Static and dynamic light scattering from liquid crystalline solutions of rodlike macromolecules

Paul van der Schoot and Theo Odijk

Department of Polymer Technology, Faculty of Chemical Technology and Materials Science, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands

(Received 27 November 1989; accepted 8 May 1990)

It is argued that concentration fluctuations in lyotropic nematics can cause significant scattering of light. We calculate the static structure factor numerically for a nematic suspension of rods in the second virial approximation. An analytical approximation is also given based on a variational principle applied to an integral equation of the Yvon type. The relation between the one-particle distribution function and the usual correlation functions is discussed. An expression is derived for the polarized dynamical structure factor. This yields the initial decay rate which emphasizes the diffusion perpendicular to the director. We show that the contribution from anisotropic scattering is negligible.

I. INTRODUCTION

There are many unresolved problems in the statistical physics of liquid crystals. One class involves the microscopic basis of continuum theory. In a nematic liquid crystal one discerns a position and time-dependent director which is the order parameter in the sense of condensed matter physics. It is postulated to be a well-defined field in nematomechanics and dynamics. But it has been asserted that the thermal excitation of the director field influences the local ordering of a molecule with respect to a laboratory fixed axis. In order to get finite expressions these authors simply introduce ad hoc cutoffs or numbers of degrees of freedom without coming to terms with a self-consistent view of the problem. Ideally a unified formal analysis should yield both the complete orientational distribution and the fluctuating order parameter or director at once, that is without further bootstrapping.

Parenthetically we note that much more sophisticated attempts at a resolution of a conceptionally similar problem have been given. In the theory of the liquid–vapor interface physicists have tried to reconcile the local density profile, as described by the van der Waals gradient, with the fluctuations of the interface calculated by the capillary wave theory. Here the fluctuating interface is similar to the fluctuating director in the nematic. The matching of the two descriptions is an unresolved problem.

The most advanced theory of liquid crystals is the statistical treatment of the slender rod model first introduced by Onsager, which has been extended in many directions. (See the reviews Refs. 13 and 14.) We stress that it is not valid for many polymer liquid crystals whose macromolecules must be regarded as semiflexible. The marked influence of semiflexibility has been taken into account. For the sake of simplicity we here concentrate on a suspension of perfectly rigid rods in the second virial approximation. We recall that higher virial terms may be disregarded when the volume fraction is much smaller than unity.

Straley first introduced the free energy of a nematic solution of rods with an inhomogeneous director field . Implicit in his analysis is the assumption that the original distribution function is only mildly perturbed i.e., |

\[ \nabla n(r) \cdot \langle \theta^2 \rangle^{1/2} \sim (\theta^2)^{1/2} \]

(Here \( \theta \) is the angle between a test rod and the director and \( L \) is the rod length.) Now the fluctuation theory of nematics shows that the self-correlation function of the director field scales essentially as

\[ \langle n_x(r_1)n_x(r_2) \rangle \sim k_B T/K |r_1 - r_2|, \]

(1.1) where the unperturbed director is along the Z axis, \( k_B \) is Boltzmann’s constant, \( K \) some combination of the elastic moduli and the subscript \( x \) indicates a perturbation in a direction perpendicular to the Z axis. Tentatively extrapolating this down to \( |r_1 - r_2| \approx L \) and using the asymptotic expressions for the moduli, we get

\[ \langle n_x(r_1)n_x(r_2) \rangle \sim DL^{-\frac{1}{2}}(\theta^2)^{1/2} \]

which is much smaller than \( \langle \theta^2 \rangle \) within the second virial approximation. Hence, this would allow us to neglect director fluctuations. Nevertheless, the introduction of \( L \) as a cutoff is to some extent arbitrary. In fact, a complete theory should not yield a divergent correlation function at all. Somehow the Straley expansion needs to be modified at short wavelengths in order to get a consistent description.

The current paradigm in thermotropic liquid crystals is that director fluctuations predominantly scatter light. De Gennes has discussed the ratio \( R \) of the scattering intensity from these fluctuations to that arising from density fluctuations

\[ R \approx \varepsilon_\sigma/e^2k^3 K\chi_T, \]

(1.2) where \( \varepsilon_\sigma \) is the anisotropic permittivity, \( e \) the average permittivity, \( k \) the magnitude of the scattering vector and \( \chi_T \) the isothermal compressibility. For the usual liquid crystals \( R \) is indeed a huge quantity. By contrast, for a nematic solution of long rods the situation is decidedly different. If we set \( e_\sigma/e = O(1), kL^{-1} \) and \( \chi_T \approx (\nu k_B T)^{-1} \) and we use the results of Refs. 17 and 18, the quantity \( R \) turns out to be of order unity so that concentration fluctuations contribute just as much to the light scattering from a lyotropic nematic.

As has been discussed above a consistent theory of both director and concentration fluctuations is nonexistent. Here we take account of concentration fluctuations in a fixed director field. Our motivation for this admittedly ad hoc prescription is twofold. Firstly, the provisional extrapolation of
Eq. (1) does show that director fluctuations do not interfere with the usual orientational distribution. Secondly, director fluctuations give rise to scattering that is depolarized, at least when the director is perpendicular to the scattering plane, whereas we focus on polarized scattering only.

The outline of this paper is as follows. In Sec. II we express the polarized dynamical structure factor in terms of the time-dependent positional and orientational distribution function. Section III introduces the kinetic equation this distribution function satisfies. The linear response theory of Sec. IV shows how the structure factor is linked to the linearized kinetic equation. Next, the static structure factor is calculated both analytically and numerically in Sec. V. We survey the initial decay rate in Sec. VI and discuss the small contribution from anisotropic scattering in Sec. VII. Finally, the limitations and main conclusions of our work are discussed in the last section.

II. THE POLARIZED DYNAMICAL STRUCTURE FACTOR

Consider light scattering from a nematic solution of long rodlike macromolecules of length $L$ and width $D$ with $L$ much larger than $D$. The scattering geometry is chosen in such a way that the director $n_0$ is parallel to the $Z$ axis, the wave vectors $k_i$ of the incident beam and $k_f$ of the scattered light are somewhere in the $XY$ plane and the scattering vector $k = k_i - k_f$ is parallel to the $X$ axis (Fig. 1). In order to obtain the polarized scattered mode the directions of polarization of the incident and scattered light are set parallel to the $Z$ axis.

The usual assumptions regarding light scattering from macromolecular solutions are made. This means that we will consider scattering only from the rodlike particles, which are assumed to have no dynamic internal structure. The condition that the length $L$ be much greater than the width $D$ is important since it permits analysis of solutions of low volume fraction. Hence, we neglect multiple scattering and apply the Rayleigh–Debye approximation. The latter approximation is applicable if the following condition is met:

$$4\pi (R_c/\lambda) |\delta n| \ll 1,$$

where $\lambda$ is the wavelength of light in vacuum, $\delta n$ the difference in refractive index of solvent and solute and $R_c$ the characteristic dimension of the scatterer. The length of the rodlike particles that form nematic phases in solution is typically of the same order of magnitude as the wavelength of light, so $L \approx \lambda$. For the scattering geometry given above the characteristic dimension $R_c$ is however not equal to $L$, but rather $L$ times the root-mean-square angle between the orientation of the rods and the director, $\langle \theta^2 \rangle^{1/2}$, as the particles are more or less aligned parallel to the $Z$ axis and perpendicular to the scattering vector $k$. Setting $R_c = L \langle \theta^2 \rangle^{1/2}$ we then have $4\pi (L/\lambda) \langle \theta^2 \rangle^{1/2} |\delta n| \ll 1$ if $\langle \theta^2 \rangle \ll 1$, because $L/\lambda \approx O(1)$ and $|\delta n| \approx O(10^{-3})$. Accordingly the Rayleigh–Debye condition is met for highly ordered nematic solutions of rodlike molecules (see also Sec. III). Note that this may not be true for isotropic solutions of rodlike molecules because for some configurations the characteristics dimension is indeed $L$, i.e., $R_c \approx L$.

