf., Eq. (33)] for odd k, permits us to calculate matrix elements such as $\langle 0|\theta|N \rangle$. Thus, from Eqs. (27) and (32) we obtain, for $N \gg 1$, the Cayley tree lattice model result

$$G(t) \approx \frac{2R}{2N+1} \sum_{\substack{k=1 \\ \text{odd}}}^{2N+1} \exp(-\mu_{k_{k}CT}^{(2N+1)})/\mu_{k_{k}CT}^{(2N+1)}, \qquad (60)$$

which is identical in functional form to G(t) obtained from a one-dimensional system of 2N+1 rods with fixed boundaries, i.e., a linear chain of rods bounded by rods fixed in their equilibrium positions.^{13,21} Just as in the cases of Sec. II, one can show that as $N \rightarrow \infty$, G(t)is independent of the particular choice of boundary conditions [cf. Eqs. (35) and Appendix A]. Thus for K=1we obtain Eq. (39) in this limit. However, for K>1 we achieve a formally identical result but with rescaled rod-rod and rod-field interactions. That is, in Eq. (39) one replaces $\hat{\boldsymbol{\epsilon}}$ by $\sqrt{K}\hat{\boldsymbol{\epsilon}}$ and $\hat{\boldsymbol{\epsilon}}'$ is replaced by $\hat{\boldsymbol{\epsilon}}'$ $+\hat{\epsilon}(\sqrt{K}-1)^2$. Thus the rod-rod interaction is increased by the factor \sqrt{K} , while for K > 1 there is an additional "rod-field" contribution $\hat{\epsilon}(\sqrt{K}-1)^2$. It is not clear whether this additional term is a peculiarity of the Cayley tree (possibly arising from the fact that it branches and never can turn back on itself) or is associated with the free energy of stabilization of the aligned phase, which in the absence of an aligning field, should not have any preferred direction, ^{8,9} except that we have constructed our model with an intrinsic preferred direction. In any event, we will be primarily interested in the rescaled $\hat{\epsilon}$, with an otherwise simple $\sin^2[k\pi/2(M+1)]$ dependence in the eigenvalues of Eq. (59).

While our emphasis in the present work is on soluble analytic models, we believe that aspects of the method used in this section could readily be extended to develop numerical solutions for extended two-dimensional arrays of coupled torsional Brownian oscillators with next nearest neighbor (and even higher order neighbor) interactions. The primary procedure that simplified our analysis of the Cayley tree is that of Lanczos tri-diagonalization, which transformed the Cayley tree

model into that of an *effective linear* chain of Brownian torsional oscillators with rescaled couplings. This procedure also allows one to directly focus on a single molecule which can be regarded as being at or near the center of the array. The Lanczos algorithm has been shown to be a powerful method for *numerically* achieving tri-diagonal form for even very large arrays in other physical problems,²⁰ and its applicability to complex diffusional problems has recently been demonstrated.^{28(a)} In the present application the Lanczos algorithm could be used to numerically tri-diagonalize the **A** matrix which is then easily diagonalized. Then the approach of Secs. II and III can immediately be employed to numerically obtain the correlation function and spectral density.

V. SCALING AND DIRECTOR FLUCTUATIONS

As noted in Sec. I, the models we have discussed in the previous sections have defects (distinct from matters of dimensionality) when compared to actual liquid crystals, a matter we attempt to deal with in this section. For example, the linear array of N + 1 rigid rods does not correspond to a "real" linear array of liquid crystal molecules in two important respects: (1) the potential between rods, E_{int} is not so large that each rod experiences only small angular deviations θ_i , and (2) in a real liquid crystal the molecules translate and exchange with their neighbors. The effect of Eq. (1) is that in a normal liquid crystal the order parameter $S \sim 0.4 - 0.6$, while the torsional limit would require $S \gtrsim 0.95$. The effect of Eq. (2) is to randomize somewhat the time-dependent fluctuations in interaction potential sensed by a particular molecule. Also, Eq. (3) the flexibility of a real liquid crystal molecule will tend to lead to a variation in the intermolecular potential acting on different parts of the same molecule. These are problems we ascribe to a proper description of localized cooperative dynamics of liquid crystalline molecules. Instead we believe our model results are more useful for dealing with long-range cooperativity of the type referred to as director fluctuations (cf, Sec. I).