In the above we have reduced a solution of rodlike macromolecules to an effective gas of rods, at least as far as the static properties are concerned. This nonideal gas exhibits both intermolecular as well as intramolecular interference in the scattering process. Dealing with the interference is facilitated if the particles are subdivided into $d_p = (L/D)$ cylindrically symmetric “segments” which are treated as the basic scattering units. Because $|k|/D \approx kD \ll 1$ each segment or scattering unit behaves like a point scatterer. Now let $p_{ij}$ be the polarizability of the scattering unit parallel to the principal axis of the macromolecule and $p_{ij}$ the polarizability perpendicular to that axis. The polarized dynamical structure factor can then be written as

$$S(k,t) = \frac{1}{N_r d_p^2} \sum_{i} \sum_{j} \langle B_i(0) B_j(t) \rangle \times \exp[i k \cdot (r_i(t) - r_i(0))]$$

$$B_i(t) = 1 + \frac{1}{2} \beta P_2 [\cos \theta_i(t)]$$,

(2.2)

where $N_r$ is the number of rods in the scattering volume, $r_i(t)$ and $\theta_i(t)$ are the position and angle with respect to the $Z$ axis of segment $i$ at time $t$, $\beta = 3(p_{ii} - p_{ij})/(p_{ii} + p_{ij})$ equals the relative anisotropy of the polarizability and $P_2$ is the second Legendre polynomial. The primes indicate a summation over all segments in the scattering volume. Expression (2.2) can be rewritten in terms of correlation functions of segment density fluctuations. Let $f(r,t,u)$ be the local rod density of rods in configuration $(r,u)$ at time $t$, $r$ being the position of the center of mass and $u$ the orientational vector of the principal axis with $|u| = 1$ (Fig. 2). Then we have

$$f(r,u;t) = \sum_{i} \delta(r - R_i(t)) \delta(u - u_i(t)).$$

(2.3)

Here $R_i(t)$ and $u_i(t)$ are the position of the center of mass and orientation of particle $i$ at time $t$. Summation is implied over all rods in the scattering volume. The Fourier
III. THE KINETIC EQUATION

As discussed in the Introduction, we let the director \( \mathbf{n}(r) \equiv \mathbf{n}_0 \) be uniform and fixed along the \( Z \) axis. Neglecting hydrodynamic interactions, the distribution function \( f(r, u; t) \) satisfies the preaveraged diffusion equation for translating, rotating, and interacting rods.\textsuperscript{23} This equation has the following form for a nematic solution in an applied external field

\[
\frac{\delta f}{\delta t} = \frac{\delta}{\delta r} \left[ D_0 \mathbf{u} \cdot \nabla + D_1 \mathbf{I} - \mathbf{u} \right] \left[ \frac{\delta f}{\delta r} + f \frac{\delta}{\delta r} (\phi + \omega) \right] + \frac{\delta}{\delta r} \hat{R} \left( \delta f + \hat{R}(\phi + \omega) \right).
\]

(3.1)

Here \( D_0 \) and \( D_1 \) are the parallel and perpendicular translational (self-) diffusion constants, \( \phi(r, u; t) \) and \( \omega(r, u; t) \) the potentials a test rod feels due to the applied external field and the molecular field created by the presence of other macromolecules, \( \hat{R} \) is the preaveraged rotational diffusion constant and \( \mathbf{I} \) is the identity operator.\textsuperscript{26} We have set \( k_B T \) equal to unity for convenience. The diffusion constants are to be taken as adjustable parameters in view of the absence of any quantitative theory describing the concentration and length dependence.

The potential \( \omega(r, u; t) \) can be handled at the pair interaction level provided the volume fraction polymer is low (implying \( L \gg D \) if the nematic state is to be feasible). Then the self-consistent molecular potential exerted on a test rod in configuration \( (r, u) \) can be written as\textsuperscript{23}

\[
\omega(r, u; t) = \int \mathcal{D}r' \int d\mathbf{u}' W(r - r', u, u') f(r', u'; t),
\]

(3.2)

where \( W(r - r', u, u') \) is the negative Mayer function of two polymers in configurations \( (r, u) \) and \( (r', u') \). Equation (3.2) is the second virial approximation of a more general expression involving the direct correlation function discussed by Schurr.\textsuperscript{44} (See our derivation of the direct correlation function Eq. (4.20) below.) For hard rods we have

\[
W(r - r', u, u') = \begin{cases} 1 & \text{if two rods overlap} \\ 0 & \text{otherwise} \end{cases}
\]

(3.3)

If we set the external field \( \phi \) equal to zero, we recover a variant of the Onsager integral equation giving the stationary solution to Eq. (3.1):

\[
\ln f_{eq}(r, u) = \text{cst} - \int d\mathbf{u}' W(r - r', u, u') f_{eq}(r', u'),
\]

(3.4)

where \( \text{cst} \) is a normalization constant.\textsuperscript{12} The solution of this integral equation can be written as

\[
f_{eq}(r, u) = f_{eq}(u) = \nu \psi(u);
\]

(3.5)

\( \psi(u) \) being the orientational distribution function. As shown by one of us,\textsuperscript{13} a useful asymptotic solution to Eq. (3.4) for the nematic phase is given by

\[
\psi(\theta) = (\alpha/4\pi) \exp(-\frac{1}{2} \alpha \theta^2), \quad 0 < \theta < \pi, \quad \psi(\pi - \theta) = \psi(\pi - \theta), \quad \frac{1}{2} \pi < \theta < \pi.
\]

(3.6)

Here \( \theta \) is the angle between the director and the rod. The parameter \( \alpha \) is related to the mean square width of the distribution through \( \langle \theta^2 \rangle = 2\alpha^{-1} \) and to the scaled concentration...
\[ c = \frac{4\pi}{\lambda^2} D \nu \]  
\[ \alpha = 4\pi^{-1}c^2 \]  
\[ c = 3.2904 \text{ and } c = 4.1910. \]

**IV. FORMALISM**

In order to calculate correlation functions like Eq. (2.8) or (2.9) we need information about the pair correlation function. At low densities, i.e., at the level of the second virial approximation, this information can be extracted from the time evolution equation of the single-particle distribution equation (3.1). The formalism that enables us to do that consists of two parts. First we calculate the static structure factor for isotropic scattering \( S_T(k,0) = S_T(k) \) with the help of a special form of the Yvon theorem. Next we use the theorem stating that correlation functions of microscopic variables follow the same kinetic equation as the macroscopic variables themselves. This allows us to construct an expression for the dynamical structure factor \( S_T(k,t) \). Part of the analysis has been inspired by the work of Doi et al.\(^{23}\)

Let us switch on some external field such that a polymer in configuration \((r,u,t)\) feels a potential \(\phi(r,u,t)\). If the external field is weak enough the distribution function consists of a sum of equilibrium distribution \(f_{\text{eq}}(u)\) in the absence of the field and a small perturbation \(\delta f(r,u,t)\) linear in \(\phi(r,u,t)\):

\[ f(r,u,t) = f_{\text{eq}}(u) + \delta f(r,u,t). \]  
\[ \text{(4.1)} \]

Upon insertion of Eq. (4.1) into Eq. (3.1), spatial Fourier transformation and linearization Eq. (3.1) becomes

\[ \frac{\delta f}{\delta t} = -\hat{\Omega} \delta f(k,u,t) - \hat{\Phi}_{\text{eq}}(u) \phi(k,u,t). \]  
\[ \text{(4.2)} \]

Here, and in the following, spatial Fourier transforms are simply denoted by the replacement of \(r\) by \(k\). The operators \(\hat{\Omega}\) and \(\hat{\Phi}\) are defined as follows: \([A(u)\) is an arbitrary function]:

\[ \hat{\Omega} A(u) \equiv \hat{\Omega} \left[ 1 + f_{\text{eq}}(u) \hat{\Phi} \right] A(u), \]  
\[ \text{(4.3)} \]

\[ \hat{\Phi} A(u) \equiv \int du' W(k,u,u') A(u'), \]  
\[ \text{(4.4)} \]

\[ \hat{\Gamma} A(u) \equiv \left[ (D_1 - D_2)(u - k)^2 + D_2 k^2 - \tilde{D} \tilde{R}^2 \right] \]
\[ \times A(u) - \tilde{D} \tilde{R} \omega_0 A(u), \]  
\[ \text{(4.5)} \]

where \(\omega_0(u)\) is the average nematic field a test rod experiences when pointing in direction \(u\):\(^{12}\)

\[ \omega_0(u) = \int dr \int du' W(r,u,u') f_{\text{eq}}(u'), \]
\[ = 8\pi c^{-1} \int du' |u \wedge u'| \psi(u'). \]  
\[ \text{(4.6)} \]

The spatial Fourier transform of the (negative) Mayer function (3.3) used in (4.4) reads\(^{23}\)

\[ W(k,u,u') = 2L^2 D |u \wedge u'| s_k(u) s_k(u') \quad \text{for} \quad kD < 1. \]  
\[ \text{(4.7)} \]

Now consider a specific external field that induces the following potential in the system at \(t = 0\) and onward:\(^{23}\)

\[ \phi(k,u) = -\epsilon s_k(u) H(t) \]  
\[ \text{(4.8)} \]

for rods, or equivalently

\[ \phi(k) = -\epsilon H(t) \]  
\[ \text{(4.9)} \]

for segments; \(H(t)\) is the Heaviside step function. In that case the stationary or equilibrium solution of Eq. (4.2) becomes

\[ \delta \Phi(k) = \left( \int du' s_k(u) \right) \times \left[ 1 + f_{\text{eq}}(u) \hat{\Phi} \right] - f_{\text{eq}}(u) s_k(u) \]  
\[ \text{(4.10)} \]

The perturbation \(\delta \Phi\) is defined analogously to \(\delta f\). It should be noted that the term \([...]^\text{-1}\) is a (formal) operator inverse. Writing the part of Eq. (4.11) between the parentheses as \(\chi(k)\) and using Eq. (4.9) we get \(\delta \Phi(k) = \chi(k) \phi(k)\), i.e., \(\chi(k)\) can be viewed as a generalized response function. This response function is linked to the static structure factor through a variant of the Yvon theorem stating that\(^{29}\)

\[ S_T(k) = -\chi(k)/\nu, \]  
\[ \text{(4.12)} \]

whence,

\[ S_T(k) = \int du s_k(u) \left[ 1 + v\psi(u) \hat{\Phi} \right] - s_k(u) \psi(u). \]  
\[ \text{(4.13)} \]

It is instructive to investigate the relation between the virial approach given above and distribution function theory. We make use of the so-called Yvon equation for weak external fields, which reads for rodlike particles:\(^{39}\)

\[ \delta f(k,u) = -f_{\text{eq}}(u) \phi(k,u) - f_{\text{eq}}(u) \]
\[ \times \int \left[ f_{\text{eq}}(u') h(k,u,u') \phi(k,u') \right], \]  
\[ \text{(4.14)} \]

where \(h(k,u,u')\) is the spatial Fourier transform of the molecular total correlation function \(h(r,u,u')\). Using potential (4.8) we obtain at equilibrium

\[ \delta f(k,u) = \left[ 1 + f_{\text{eq}}(u) \hat{\Phi} \right] f_{\text{eq}}(u) s_k(u) \]  
\[ \times \int du' f_{\text{eq}}(u') \phi(k,u') \]  
\[ \text{(4.15)} \]

The operator \(\hat{\Phi}\) is defined as

\[ \hat{\Phi} A(u) \equiv \int du' h(k,u,u') A(u'), \]  
\[ \text{(4.16)} \]

where again \(A(u)\) is an arbitrary (integrable) function. Following the same line of reasoning as in deriving Eq. (4.13), we get

\[ S_T(k) = \int du s_k(u) \left[ 1 + v\psi(u) \hat{\Phi} \right] s_k(u) \psi(u). \]  
\[ \text{(4.17)} \]

(See also Schneider et al.\(^{30}\)) Comparison of Eqs (4.15) and (4.10) proves the equivalence of the operators \([1 + v\psi(u) \hat{\Phi}]^{-1}\) and \([1 + v\psi(u) \hat{\Phi}]\) at least at the level of...
the second virial approximation. Next we expand the inverse operator formally as

$$[1 + \nu \psi(u) \hat{W}]^{-1} = 1 - \nu \psi(u) \hat{W}$$

$$+ \nu \psi(u) \hat{W} (\nu \psi(u) \hat{W}) - \cdots.$$  (4.18)

An expansion of the operator $[1 + \nu \psi(u) \hat{W}]$ is obtained in terms of the direct correlation function $C(r, u, u')$ by recursively solving the Ornstein–Zernike equation:  

$$h(k, u, u') = C(k, u, u')$$

$$+ \int du' f_{eq}(u') C(k, u, u') h(k, u', u').$$  (4.19)

Equating terms of like order in the two series shows that

$$C(k, u, u') = - W(k, u, u').$$  (4.20)

This shows that in the treatment of Doi et al. and ourselves the direct correlation function equals the Mayer function, i.e., one truncates the diagrammatic expansion of the direct correlation function after the first term.

We now proceed to incorporate dynamics into our analysis. Equation (2.8) can be reformulated with the help of Eq. (2.4),

$$S_f(k, t) = \int du \int du' s_k(u)s_k(u')$$

$$\times \langle \delta f(-k, u; 0)\delta f(k, u'; t) \rangle / \nu V.$$  (4.21)

In the absence of an external field $\delta f(k, u'; t)$ follows the kinetic equation (4.2)

$$\frac{\delta}{\delta t} \delta f(k, u'; t) = -\hat{\Omega} \delta f(k, u'; t).$$  (4.22)

The primed operator $\hat{\Omega}'$ is equivalent to $\hat{\Omega}$ except that all $u$ are replaced by $u'$. But if $\delta f(k, u'; t)$ satisfies Eq. (4.22), then also

$$\frac{\delta}{\delta t} \langle \delta f(-k, u; 0)\delta f(k, u'; t) \rangle$$

$$= -\hat{\Omega}' \langle \delta f(-k, u; 0)\delta f(k, u'; t) \rangle$$  (4.23)

as follows from general kinetic theory. The solution of Eq. (4.23) is

$$\langle \delta f(-k, u; 0)\delta f(k, u'; t) \rangle$$

$$= \int du'' \langle \delta f(-k, u; 0)\delta f(k, u''; 0) \rangle G(k, u'', u'; t),$$  (4.24)

where the Green’s function $G(k, u'', u'; t)$ satisfies

$$\left( \frac{\delta}{\delta t} + \hat{\Omega}' \right) G(k, u'', u'; t) = 0$$  (4.25)

and

$$G(k, u'', u'; 0) = \delta(u'' - u').$$

This result can be inserted in Eq. (4.21) to obtain

$$S_f(k, t) = \int du' \int du'' s_k(u') G(k, u'', u'; t) F(k, u''),$$  (4.26)

defining the function $F(k, u'')$ as

$$F(k, u'') = \int du \ s_k(u) \langle \delta f(-k, u; 0)\delta f(k, u''; 0) \rangle / \nu V.$$  (4.27)

For $t = 0$ Eq. (4.26) reduces to

$$S_f(k, 0) = S_f(k) = \int du' \ s_k(u') F(k, u')$$  (4.28)

which establishes $F(k, u'')$ since expression (4.28) should be identical to Eq. (4.13) for all $k$. We thus arrive at the conclusion that

$$S_f(k, t) = \int du \int du'' \ s_k(u') G(k, u'', u'; t)$$

$$\times [1 + \nu \psi(u'') \hat{W}]^{-1} s_k(u') \psi(u'').$$  (4.29)

For isotropic solutions an analogous equation was obtained by Doi et al. but via a different method.

Equation (4.29) can also be derived from the so-called Vineyard convolution approximation. The derivation starts from the formal expression for the dynamic structure factor (see the Appendix)

$$S_f(k, t) = \int du \int du' \ s_k(u) s_k(u') \psi(u') G(k, u, u'; t)$$

$$+ \nu \int du \int du' \ s_k(u) s_k(u') \psi(u') \psi(u') g(k, u, u'; t),$$  (4.30)

where $g(r, u, u'; t)$ is the time-dependent equivalent of the molecular pair correlation function, and $g(k, u, u'; t)$ its spatial Fourier transform. The Vineyard convolution approximation states that the time evolution of the molecular pair distribution $f^{(2)}(r - r', u, u'; t)$ (see also the Appendix) can be approximated by

$$f^{(2)}(k, u, u'; t) \approx \int du'' f^{(2)}(k, u, u''; 0) G(k, u'', u'; t)$$  (4.31)

which is equivalent to

$$\psi(u') g(k, u, u'; t) \approx \int du'' \psi(u'') g(k, u, u''; 0) G(k, u'', u'; t).$$  (4.32)

The function $G(k, u, u'; t)$ is again the solution of the single-particle time evolution equation (4.25) and $g(k, u, u'; 0) \equiv g(k, u, u')$ is the usual pair correlation function. Insertion of Eq. (4.32) in Eq. (4.30) and replacing the pair correlation function by the total correlation function result in

$$S_f(k, t) \approx \int du \int du' \ s_k(u') G(k, u, u'; t)$$

$$\times [1 + \nu \psi(u) \hat{W}] s_k(u) \psi(u).$$  (4.33)

This is identical to Eq (4.29) in the second virial approximation because of identity (4.20). Hence the Vineyard convolution approximation can be justified but only at the pair interaction level, i.e., at low densities.