In order to see this, we need to introduce simple, but current ideas on scaling and renormalization. In particular, we might argue that Eqs. (1)-(4), before we restrict the θ_i to only small fluctuations, might still be a good starting point for a molecular description. We could improve on this description by allowing for (a) translational diffusion of each molecule and (b) full phase-space treatment in the angular motion, i.e., angular momentum or inertial effects. Instead, we shall divide our lattice of rods with nearest neighbor coupling into blocks of length $a' \equiv La$, where a is again the distance between rods. Now we reconsider our model as a model of blocks of L rods with nearest neighbor interaction between these blocks. If these blocks are large enough, then the effective interaction between neighboring blocks should be large enough that they become strongly coupled in the sense that $(\theta_i - \theta_{i\pm 1})$ becomes very small, where now θ_i refers to the director orientation of the *i*th block. Also, for large enough blocks, the translational diffusion of molecules within each block and between adjacent blocks should be of little significance to the property of the blocks themselves,^{28(b)} nor should any inertial effects be important.

Thus, we redefine our problem in terms of blocks which again obey Eqs. (1)-(4) but with rescaled energies: $E_{int}^{(L)}$ and $E_{ext}^{(L)}$ and with rescaled rotational diffusion coefficient $R^{(L)}$. In this limit, molecular details have been averaged out, and the approximations leading to Eqs. (5) and (6) become applicable. We do, however, give up details of order a' or less (i.e., wave vector $q \ge \pi/aL$), and for the present we are not attempting to calculate the rescaled parameters $E_{int}^{(L)}$, $E_{ext}^{(L)}$, and $R^{(L)}$ in terms of true molecular properties.

Instead, we now consider the opposite limit of long wave vectors, q. In this limit we should obtain the hydrodynamic results appropriate for director fluctuations. It is not, at present, possible to perform this comparison rigorously, since the models we could solve for analytically are not true three dimensional cases, so we must use a weaker inferential approach. In particular, let us suppose we can use the results of the previous sections as approximations to modes in three dimensions.

Thus the mean-square fluctuation for the kth normal mode may be given by

$$\langle \xi_{k}^{2} \rangle = \langle 0_{k} | \xi_{k}^{2} | 0_{k} \rangle = R^{(L)} / \mu_{k}^{(L)}$$

$$= \left[4\beta E_{int}^{(L)} \sin^{2} \left(\frac{k\pi}{2(N+1)} \right) + \beta E_{oxt}^{(L)} \right]^{-1} , \quad k = 0, 1, \dots, N,$$
(61)

where we have introduced rescaled parameters (which also includes the rescaling due to the K nearest neighbors cf. Sec. V). Then in the limit of $(k/N) \rightarrow 0$ we have

$$\lim_{(k/N)\to 0} \langle \xi_k^2 \rangle = \left| \beta E_{\text{int}}^{(L)} \frac{\pi^2 k^2}{(N+1)^2} + \beta E_{\text{ext}}^{(L)} \right|^{-1}, \quad (62)$$

which we wish to relate to the known hydrodynamic expression^{θ , θ} for liquid crystals. In this theory one writes the distortion free energy for the nematic state in the simplified one-constant approximation as

$$F_{d} = \frac{1}{2} \sum_{q} \left(Kq^{2} + \chi_{a} H^{2} \right) \left[\left| n_{x}(q) \right|^{2} + \left| n_{y}(q) \right|^{2} \right], \quad (63)$$

where the Fourier components of $n_x(\mathbf{r})$ and $n_y(\mathbf{r})$ are defined by

$$n_{\mathbf{x}}(\mathbf{q}) \equiv \frac{1}{V} \int n_{\mathbf{x}}(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}$$
 (64)

and where V is the sample volume, while K is the force constant for the distortion modes, and $\chi_a H^2(n_x^2 + n_y^2)$ is a magnetic free energy of distortion per unit volume. The mean square fluctuations of the director modes is given by

$$\langle |n_{\mathbf{x}}(q)|^2 \rangle = \langle |n_{\mathbf{y}}(q)|^2 \rangle = (\beta V)^{-1} / (Kq^2 + \chi_a H^2)$$
(65)

and each mode has a relaxation rate:

$$\tau(q)^{-1} = Kq^2/\eta + \chi_a H^2/\eta .$$
 (66)