V. THE STATIC STRUCTURE FACTOR

A. Analytical evaluation

It is convenient to define an as yet unknown function $b(k, u)$ that has the property

$$F(k, u'') = \int du \ s_k(u) \langle \delta f(-k, u; 0)\delta f(k, u''; 0) \rangle / \nu V.$$  (4.27)
\[ S_i(k) = \int du \ s_k(u) \psi^{1/2}(u)b(k,u). \]  

(5.1)

As can be seen from Eq. (4.13) this function \( b(k,u) \) satisfies the following Fredholm integral equation of the second kind:

\[ b(k,u) + (8/\pi)c \hat{K}b(k,u) = s_k(u) \psi^{1/2}(u), \]  

(5.2)

where the (symmetric) operator \( \hat{K} \) is defined as

\[ \hat{K}b(k,u) = s_k(u) \psi(u)^1/2 \times \int du' |u \wedge u'| s_k(u') \psi(u')^{1/2}b(k,u'). \]  

(5.3)

The equivalence of Eq. (4.13) and the combination (5.1) and (5.2) is easily seen by noting that \( c \) is the dimensionless concentration defined in Sec. III.

To the lowest order of approximation the concentration-dependent term in Eq. (5.2) can be dropped, i.e., we set \( b(k,u) \approx s_k(u) \psi^{1/2} \), to get the so-called self-intermediate scattering function or form factor

\[ S_i^{(0)}(k) = \int du \ s_k(u)^2 \psi(u) = \int du \left( \frac{\sin K\bullet u}{K\bullet u} \right)^2 \psi(u). \]  

(5.4)

The evaluation of Eq. (5.4) is simple in the Gaussian approximation to the orientational distribution function equation (III.6). First it has to be borne in mind that given the scattering geometry as described in Sec. II, the scattering vector \( K \) is chosen in the direction of the \( X \) axis while the director \( n_0 \) is chosen parallel to the \( Z \) axis. Consequently, \( K\bullet u = K \sin \theta \cos \phi \) in the usual polar coordinates (recall that \( |K| = K \) and \( |u| = 1 \)). For highly ordered systems or, equivalently, \( \alpha \gg 1 \) in Eq. (3.6), the approximation \( K\bullet u \approx K^2 \cos \phi \) is permissible. Defining the rescaled magnitude of the scattering vector as \( z = \frac{K}{K_0} - 1/2 \) and changing the variables of integration in Eq. (5.4) to \( x = \alpha^{1/2} \cos \phi \) and \( y = \alpha^{1/2} \sin \phi \), we obtain

\[ S_i^{(0)}(z) = \left(\frac{2\pi}{\alpha} \right)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \frac{\sin z x}{z x} \right)^2 \exp(-i x^2 - iy^2) dx dy (1 + O(\alpha^{-1})). \]  

(5.5)

Integration by parts and omitting terms of \( O(\alpha^{-1}) \) then lead to

\[ S_i^{(0)}(z) = \frac{1}{2}(e^{-2z} + 1) + \left( \frac{\pi}{2} \right)^{1/2} z^{-1} \text{erf}(2^{1/2}z), \]  

(5.6)

where \( \text{erf}(x) \) is the error function. The kernel of the operator \( K \) vanishes for \( z \to \infty \) so that

\[ \lim_{z \to \infty} S_i(z) = S_i^{(0)}(z). \]  

(5.7)

and the asymptotic behavior of \( S_i(z) \) for large \( z \) is described by Eq. (5.6).

A naive method of solving integral equations like the one given by Eq. (5.2) is by means of the iteration

\[ b^{(0)}(k,u) = s_k(u) \psi(u)^{1/2}, \]  

and

\[ b^{(i+1)}(k,u) = s_k(u) \psi(u)^{1/2} - (8/\pi)c \hat{K}b^{(i)}(k,u), \]  

(5.8)

the superscript \( i \) denoting the \( i \)th iterative step. This Neumann iteration converges only if the following requirement is met: \(^{24}\)

\[ (8/\pi)c |\hat{K}| < 1. \]  

(5.9)

In the nematic phase Eq. (5.9) can be shown to hold only for large enough \( z \). It should be noted however that Eq. (5.9) is obeyed for all \( K \) in the case of the isotropic phase, provided the concentration \( c \) is not too high. For instance, defining \( S_i^{(0)}(0) \) as the outcome of the \( i \)th iteration of Eq. (5.1) and (5.8) for \( K = 0 \), we get

\[ \lim_{i \to \infty} S_i^{(0)}(0) = 1/1 + 2c \quad \text{(isotropic phase, } c < 0.5) \]  

(5.10)

which is in agreement with the result of Doi et al. \(^{23,24}\) We return to a numerical evaluation of the Neumann expansion in the next section.

A different method of solving Eq. (5.2) approximately is via a variational principle akin to those of the Schwinger type. \(^{34}\) It exploits the fact that \( \hat{K} \) is symmetric and Eq. (5.1) has an extremum when \( b(k,u) \) is the exact solution of Eq. (5.2). To show this we let \( \delta b(k,u) \) be a small variation in \( b(k,u) \) and \( I(b) \) be defined by Eq. (5.1), i.e., \( I(b) = S_i(k) \).

Then we have \(^{35}\)

\[ I(b + \delta b) = I(b) - \int du \delta b(k,u)^2 \]  

\[ - \frac{8}{\pi} c \int du \int du' |u \wedge u'| s_k(u) s_k(u') \times \psi(u)^{1/2} \psi(u')^{1/2} \delta b(k,u) \delta b(k,u'). \]  

(5.11)

Hence, any variation of order \( \delta b \) in \( b \) leads to a variation of order \( \delta b \) squared in the final result. Now let \( h(u) \) be an estimate of \( b(k,u) \). In order to render \( I(h) \) invariant to the scale of \( h \), we write \( h(u) = \gamma \Phi(u) \), where \( \gamma \) is a variational parameter and \( \Phi(u) \) is a trial function momentarily held fixed. The best estimate for \( h \) is the one for which \( I(h) \) shows an extremum in \( \gamma \). \(^{35}\) Setting \( \delta I/\delta \gamma = 0 \) we get

\[ I(\Phi) = \frac{A^2}{B+C} \]  

(5.12)

and

\[ A = \int du s_k(u) \psi(u)^{1/2} \Phi(u), \]  

(5.13)

\[ C = \frac{8}{\pi} c \int du \int du' s_k(u) s_k(u') \times \Phi(u) |u \wedge u'| \Phi(u') \psi(u')^{1/2} s_k(u'). \]  

(5.14)

The trial function \( \Phi(u) \) may be chosen with or without an adjustable parameter.

In the limit \( z \to \infty \) the solution of Eq. (5.2) is \( b(k,u) = s_k(u) \psi(u)^{1/2} \). A reasonable zero-order trial function for the large \( z \) range is therefore \( \Phi(u) = s_k(u) \psi(u)^{1/2} \) and

\[ A = B = S_i^{(0)}(k), \]  

(5.15)

\[ C = \frac{8}{\pi} c \int du \int du' s_k(u) s_k(u') \Phi(u) |u \wedge u'| s_k(u')^2 \psi(u'). \]
To render $C$ tractable we replace $|u \wedge u'|$ by its average $(\pi/4)\rho$,

$$
\rho = \frac{4}{\pi} \int du \int du' \psi(u) \psi(u') |u \wedge u'|
$$

(5.15)

which yields

$$
S_f(k) \approx \frac{S_f^{(0)}(k)}{1 + 2c \rho S_f^{(0)}(k)}.
$$

(5.16)

This result is similar to the conventional Random Phase Approximation expression for static scattering from isotropic solutions of polymers, except for the factor $\rho$ exhibiting the decrease of the excluded volume interaction in the nematic phase. In the Gaussian approximation $\rho \approx 4/(\pi a)^{-1/2}$.

Expression (5.16) is not expected to be accurate for small $z$.

We may improve our estimate of the static structure factor by using a Gaussian ansatz, together with a preaveraging approximation which presumably introduces only a small error. Having redefined the trial function $\Phi(u)$ by $\Phi(u)_{\nu} \psi(u)_{\nu}$, the result of the preaveraging becomes

$$
A \approx S_f^{(0)}(k) \int du \psi(u) \Phi(u),
$$

$$
B \approx S_f^{(0)}(k) \int du \psi(u) \Phi(u)^2,
$$

$$
C \approx S_f^{(0)}(k)^2 \int du \int du' \psi(u) \Phi(u) \Phi(u')
$$

(5.17)

Our Gaussian trial function reads

$$
\Phi(\theta) = \exp(-\mu(\epsilon - 1)\theta^2), \quad 0 < \theta < \pi/2,
$$

$$
\Phi(\theta) = \Phi(\pi - \theta),
$$

where the adjustable parameter $\epsilon$ is a function of $z$. Insertion of Eq. (5.18) into Eq. (5.17) and the use of Eq. (3.6) lead to

$$
S_f(k) \approx \frac{S_f^{(0)}(k)}{(\epsilon^2/2\epsilon - 1) + S_f^{(0)}(k)\epsilon^{-1/2}}.
$$

(5.19)

This function has an extremum in $\epsilon$ if $\epsilon$ satisfies

$$
\epsilon^{7/2} - \epsilon^{5/2} - S_f^{(0)}(k)(2\epsilon - 1)^2 = 0.
$$

(5.20)

A standard numerical investigation of the roots of Eq. (5.20) provides an empirical but very accurate solution

$$
\epsilon = 0.9139 + 1.7127 \times S_f^{(0)}(k).
$$

(5.21)

The error in Eq. (5.21) is less than 0.2% for $0 < z < 6$ and less than 2% for $6 < z < 9$. In the following section the above estimates for the static structure factor will be compared with numerical results.

**B. Numerical evaluation**

Use of the Gaussian approximation to the orientational distribution function (3.6) leads to expressions for equilibrium properties of the nematic that are correct to leading order. The evaluation of Eq. (5.2) has to be performed with the same degree of accuracy. With this in mind we obtain for the static structure factor in the Gaussian approximation

$$
S_f(z) \approx \frac{1}{\pi} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2
$$

$$
\times \left( \frac{\sin^{1/2}\langle z_1 \rangle \langle z_2 \rangle}{2^1/2\langle z_2 \rangle} \right)^2 \exp(-x^2) b(z,x),
$$

(5.22)

where $b(z,x)$ is the solution to

$$
b(z,x) = 1 - (8/\pi) c \hat{K} b(z,x),
$$

(5.23)

$$
\frac{8}{\pi} c \hat{K} b(z,x) = \left( 2 \frac{2}{\pi} \right)^{3/2} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \langle x - x' \rangle
$$

$$
\times \left( \frac{\sin^{1/2}\langle z_1 \rangle \langle z_2 \rangle}{2^1/2\langle z_2 \rangle} \right)^2 \exp(-x^2) b(z,x').
$$

Here $x \equiv (x_1,x_2)$ are new variables, related to the polar coordinates $\theta$ and $\phi$ through $x_i = (\alpha/2)^{1/2} \cos \phi$ and $x_2 = (\alpha/2)^{1/2} \sin \phi$, and $|x - x'|^2 \equiv (x_1 - x_1')^2 + (x_2 - x_2')^2$. Note that we have redefined the function $b$. The attractiveness of the above approximate integral equation over the original equation is due to the fact that the latter involves a two-parameter calculation while the former contains only one parameter, the magnitude of the scaled scattering vector $z = K \alpha^{-1/2}$.

There are several methods by which one can solve Eq. (5.23) numerically, e.g., quadrature and expansion methods. The most straightforward is numerical quadrature which boils down to a discretization of the problem. Let $g_i$ represent gridpoints "$i"$ (actually a vector since we are dealing with a double integration) and let $w_i$ be the weights associated with that gridpoint. The values of $b(z,x)$ in the gridpoints $g_i$ are determined by solving

$$
b(z,g_i) = 1 - \sum_i \frac{8}{\pi} c K' (g_i,g_i) b(z,g_i).
$$

(5.24)

Defining the vector elements $b_i \equiv b(z,g_i)$ and the matrix elements $K_{ij} \equiv 8 \pi^{-1} c K' (g_i,g_j) w_i$, Eq. (5.24) is recast into the form of a matrix equation

$$
(I + \hat{K}) \mathbf{b} = \mathbf{E}.
$$

(5.25)

In Eq. (5.25) the matrix I represents the unit matrix and the vector $E$ a vector of which all elements have a value equal to unity. The matrix equation can either be solved directly by standard methods or by using the numerical equivalent of the Neumann expansion (5.8), i.e., $b^{(0)} = E$ and $b^{(i+1)} = E - K b^{(i)}$.

Let us first deal with the direct method. The occurrence of an $\exp(-x^2)$ term in the integrand suggests a Gauss-Hermite quadrature in order to discretize Eq. (5.1) and generate matrix $K$. In terms of a product rule of $N \times M$ gridpoints the discretized static structure factor becomes

$$
S_f(z) \approx \frac{1}{\pi} \sum_{i=1}^{N} \sum_{j=1}^{M} w_{i,M} w_{j,N}
$$

$$
\times \left( \frac{\sin^{1/2}\langle z_{i,M} \rangle \langle z_{j,N} \rangle}{2^1/2\langle z_{j,N} \rangle} \right)^2 b(z_i,g_{i,M},g_{j,N}),
$$

(5.26)

where $g_{i,M}$ are the roots of the Hermite polynomial $H_M$ and $w_{j,N}$ the accompanying weights (see e.g., Ref. 38 for details). The matrix equation cf. Eq. (5.25) can be obtained straightforwardly from
\[ b(z, (g_{k,M}, g_{l,N})) = 1 - 2 \left( \frac{2}{\pi} \right)^{1/2} \sum_{i=1}^{N} \sum_{j=1}^{M} w_{i,N} w_{j,M} \left( \frac{\sin 2^{1/2} z g_{i,j}}{2^{1/2} z g_{i,j}} \right)^2 \times \left[ (g_{i,M} - g_{k,M})^2 + (g_{l,N} - g_{l,N})^2 \right]^{1/2} \times b(z, (g_{i,j}, g_{l,N})) \]  
\tag{5.27}

For small \( z \) the integrand is almost symmetrical, so that we choose \( N = M \). The number of constituent elements of matrix \( K \) then equals \( N^2 \times N^2 \) or, equivalently, the number of gridpoints squared. This means that computer storage becomes problematical with increasing values of \( z \), because this requires an increasing number of gridpoints.

Because the kernel of operator \( \tilde{K}' \) in Eq. (5.23) has a weak singularity in its derivative at \( x = x' \) (or \( u = u' \)), the quadrature method described above is expected to converge relatively slowly, as is illustrated in Fig. 3. The figure shows that the numerical static structure factor via quadrature for \( z = 0 \) is a linear function of the inverse number of gridpoints \( N^{-2} \) when \( N^2 \geq 250 \). Extrapolation to infinite \( N \) yields

\[ S_f(0) = 0.2794 \quad \text{(quadrature)}. \]  
\tag{5.28}

Rather surprisingly, the coefficient of the quadratic term in the small \( z \) expansion of the static structure factor converges more rapidly than the constant term \( S_f(0) \). In fact, we have obtained

\[ S_f(z) \approx S_f(0) - \frac{1}{15} z^2 \quad (z \leq 0.3) \]  
\tag{5.29}

to high accuracy. The error was determined to be less than 0.06%, 0.04%, 0.02% and 0.01% for \( N^2 \) equal to 400, 576, 1024, 2304, respectively. In order to establish Eq. (5.29) we have not used Eq. (5.28) but rather the value of \( S_f(0) \) pertaining to the relevant number of gridpoints.

In Fig. 4 we have plotted the results of the numerical computations in the range \( 0 < z < 10 \). The data were obtained using \( N^2 = 1024 \) gridpoints, which is sufficient to gain a reasonable accuracy for small values of \( z \) \([ S_f(0) \] as calculated with 1024 gridpoints differs roughly 0.5% from the extrapolated value Eq. (5.28)). For large values of \( z \) (larger than roughly 3) the accuracy is expected to deteriorate rapidly because the number of gridpoints becomes increasingly insufficient to keep track of all oscillations of the integrand. For the high \( z \) range it is however also possible to apply the Neumann iterative scheme in order to solve matrix equation (5.25). Then exorbitant memory usage can be avoided by generating the matrix elements at the moment they are needed in the iterative process. Ideally, the results of both methods should match at some point.