We now require that Eq. (62) be equivalent to Eq. (65). This is readily achieved by first letting [cf. Eq. (7)]

$$q_k = \frac{\pi}{a'} \frac{k}{(N+1)}$$
, $k = 0, \dots, N$ (67)

and then recognizing that $E_{int}^{(L)}$ represents internal energy

(68)

per block of volume a'^3 , etc. One obtains

$$E_{i}^{(L)} = Ka'$$

and

$$E_{\rm ext}^{(L)} = a^{\prime 3} \chi_a H^2 .$$
 (69)

When we use Eqs. (67)-(69) as well as the renormalized form of Eq. (9) in the limit $k \rightarrow 0$, we obtain

$$\eta^{-1} = 2\beta R^{(L)} a^{\prime 3} . \tag{70}$$

{Recall for a sphere of radius *a* undergoing Stokes-Einstein rotational diffusion $\tau_l = [Rl(l+1)]^{-1} = 8\pi a^3 \eta \beta / l(l+1)$, for the *l*th spherical Harmonic, which is quite similar, but not identical to Eq. (70).}

We summarize our point of view by rewriting Eq. (63) as

$$F_{d} = 2 \sum_{q} \left[K/a^{\prime 2} \right) \sin^{2} \frac{a^{\prime}}{2} q + \frac{1}{4} \chi_{a} H^{2} \right] \left[\left| n_{x}(q) \right|^{2} + \left| n_{y}(q) \right|^{2} \right],$$
(71)

while Eq. (66) becomes

 $I(t) \equiv \langle n(\mathbf{r}, t=0)^* n(\mathbf{r}, t)_+ \rangle$

$$\tau(q)^{-1} = (2/a')^2 K \sin^2\left(\frac{a'}{2}q\right) / \eta(q) + \chi_a H^2 / \eta(q) .$$
 (72)

In summary, this scaling approach suggests a simple form to extend the hydrodynamic approach to large q in a way that reflects upon microscopic noncontinuum behavior of the system. Instead of the q^2 dependence of the distortion free energy and relaxation frequency of the qth mode, we obtain the $\sin^2(a'/2)q$ dependence. This is important in the calculation of spectral densities as shown below. However, it should be noted that we do not avoid the need to invoke a maximum or cutoff q_c as is usually employed in calculations based on the hydrodynamic model. In that model, q_c is arbitrarily taken as of molecular dimension representing the extreme upper limit that a hydrodynamic model could be pushed. Our approach based on scaling suggests instead a $q_c \sim \pi/a' = \pi/La [cf. Eq. (67)]$ where L is chosen as small as possible but consistent with a renormalized form of Eq. (1) in which molecular detail has been smoothed out. This a' or q_c then enters explicitly into our expressions. It represents the fact that there are still localized degrees of freedom or localized modes on a molecular scale which have not been included. These localized modes should have faster relaxation rates, so they would sense the instantaneous distribution of values of the cooperative modes analyzed here. Thus, methods of combining both types of modes: long-range and short range may be developed along lines previously discussed. 5, 17, 29

VI. A MODIFIED SPECTRAL DENSITY FOR THREE DIMENSIONS

We use the results of the previous section to obtain a spectral density function for director fluctuations in three dimensions. We start with the standard expression based upon hydrodynamic theory^{2,7} but we make use of Eqs. (71) and (72). That is, we write for the correlation function for $n_{\pm} = n_{x} \pm in_{y}$,

$$= \frac{1}{(2\pi)^3} \int_0^{q_c} \frac{2k_B T \exp[-(4K/a'^2\eta) \sin^2\left(\frac{a'}{2}q\right)t - \chi_a H^2 t/\eta]}{[(4K/a'^2) \sin^2\left(\frac{a'}{2}q\right) + \chi_a H^2]} 4\pi q^2 dq , \qquad (73)$$

which reduces to the standard hydrodynamic expression^{5,7} if we let $\sin^2((a'/2)q) \approx ((a'/2)q)^2$. Here q is given by Eq. (67) and $q_c = \pi/a'$. Now let $q = \theta/a'$ with $\theta = \pi k/(N+1)$ and $0 \le \theta \le \pi$. Substituting into Eq. (73) we have:

$$\langle n(\mathbf{r},0)^*_n(\mathbf{r},t)_* \rangle$$

$$=\frac{8\pi k_{B}T}{(2\pi)^{3}a'^{3}}\int_{0}^{\pi} \frac{\exp\left[-\frac{4Kt}{a'^{2}\eta}\sin^{2}\left(\frac{\theta}{2}\right)-\frac{\chi_{a}H^{2}}{\eta}t\right]}{\frac{4K}{a'^{2}}\sin^{2}\left(\frac{\theta}{2}\right)+\chi_{a}H^{2}}\theta^{2}d\theta = \frac{8\pi k_{B}T}{(2\pi)^{3}}\int_{0}^{\pi} \frac{\exp\left[-4(E_{int}^{(L)}t/\beta R)\sin^{2}(\theta/2)-E_{ext}^{(L)}t/2\beta R\right]}{4E_{int}^{(L)}\sin^{2}(\theta/2)+E_{ext}^{(L)}}\theta^{2}d\theta ,$$
(74)

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where we have used Eqs. (68)-(70) to obtain the second equality in Eq. (74). It is seen to be our three dimensional extension of the one-dimensional correlation function (35) in the limit of large N (where summation over k is replaced by an integration), and is independent of N.^{30(a)}

We now introduce the new constants (in units of s^{-1}):

$$C = \frac{k_B T}{a^{\prime 3} \pi^2 \eta} \quad , \tag{75}$$

 $\alpha \equiv 2K/a^{\prime 2}\eta , \qquad (76)$

 $b \equiv \chi_a H^2 / \eta , \qquad (77)$

$$\lambda = \lambda(j) \equiv 2\alpha \sin^2(\theta/2) + b = (\alpha + b) - \alpha \cos(\theta) .$$
 (78)

Then Eq. (74) is written as

$$I(t) = C \int_0^{\tau} \frac{\exp\{-\lambda t\}}{\lambda} \theta^2 d\theta = C \int_0^{\tau} \int_t^{\infty} \exp(-\lambda t') \theta^2 dt' d\theta ,$$
(79)

reversing the order of integration yields

$$I(t) = C \int_{t}^{\infty} dt' \exp[-(\alpha+b)t'] \int_{0}^{\tau} \exp[(\alpha t' \cos(\theta)] \theta^{2} d\theta .$$
(80)

The integrand of the θ integral from Eq. (80) can be expanded in terms of the modified Bessel functions. The

resulting θ integrals are easily evaluated, leading to the most general result:

$$I(t) = C \left[\frac{\pi^3}{3} \int_t^{\infty} dt' \exp[-(\alpha + b)t'] I_0(\alpha t') + 4\pi \sum_{k=1}^{\infty} \frac{(-1)^k}{k^2} \int_t^{\infty} dt' \exp[-(\alpha + b)t'] I_k(\alpha t') \right].$$
(81)

For short times, $\alpha t' \ll 1$, we can rewrite the integrals of Eq. (73). In this limit $I_0(\alpha t') \approx 1$, $I_k(\alpha t') \approx 0$ for k > 0, leaving for $\alpha t' \ll 1$ the approximation

$$I(t) \cong C \left[\frac{\pi^3}{3} \frac{1}{\sqrt{b(2\alpha+b)}} + 4\pi \sum_{k=1}^{\infty} \frac{(-1)^k [\alpha+b\sqrt{b(2\alpha+b)}]^k}{(k^2)\alpha^k \sqrt{b(2\alpha+b)}} - \frac{\pi^3}{3} \left(\frac{1-\exp[-(\alpha+b)t]}{\alpha+b} \right) \right].$$
(82)

[Note I(0) is equal to the first two terms of Eq. (82).]