For increasing values of \( z \) we found it more convenient to use a higher order Newton–Cotes integration rule instead of the Gauss–Hermite rule. The discretized versions of the static structure factor (5.22) and integral equation (5.23) using the Newton–Cotes rule are almost identical to the ones obtained for the Gauss–Hermite rule, except for an \( \exp(-g_{i,j}^2 - g_{l,k}^2) \) term appearing in the summand. We chose a repeated 11-point rule of \( N \times M \) gridpoints. The exact position of the gridpoints depends on the choice of the integration boundary \( R \), unlike the Gauss–Hermite rule where we automatically used \( R = \infty \). Because the oscillatory behavior of the integrand is asymmetrical with respect to the integration variables, we chose \( N \) unequal to \( M \) in order to minimize the total number of gridpoints. Now, the variables \( N, M, \) and \( R \) have to be determined empirically as a function of \( z \) by systematically increasing their values till they asymptote toward constants. In our case an accuracy of about 0.2% was thought acceptable. The Neumann iteration proved to converge only if \( z \) was greater than roughly 4. At most 20 iterations were required to attain the limiting value of \( S_f(z) \) from the converging series. This was possible to high accuracy (much better than the aforementioned 0.2%) because the iterations of even and odd numbers could be separated into two convergent series.

In Fig. 4 we have also plotted the results of the Neu-
mann iteration. They match nicely to the quadrature results at \( z = 4 \). Combining the results of both methods we get a consistent curve for the static structure factor as a function of the scaled magnitude of the scattering vector. This curve is plotted in Fig. 5, together with those of the various approximate expressions derived in the preceding section. As expected, the self-intermediate scattering function grossly overestimates the numerically obtained structure factor. On the other hand, the approximate variational results underestimate the numerical values. Expressions (5.16) and (5.19) almost coincide for \( z > 5 \), both underestimating the numerical curve by about 11%. For small \( z \), Eq. (5.16) becomes substantially less accurate, being off by a maximum of 29%. Expression (5.19) does comparatively well in that range, the discrepancy being only 12% for \( z = 0 \); the maximum error of 17% occurs at \( z \approx 2.5 \). Apparently the approximate variationally obtained expressions give a fair estimate of the static structure factor; a better trial function would improve this estimate.

At the end of this section we describe briefly an alternative method for solving integral equation (5.2) numerically when \( z = 0 \) (see also Ref. 39). Equations (5.1) and (5.2) can be written as

\[
S_f(0) = \int du \, \psi(u) b(u),
\]

\[
b(u) + \frac{8}{\pi} c \int du' |u \land u'| \psi(u') b(u') = 1.
\]

Symmetry considerations lead to the conclusion that \( b(u) = b(\theta) \), i.e., \( b \) depends only on the polar coordinate \( \theta \) and not on \( \phi \). Next we write \( b \) as a series expansion in Legendre polynomials:

\[
b(\theta) = \sum_{l=0}^{\infty} b_l P_l(\cos \theta)
\]

and note that

\[
(2\pi)^{-1} \int_{0}^{2\pi} d\phi \sin \gamma = \sum_{n=0}^{\infty} d_{2n} P_{2n}(\cos \theta) P_{2n}(\cos \theta'),
\]

where \( \gamma \) is the angle between \( u \) and \( u' \), \( d_0 = \pi/4 \), \( d_2 = -5\pi/32 \), and

\[
d_{2n} = -\frac{\pi(4n + 1)(2n - 3)!!(2n - 1)!!}{2^{2n + 2} n!(n + 1)!},
\]

when \( n > 1 \). Inserting Eqs. (5.32) and (5.33) into Eqs. (5.30) and (5.31), we obtain

\[
S_f(0) = \sum_{k=0}^{\infty} b_{2k} \langle P_{2k}(\cos \theta) \rangle
\]

the expansion coefficients \( b_{2k} \) satisfying

\[
b_{2k} + 8\pi^{-1} c \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} d_{2k} b_{2l}(4m + 1) X_{2k,2l,2m} \langle P_{2m}(\cos \theta) \rangle = \delta_{k,0}.
\]

Here

\[
I_{2k,2l,2m} = \frac{1}{2} \int P_{2k}(x) P_{2l}(x) P_{2m}(x) dx
\]

which is equal to 0 if \( k + l - m < 0 \), or \( k - l + m < 0 \), or \(-k + l + m < 0 \), and

\[
I_{2k,2l,2m} = \frac{(k + l + m)!}{(k + l - m)!(k - l + m)!( - k + l + m)!}
\]

I_{2k,2l,2m} \quad \text{otherwise. The angular brackets in Eqs. (5.35) and (5.36) denote an average over all orientations}

\[
\langle \cdots \rangle = \int du \, \psi(u) (\cdots).
\]

In practice only a limited number of expansion coefficients \( b_{2k} \) are needed to get an accurate description. Upon replacing \( \infty \) in the upper limit of the summations by \( n_{\text{max}} \), Eq. (5.36) reduces to an ordinary matrix equation, provided
the averages \( \langle P_{2m} \rangle \) are known. We calculated these averages with the Gaussian angular distribution function (3.6), using the aforementioned repeated 11-point Newton–Cotes quadrature rule. The numerical integrations were carried out without using additional approximations similar to those in deriving Eqs. (5.22) and (5.23) so that the end result depends on \( \alpha \). The number of required expansion coefficients \( n_{\text{max}} + 1 \) was determined by systematically adding extra terms until a constant value of \( S_f(0) \) was reached within a chosen accuracy of 0.1%. It turns out that \( n_{\text{max}} \approx 1.5 \alpha^{1/2} \) (see also Ref. 40).

The results of the calculations are plotted in Fig. 6. The static structure factor is found to depend linearly on \( \alpha^{-1} \), if \( \alpha \) is large enough. Extrapolation leads to

\[
S_f(0) = 0.2783 \left[ 1 + O(\alpha^{-1}) \right] \quad \text{(expansion).} \quad (5.40)
\]

This is in good agreement with the previous result (5.28).

VI. INITIAL DECAY RATES

Analytical evaluation of the expression for the dynamic structure factor does not seem feasible at present. The initial decay rate \( \Gamma_f(k) \) however can be calculated analytically for all \( K \) or \( z \), since the Green's function \( G(k,u,u';t) \) need not be known.\(^{26}\)

\[
\Gamma_f(k) \equiv - \frac{\delta}{\delta t} \ln S_f(k,t) \bigg|_{t=0} = \int d u S_k(u) \hat{\Delta}_s(u) \hat{G}_s(u) \psi(u) \quad S_f(k) \quad (6.1)
\]

A somewhat tedious calculation shows that for the Gaussian distribution (3.6) and the nematic potential that is linked with this distribution,\(^{41}\)

\[
\omega_0(u) \approx \omega_0(0) + |\alpha \theta^2 + \cdots|,
\]

the following expression is obtained

\[
S_f(z) = - \alpha (\tilde{D}_r - \tilde{D}_z z^2 - 4L^{-2} D_1 z^2) S_f^{(0)}(z) + 2L^{-2} (D_1 - D_1) (1 - e^{-z^2}) + 2^{-3/2} \pi^{1/2} \alpha \tilde{D}_z z \text{erf}(2^{1/2} z)
\]

\[
- 2 \alpha \tilde{D}_z z \left[ 3^{-1}(\pi/2)^{1/2} z \text{erf}(2^{-1/2} z) - \sum_{m=0}^{\infty} \frac{(m+2)(2m+5)!}{(2m+2)^{2m+1}} \text{exp}(-z^2/2) H_{2m+1}(2^{-1/2} z) \right].
\]

(6.3)

Here \( S_f^{(0)}(z) \) is given by Eq. (5.6) and terms of \( O(\alpha^{-1}) \) have been omitted. Expanding Eq. (6.3) in powers of \( z \),

\[
\Gamma_f(z) \approx (a_1 z^2 + a_2 z^4 + \cdots) / S_f(z),
\]

\[
a_1 = 4 \alpha L^{-2} D_1 + 4L^{-2} (D_1 - D_1),
\]

\[
a_2 = 4 \alpha L^{-2} \tilde{D}_z - 4 \alpha L^{-2} D_1 - 4L^{-2} (D_1 - D_1).
\]

Note that the diffusion coefficients \( D_1 \) and \( \tilde{D}_r \) appear in combination with the factor \( \alpha \), which is greater than roughly 20. Although both \( D_1 \) and \( \tilde{D}_r \) are probably small in nematic solutions, they may as a result of this still contribute to the initial decay rate. The preaveraged rotational diffusion constant \( \tilde{D}_r \) does not influence the initial decay rate at small scattering angles because it does not show up in the \( O(\alpha^2) \) term. The extraction of \( \tilde{D}_r \) from experimental data is therefore possible only at relatively large scattering angles (see below).