The long-time limit of Eq. (79) may be obtained by recognizing that the values of λ near its minimum will dominate.^{30(b)} Thus by letting $\lambda \simeq b + (1/2)\alpha\theta^2$, replacing π by ∞ in the limit of the second integral, and exchanging the order of the integrals one obtains

$$I(t) \simeq C \sqrt{\frac{\pi}{2}} \int_{t}^{\infty} \frac{\exp(-bt')}{(\alpha t')^{3/2}} dt' .$$
(83a)

In the limit that $b \rightarrow 0$, (i.e., b becomes infinitesimal), then

$$I(t) \simeq C \sqrt{2\pi} / \alpha^{3/2} t^{1/2}$$
, (83b)

which is identical to the result from the equivalent hydrodynamic model in the absence of a cutoff q_c .^{5,7} In this long-time limit, I(t) given by Eqs. (83a) or (83b) is independent of a' (i.e., it exhibits scaling behavior).

From Eq. (79) we obtain the Fourier transform where $s = i\omega$

$$J(\omega) = 2\operatorname{Re} \int_{0}^{\infty} dt \exp(-st) I(t)$$

= $2\operatorname{Re} \left[C \int_{0}^{\infty} dt \exp(-st) \int_{t}^{\infty} dt' \int_{0}^{\tau} \exp(-\lambda t') \theta^{2} d\theta \right]$
= $2\operatorname{Re} \left[C \int_{0}^{\infty} dt \exp(-st) \int_{0}^{\infty} dt' \int_{0}^{\tau} \exp(-\lambda t) \theta^{2} d\theta - C \int_{0}^{t} dt' \int_{0}^{\tau} \exp(-\lambda t') \theta^{2} d\theta \right].$ (84)

Note the first term yields a $[const/(i\omega)]$ which is pure imaginary and can be extracted immediately from our solution.

Using the same analysis of the $\exp(-\lambda t')$ term used earlier to calculate I(t) gives

$$J(\omega) = 2\operatorname{Re}\left[-C \int_{0}^{\infty} dt \exp(-st) \int_{0}^{t} dt' \exp[-(\alpha+b)t'] \times \left[\frac{\pi^{3}}{3} I_{0}(\alpha t') + 4\pi \sum_{n=1}^{\infty} I_{n}(\alpha t')(-1)^{n}/n^{2}\right]\right].$$
(85)

Performing the integrals yields the formal result written in standard form as

$$J(\omega) = 2\operatorname{Re}\left[C\frac{i}{\omega}\left[\frac{\left[(bB-\omega^2)-i\omega(b+B)\right]}{(b^2+\omega^2)(B^2+\omega^2)}\right]^{1/2}\right]$$



FIG. 1. Graph of spectral density $J(\omega)$ vs frequency to the inverse one-half power in dimensionless units. The ordinate is given in units of $\hat{J}(\bar{\omega}) \equiv J(\omega)\alpha$ where α is defined by Eq. (76), while the absicca is given in units of $\bar{\omega}^{-1/2}$, where $\bar{\omega} \equiv \omega/\alpha$ $= (\pi^2/2)\omega/\omega_c$. Also shown on the abscissa is the value of $\nu^{-1/2}$ $= (\omega/2\pi)^{-1/2}$ in (MHz)^{-1/2} for the typical values of $K = 6.3 \times 10^{-7}$ dyn, $\eta = 1.3p$, and a' = 15 Å. The solid lines correspond to Eq. (86) and the modification for finite diffusion coefficient D. This is compared to the predictions of the hydrodynamic theory (dashed lines) obtained from Eq. (74) by replacing $\sin^2(\theta/2)$ by $\theta^2/4$. The curves labelled a, b, and c correspond to values of dimensionless $\hat{D} \equiv D/\alpha a'^2 = (D\eta/2K)$ of 0, 0.62, and 1.03, respectively. (Using the above values of K and η they become 0, 6×10^{-7} , and 1×10^{-6} cm²/s, respectively.) [Note $\chi_a H^2/\eta$ is kept small enough so as not to affect the results.]

$$\times \left(\frac{\pi^3}{3} + 4\pi \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \frac{\left[(i\omega + \alpha + b) - \sqrt{(i\omega + \alpha + b)^2} - \alpha^2\right]^n}{\alpha^n}\right)$$
(86)

with $B \equiv 2\alpha + b$. [The apparent divergence in the coefficient ~ ω^{-1} may be shown to disappear, as $\omega \to 0$ by analogy to the discussion of Eqs. (47)-(50).] We note, that Eq. (86) [and also Eq. (81)] must be multiplied by $3S^2/2$, where S is the mean ordering of the molecule, in order to correspond to the usual spectral density (and correlation function) needed in magnetic resonance (cf. Ref. 5).

We compare the result of Eq. (86) with the standard hydrodynamic result^{2,5,7} in Figs. 1 and 2 as a function of ω over the range of interest to NMR relaxation experiments (viz., 10^4-10^8 Hz). ¹⁻⁶ These figures are actually in dimensionless units: $\overline{\omega} \equiv \omega/\alpha$ ($\overline{\omega}_c \equiv \omega_c/\alpha$ $\equiv \pi^2/2$) and $\hat{J}(\overline{\omega}) \equiv J(\omega)\alpha$. If follows from Eq. (83b) that for low frequencies $J(\omega) \propto \omega^{-1/2}$, as in the hydrodynamic result, $\hat{J}(\overline{\omega})_{\text{HD}}$. ^{5,7} There is only a small increase (approaching a factor of two) in the ratio $\hat{J}(\overline{\omega})/$ $\hat{J}(\overline{\omega})_{\text{HD}}$ as $\omega_c^{>}\omega_c$ (cf. Fig. 2) and for $\omega \gg \omega_c$ (typically





FIG. 2. Ratio of spectral density $\hat{J}(\bar{\omega})$ to the hydrodynamic result $\hat{J}(\bar{\omega})_{\text{HD}}$ as a function of $\bar{\omega}^{-1/2}$ and $\nu^{-1/2}$ (in MHz^{-1/2} for $K=6.3\times10^{-7}$ dyn, $\eta=1.3p$, and a'=15 Å). The curves labeled a, b, and c correspond to values of dimensionless D of 0, 0.62, and 1.03 (cf. Fig. 1).

greater than 100 MHz) both results become comparable. This is in agreement with the identical asymptotic form of $J(\omega) \simeq 2\pi R^{(L)}/3\omega^2$ with $R^{(L)}$ given by Eq. (70) that may be obtained from the above expressions. Thus, there are just modest differences predicted by the two theories in the absence of translational diffusion of the molecules.

Translational diffusion of the molecules may be introduced²⁸ with the multiplicative factor $\exp[-q^2Dt]$ into the integrand of Eq. (73). Here D is the translational diffusion coefficient.^{2,5,31} Results³² for $\hat{D} = D/$ $\alpha a'^2$ of 0.62 and 1.03 (which correspond to $D = 6 \times 10^{-7}$ and 1×10^{-6} cm²/s if we use typical values of K = 6.3 $\times 10^{-7}$ dyn, $\eta = 1.3p$, and a' = 15 Å) are shown in Figs. 1 and 2. For low frequencies even better agreement is found between the two theories, and for $\omega \ge \omega_c$ the differences are somewhat suppressed. However, the asymptotic limiting results are somewhat greater for the present model, and this deviation is increasing with increasing D_{\bullet} Such frequencies are accessible to modern NMR experiments, although this is the regime where $J(\omega)$ is small and therefore more difficult to measure. However, the current theory predicts an enhancement of this mechanism for finite diffusion indicating that it could be a little easier to detect. A recent NMR study demonstrates the subtle detail with which $J(\omega)$ from director fluctuations may be examined as a function of frequency.^{$6(\bullet)$} Effects of a finite D on

the present predictions³³ could be tested by performing experiments with molecular probes of varying size as a function of frequency if there is sufficient sensitivity to this mechanism.

The reason for this effect from a finite D is as follows. The decay constant from the qth mode (for $b \approx 0$) becomes $\lambda' = 4K/a'^2 \eta \sin^2(a'q/2) + Dq^2$, while the mean square fluctuation remains just λ [cf. Eq. (78)]. Thus the qth mode contributes the amount $J_q(\omega) \propto (\lambda'/\lambda) \{1/[\omega^2 + {\lambda'}^2]\}$ to the total spectral density $J(\omega)$, which for large ω becomes: $\lambda'/\lambda\omega^2$. Now the $\sin^2 a'q/2$ term suppresses the importance of the first term in λ' relative to Dq^2 for the higher q modes (which are important at higher frequencies) and $\lambda'/\lambda = 1 + (D\eta/K) [(a'^2q^2/4)/\sin^2(a'q/2)]$. Thus the high frequency results show a greater sensitivity to D than the hydrodynamic result, wherein $\lambda' = [K/\eta + D]q^2$ and $\lambda'/\lambda = 1 + D\eta/K$.