Of particular interest is the apparent cooperative diffusion coefficient defined as\(^{26}\)

\[
D_{\text{coop}} \equiv \lim_{k \to 0} \frac{\Gamma_f(k)}{k^2}
\]

(6.5)

which becomes after insertion of Eqs. (6.4) and (2.7),

\[
D_{\text{coop}} \approx (D_1 + \tilde{D}_z (D_1 - D_1)) \text{erf}(-z^2) / S_f(0),
\]

(6.6)

where \( S_f(0) \approx 0.28 \left[ 1 + O(\alpha^{-2}) \right] \) is only weakly concentration dependent since \( \alpha \gtrsim 4 \) in the nematic phase. The numerator of Eq. (6.6) is equal to the (orientational) average of the translational diffusion constant in the direction of the scattering vector \( D_G \equiv \langle \hat{\mathbf{k}} \cdot \mathbf{D} \hat{\mathbf{k}} \rangle; \hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|, \mathbf{D} = D_1 uu + \tilde{D}_z (1 - uu) \rangle \) is the previously defined orientational average (5.39). This diffusion coefficient \( D_G \) is concentration dependent due to the concentration dependence of the average orientation of the macromolecules.

In the limit \( z \to \infty \), Eq. (6.3) reduces to

\[
\Gamma_f(k) \approx D_1 k^2 + \tilde{D}_z k^2.
\]

(6.7)

The apparent diffusion coefficient reaches a plateau value in this limit:

\[
D_{\text{plat}} \equiv \lim_{k \to \infty} \frac{\Gamma_f(k)}{k^2} \approx D_1 + \tilde{D}^2 z \tilde{D}_z.
\]

(6.8)

This expression is identical to the one obtained for dilute solutions of rigid rodlike polymers.\(^{42}\)

We conclude this section by giving qualitative curves of initial decay rates for different concentrations of the virus TMV in nematic solution as predicted by Eq. (6.4). We im-

![Fig. 6. The static structure factor \( S_f \) at \( z = 0 \) as a function of the inverse of the parameter \( \alpha \), defined in Sec. III. The data were obtained by means of the expansion method.](image-url)
mediate addition that TMV might not be so good an example. Since $L \approx 300$ nm and $D \approx 18$ nm we know the aspect ratio is about 17 which may just not be large enough for the second virial approximation to be valid. The effective aspect ratio is in fact even smaller than 17 due to the presence of an electrical double layer.

For qualitative purposes we assume that the parallel translational diffusion coefficient equals its value in dilute solution, so $D_p = D_{0,0}$, and the perpendicular translational diffusion coefficient equals zero, i.e., $D_q = 0$. (This assumption may be too strong.) We also need an expression for the static structure factor: $S_0(z) \approx 0.28 - \beta z^2$ for $z \leq 0.3$ (see Sec. V). The restriction $z \leq 0.3$ implies that we are limited to relatively modest scattering angles; smaller than roughly 80° if the wavelength of the incident light is 500 nm (in vacuo) and $4 < c < 10$.

In Fig. 7 we have plotted the initial decay rate $\Gamma_1(k)$ for various concentrations, using the above suppositions and $D_{0,0} = 5.9 \times 10^{-12}$ m$^2$ s$^{-1}$; $D_{0,0}$ is the average translational diffusion coefficient in dilute solution. For each concentration we have used two extremes for the rotational diffusion constant: $D_r = 0$ s$^{-1}$ and $D_r = 318$ s$^{-1}$, the value in dilute solution. The strong concentration dependence of $\Gamma_1$ and its weak dependence on the rotational diffusion constant in the small $K$ range are clearly illustrated.

VII. ANISOTROPIC SCATTERING

Following Sec. II the contribution of the anisotropic scattering to the total scattering is expressed in an anisotropic structure factor $S_4(k,t)$:

$$S_4(k,t) = \frac{\beta^2}{\gamma V} \left( c(-k,0)c(k,t) / \gamma V + O(\beta^2) \right)$$

The two terms on the right-hand side of this expression are identical as one can show by noting that the structure factor is invariant to the transformation $k \rightarrow -k$ and that, since we are dealing with a stationary microscopically reversible system, the averages are invariant to the transformation $(0,t) \rightarrow (-t,0)$ and $t \rightarrow -t$. Consider first the static form of Eq. (7.1) by setting $t = 0$. Then with the help of Eqs. (2.3), (2.4), and (2.6) we obtain

$$S_4(k) = \frac{\beta^2}{\gamma V} \int d(u_s(u)P_z(n_u) \left[ 1 + \nu\psi(u)\hat{H} \right] s_k(u) \psi(u))$$

(7.2)

(see also the Appendix). Here $\hat{H}$ is again the integral operator (6.16) associated with the molecular total correlation function $h(r_u,uu')$. We recall that in the second virial approximation the Mayer function acts as the direct correlation function, and that therefore Eq. (7.2) can be written as (cf. Sec. IV)

$$S_4(k) \approx \frac{\beta^2}{\gamma V} \int d(u_s(u)P_z(n_u) \left[ 1 + \nu\psi(u)\hat{H} \right] s_k(u) \psi(u))$$

(7.3)

Since the orientational distribution function $\psi(u)$ is sharply peaked around the director, the small angle expansion

$$P_z(n_u) \approx 1 - \beta^2 + \cdots$$

(7.4)

is applicable. Using the Gaussian distribution (3.6) it appears from Eqs. (7.3) and (7.4) that

$$S_4(k) \approx \beta S_0(k) \times (1 + O(\alpha^{-1}))$$

(7.5)

We have checked this relation numerically for $k = 0$ by means of the expansion method described in Sec. V. It turns out that when $20 \leq \alpha \leq 80$ the relative error is less than 2%. Finally we get to leading order for large $\alpha$,

$$S(k) = S_4(k) + S_4(k) \approx S_0(k) (1 + \beta)$$

(7.6)

The correction to the static structure factor on account of anisotropic scattering is accordingly about 10%.

The anisotropic dynamic structure factor is obtainable in a fashion similar to the derivation of the isotropic dynamical structure factor. We refer to Sec. IV for details. The resulting expression is found to be

$$S_4(k,t) = \frac{\beta^2}{\gamma V} \int d(u_s(u)P_z(n_u)G(k,u*,u';t)$$

$$\times (1 + \nu\psi(u*)\hat{H} \right] s_k(u*) \psi(u))$$

where $G(k,u*,u';t)$ satisfies Eq. (4.25). From this the initial decay rate can be calculated,

$$S_4(k) \Gamma_4(k) \approx \frac{\beta^2}{\gamma V} \int d(u_s(u)P_z(n_u)\hat{H} s_k(u) \psi(u))$$

(7.7)

Next the expansion of the Legendre polynomial (7.4) is inserted to yield the leading order behavior for large $\alpha$,

$$S_4(k) \Gamma_4(k) \approx \beta S_0(k) \Gamma_4(k) (1 + O(\alpha^{-1}))$$

(7.8)

Hence it follows that

$$\Gamma(k) = S_4(k) \Gamma_4(k) + S_4(k) \Gamma_4(k)$$

$$\approx \beta S_0(k) \Gamma_4(k) (1 + O(\beta \alpha^{-1}))$$

(7.9)

J. Chem. Phys., Vol. 93, No. 5, 1 September 1990
Downloaded 02 Aug 2007 to 130.161.132.53. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp
Since $\alpha \gg 1$ and $\beta \ll 1$ the correction to the initial decay rate is negligible.

**VIII. CONCLUDING REMARKS**

There are many limitations in our analysis. The kinetic equation (3.1) hinges on preaveraged diffusion coefficients; whether such preaveraging is legitimate is an unresolved problem. Here we have left the precise form of the coefficients unspecified. Conceivably they might well vary according to the time scale of the light scattering experiment. For instance the diffusion coefficients should adopt bare values at very short times where little or no entanglement takes place whereas effective values would be needed at longer times. The kinetic theory embodied in Eq. (3.1) emphasizes the influence of the self-consistent nematic potential.

Hydrodynamic interactions have also been ignored. Although no really satisfactory theory for semidilute rods exists, it is generally believed that hydrodynamic screening would merely change the effective diffusion coefficients by a factor of order $\log(\nu L^3)$. Since other effects like entanglement and excluded volume cause a much stronger dependence on the concentration, hydrodynamic interactions are often disregarded altogether.