VII. CONCLUDING REMARKS

The results we have obtained for the spectral density $J(\omega)$ may be used in an identical fashion to that from the hydrodynamic model in the analysis of spin-relaxation studies.¹⁻⁷ It leads to predictions for the dependence of $J(\omega)$ on ω in the experimentally accessible regime¹⁻⁶ of 1-100 MHz that can differ somewhat from the form obtained from the hydrodynamic model. The present theory shows greater sensitivity to changes in translational diffusion coefficient at the highest frequencies, where the largest differences from the hydrodynamic result are for diffusing molecules. These effects are not large and it would be important to first separate out the other mechanisms of spin relaxation in any experimental test (we note that good progress has been made along these lines⁶). Most important of all is the realization that the present theory (as well as the hydrodynamic theory) is necessarily incomplete in not including relaxation on a molecular scale, and only when that failing is removed can the somewhat arbitrary choice of scaling length a' be remove. Nevertheless, as we already noted, convenient methods for combining the effects of dynamic cooperativity on a molecular level with the more long-range cooperativity that we addressed in this work are currently available.^{5,17,34}

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APPENDIX A

Similar to the derivation in Sec. II employing free boundary conditions, the time dependent correlation function G(t) and spectral density $J(\omega)$ can be obtained in the case of periodic boundary conditions. For periodic boundary conditions, however, we require the (N+1)th rod to exhibit identical motion to the first. Thus, we need only consider the N rods labelled 1 through N. The implications of this choice of boundary condition upon the force terms entering Eq. (6) are exhibited by a slight modification of A to form a circulant matrix such that $A_{ii} = 2$, $A_{i,i\pm 1} = -1$, $A_{1,N} = A_{N,1} = -1$, i = 1 to N, with all other elements equal to zero. This symmetric cyclic matrix is diagonalized by the Fourier matrix transformation³⁵

$$Q_{jk} = N^{-1/2} \exp\left[2\pi i (j-1)(k-1)/N\right], \quad 1 \le j, k \le N.$$
 (A1)

The N eigenvalues of A' are then

$$\mu_{k,\text{PBC}} = 4\hat{\epsilon} \sin^2[(k-1)/N] + \hat{\epsilon}', \quad 1 \le k \le N$$
 (A2)

and $P(\xi^{\circ}|\xi, t)$ is given by Eq. (10) in terms of the N normal mode coordinates. (The expression of each $\phi_k(\xi_k^0|\xi_k, t)$ must now include the eigenvalues $\mu_{k, PBC}$.) Subsequent expressions for equilibrium probability distributions follow as in the discussion of Eqs. (12) and (13).

In order to calculate G(t) from Eq. (27) for periodic boundary conditions we start by writing θ_i in terms of the normal mode coordinates Eq. (28) and consider the rod i = (N/2) + 1 (N is even). From Eq. (A1) we find

$$\theta_{(N/2)+1} \equiv \theta \equiv N^{-1/2} \sum_{k=1}^{N} (-1)^{k-1} \xi_k .$$
 (A3)

Analogous to Eqs. (32) and (33) we obtain

$$\langle \mathbf{0} | \boldsymbol{\theta} | \mathbf{n} \rangle = \sum_{k=1}^{N} T_{k_{*} PBC} \langle \mathbf{0} | (R_{k^{*}} + R_{k^{-}}) | \mathbf{n} \rangle$$
$$= \sum_{k=1}^{N} T_{k_{*} PBC} \delta_{n_{0},0} \delta_{n_{i},0} \cdots \delta_{n_{k^{*}}1} \cdots \delta_{n_{N},0} , \qquad (A4)$$

where

$$T_{k_{\rm PBC}} = (-1)^{k-1} [R/N\mu_{k_{\rm PBC}}]^{1/2}$$
(A5)

with the $\mu_{k_{\rm s} \rm PBC}$ given by Eq. (A2), and thus from Eq. (27) ,

$$G(t) = (R/N) \sum_{k=1}^{N} \exp(-\mu_{k_{*} \text{PBC}}) / \mu_{k_{*} \text{PBC}} .$$
 (A6)

In the particular limit of $N \rightarrow \infty$, G(t) for periodic boundary conditions equals the integral (39), consistent with the assertion that model boundary conditions have negligible effect in this limit of many coupled rods. For $N \rightarrow \infty$ and periodic boundary conditions $J(\omega)$ is then, of course, equal to that shown in Eqs. (44)-(52).