We have modeled stiff macromolecules as slender rods. This means that the theory strictly applies to almost rigid particles like schizophyllan and fd-virus (provided they are short enough). Generally most semiflexible polymers have to be viewed as wormlike chains which conform to a different theory. We have disregarded third- and higher-order virial terms implying that the volume fraction must be quite smaller than unity.

We postulate that director fluctuations do not entangle with those concentration fluctuations we focus attention on. We have mentioned two reasons why such a hypothesis is reasonable: (a) Director fluctuations do not contribute to polarized scattering when the director is perpendicular to the scattering plane. (b) When these fluctuations are provisionally extrapolated down to a molecular length scale, they remain negligible compared with concentration fluctuations.

We have shown that the static scattering of a highly ordered nematic depends solely on the dimensionless variable $z = kL/2\alpha^{1/2}$. This fact accelerates the numerical evaluation of the structure factor $S_L$. Our variational estimates give a semiquantitative idea of the analytical behavior of $S_L$. We have not been able to discover an exact relation between $S_L(0)$ and the osmotic compressibility. Adopting the usual identity valid for isotropic liquids would give $S_L(0) = \xi$ in the Gaussian approximation. This disagrees with Eq. (5.28).

Because we have set the director $n_0$ perpendicular to the scattering plane, diffusion perpendicular to $n_0$ is emphasized. Thus in Eq. (6.6) we see that a relatively small value of $D_i$—small possibly because of entanglement—could still dominate parallel diffusion. In the higher-order terms of Eq. (6.4) both rotational and perpendicular diffusion are also weighted by the large factor $\alpha$. Accordingly, dynamic light scattering could be a useful tool in assessing the diffusion across the nematic potential.

Finally, we stress that what one intuitively expects for isotropic systems does not hold for nematic liquid crystals. In an isotropic solution of repulsive hard rods the structure factor at small $K$, i.e., $S(0)$, would decrease with increasing rod concentration and the cooperative diffusion coefficient would be enhanced. In a nematic solution the direct forces do increase with increasing volume fraction of rods but the cooperative alignment also increases. Hence, the average of the Mayer or direct correlation function proportional to an excluded volume decreases as the rods align. The diminishing excluded volume offsets the increasing volume fraction so that $S(0)$ is essentially a constant [see Eqs. (5.28) and (5.40)] and $D_{coop}$ decreases [see Eq. (6.6)].

**APPENDIX**

We seek to derive an expression for the dynamic structure factor of rodlike particles from the perspective of distribution function theory. The starting point is Eq. (4.21), which can be written in terms of the local particle density (5.3) as

$$
S_L(k,t) = \int du \int du' s_k(u)s_k(u') \int dr \int dr' \exp(ik\cdot(r-r'))
\times \left( \sum_i \sum_j \delta(r - R_i(t))\delta(r' - R_j(0))\delta(u - u_i(t))\delta(u' - u_j(0)) \right)/\nu V. \quad (A1)
$$

The double summation between the angular brackets allows the separation of like and unlike terms such that

$$
S_L(k,t) = \int du \int du' s_k(u)s_k(u')(\mathcal{L} + \mathcal{Q}), \quad (A2)
$$

where

$$
\mathcal{L} = \sum_i \langle \exp(ik[ R_i(t) - R_i(0) ])\delta(u - u_i(t)) \rangle/\nu V, \quad (A3)
$$

and

$$
\mathcal{Q} = \int dr \int dr' \exp(ik\cdot(r-r'))
\times \left( \sum_i \sum_j \delta(r - R_i(t))\delta(r' - R_j(0))\delta(u - u_i(t))\delta(u' - u_j(0)) \right)/\nu V. \quad (A4)
$$

The part of the dynamic structure factor that stems from intramolecular scattering is associated with the like terms $\mathcal{L}$ and can be simplified by noting that all particles are iden-
tical and that the total number of particles equals \( nV \). Thus we have
\[
\int \, dv \int \, dv' s_k(u) s_k(u') \mathcal{L}'
= \langle \exp[\frac{i}{\hbar} \mathbf{k} \cdot (r(t) - r(0))] s_k(u(t)) s_k(u(0)) \rangle
\]  
(A5)
in which \( r(t) \) and \( u(t) \) pertain to the position of the center of mass and the orientation of an arbitrary rodlike particle at time \( t \). As shown elsewhere, the right-hand side of Eq. (A5) is identical to
\[
\int \, dv \int \, dv' s_k(u) s_k(u') G(k,u,u';t) \psi(u),
\]  
(A6)

where \( G(k,u,u';t) \) is the previously defined Green's function. In the summation of the unlike terms of Eq. (A1) one recognizes the time-dependent equivalent of the molecular pair distribution \( f^{(2)}(r-r',u,u';t), 22 \)
\[
f^{(2)}(r-r',u,u';t) = \left( \sum_{j=1}^{N} \sum_{i=1}^{N} \delta(r-R_j(t)) \delta(r-R_i(0)) \delta(u-u_j(t)) \right.
\]
\[
\times \delta(u'-u_j(0)) \right) \]  
(A7)

It is related to the time-dependent molecular pair correlation function \( g(r-r',u,u';t) \) through
\[
f^{(2)}(r-r',u,u';t) = \nabla^2 \psi(u) \psi(u') g(r-r',u,u';t). \]  
(A8)

Consequently, inserting Eq. (A8) into Eq. (A4), we have
\[
\Psi = \nu \psi(u) \psi(u') g(k,u,u';t) \]  
(A9)

The \( k \) appearing in \( g \) indicates as before that we are dealing with a spatial Fourier transform. Combining Eqs. (A2), (A5), and (A9) establishes the final expression for the dynamical structure factor
\[
S_f(k,t) = \int dv \int dv' s_k(u) s_k(u') G(k,u,u';t) \psi(u)
+ \nu \int dv \int dv' s_k(u) s_k(u') \psi(u) \psi(u') g(k,u,u';t).
\]  
(A10)

For \( t = 0 \), Eq. (A10) becomes equal to the static structure factor (4.17) since \( G(k,u,u';0) = \delta(u-u') \) and \( g(k,u,u';0) = g(k,u,u') = h(k,u,u') \) apart from an unimportant \( \delta(k) \) term.

15 This is explicitly seen as follows. Reference 13 states that we have to compare the inverse aspect ratio \( D/L \) signifying the "internal" orientational angle of a rod with the root-mean-square angle given by the orientational distribution function [Eq. (3.6)]: \( D/L \rightarrow \alpha^{-1/2} \). Equations (3.7) and (3.8) thus show that the volume fraction approximately given by \( LD^2 \) must be small.
17 T. Odijk, Liquid Crystals 1, 553 (1986).
43 J. A. Peetersman, Max-Planck-Institut für Festkörperforschung, Grenoble (personal communication).
44 J. M. Schurr, Chem. Phys. 111, 55 (1987) and references therein. Our informal analysis leading to Eq. (4.20) may be a useful physical picture of the general formalism surveyed in this reference.
45 Multiple scattering is often thought to be low in lyotropic liquid crystals. See e.g., V. G. Taratuta, A. J. Hurd, and R. B. Meyer, Phys. Rev. Lett. 55, 246 (1985).
We inadvertently omitted the explicit form of the functional $I(\eta)$ which renders Sec. V A incomprehensible. The paragraph beginning with "A different method..." and ending "... we have" should read:

"A different method of solving Eq. (5.2) approximately is via a variational principle akin to those of the Schwinger type but not necessarily pertaining to definite operators. The functional $K$ is symmetric which simplifies the principle. The functional

$$I(\eta) = 2 \int du s(\eta(u))\psi(\eta)^{1/2}h(k,u) - \int du h^2(k,u)$$

$$- \frac{\delta \psi}{\pi} \int d\epsilon d\epsilon' s(\eta(u))\psi(\eta)^{1/2}$$

$$\times h(k,u) |u \wedge u'| s(\eta(u'))\psi(\eta')^{1/2}h(k,u')$$

has an extremum when $h(k,u) = b(k,u)$, i.e., the exact solution to Eq. (5.2). To show this we write $h = b + \delta b(k,u)$, where $\delta b$ is a small variation and $I(b) = S(k)$ [see Eqs. (5.1) and (5.2)]. Then we have."

We have also used a similar principle in the isotropic case to go beyond the random phase approximation. See P. van der Schoot and T. Odijk, Macromolecules 23, 4181 (1990).