APPENDIX B

Using a generalization of the method of Uhlenbeck and Ornstein,¹⁰ we can rederive the Gaussian form of $\phi_k(\xi_k^\circ|\xi_k, t)$ of Eq. (11) starting with the discrete state, Hilbert space, representation given by Eq. (20). This is accomplished by writing Eq. (20) expanded as

$$\phi_{k}(y_{0}|y,x) = Ae^{-y} \sum_{n=0}^{\infty} e^{-nx} \frac{H_{n}(y)H_{n}(y_{0})}{2^{n}n!}$$
(B1)

with

$$y = [\mu_k / 2R]^{1/2} \xi_k, y_0 = [\mu_k / 2R]^{1/2} \xi_k^\circ, \quad x = \mu_k t, \quad n = n_k,$$

and

$$A = [\mu_k/2\pi R]^{1/2}$$
.

Defining,

$$M(x) = \sum_{n=0}^{\infty} e^{-nx} \frac{H_n(y) H_n(y_0)}{2^n n!}$$
(B2)

and using the Hermite polynomial recurrence relation successively,¹⁸ we obtain the ordinary differential equation satisfied by M,

$$\frac{dM}{dx} = 2yy_0 M e^{-x} - e^{-2x} \frac{dM}{dx} - M' , \qquad (B3)$$

where M

$$M' = 2[y^2 + y_2^0 - \frac{1}{2}]e^{-2x}M - M'', \qquad (B4)$$

$$M'' = [4yy_0 e^{-3x} - e^{-4x}]M - e^{-2x}M' .$$
 (B5)

Equation (B3) can then be integrated directly by yield,

$$M = \frac{C(y, y_0)}{(1 - e^{-2x})^{1/2}} \exp\left[\frac{-(y^2 + y_0^2 - 2yy_0 e^{-x})}{(1 - e^{-2x})}\right]$$
(B6)

and

$$1 = \lim_{x \to \infty} M = C(y, y_0) \exp[-y^2 + y_0^2], \qquad (B7)$$

so

$$C(y, y_0) = \exp[(y^2 + y_0^2)],$$
 (B8)

thus

$$M = (1 - e^{-2x})^{-1/2} \exp\left[\frac{-(y - y_0 e^{-x})^2}{(1 - e^{-2x})}\right] \exp[+y^2], \quad (B9)$$

the equivalent of Eq. (B2), which after substitution in Eq. (B1) and a change of variables gives Eq. (11).

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expressions for convenience in presentation so far, but we do in Sec. VII.

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- ³¹We also change the definition of I(t) in Eq. (84) to $I(t) = \langle n(\mathbf{r}_{B,0}, t = 0)^*, n(\mathbf{r}_B, t)_{\pm} \rangle$ where $\mathbf{r}_{B,0}$ and \mathbf{r}_B give the location of the diffusing molecule at time t = 0 and t, respectively (Ref. 5).
- ³²For finite D we could find no closed form expansion such as Eq. (95). We therefore numerically integrated the Fourier-transformed form of Eq. (84) including the additional exponential form in Dq^2t .
- ³³Of course, for large enough q we would have $D = D(q, \omega)$, but if a' is of the order of several molecular lengths, then we would expect $D(q_c) \cong D(q=0)$.
- ³⁴As shown in Ref. 5 there is also a cross term in the spectral density arising from the director fluctuations and the rotational tumbling of the molecule with correlation time τ_R . For the present model we can write the cross-term correlation function as $I^{(3)}(t) = -e^{-t/\tau_R}I(t)$ where I(t) is given by Eq. (88). Then, since $\tau_R^{-1} \gg \lambda_{\theta}$ given by Eq. (87), we can let $I^{(3)}(t) \cong -e^{-t/\tau_R}I(0)$, where I(0) is obtained from Eq. (91). Then the cross-term spectral density, $J^{(3)}(\omega) = -I(0)\tau_R/[1+\omega^2\tau_R^2]$.
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