For the T2 sums, simple integration is not reasonable. A good approximation for $S_{\rm i}$, the inner sum, i.e. the sum of U from $j = 1$ to $k^*/2$, where $U = [k + \{q(k-j)j\}^{1/2}]^{3/2}\{(k-j)j\}^{-5/2}$, was found empirically, for high k, to approach $1.354/k$. Substituting this value into eq 19 of the main paper, we get

$$\phi'(x,5/2) \simeq \sum_{k=2}^{m} x^k(S_{\rm i}) + 1.354 \int_m^\infty x^k/k \, {\rm d}k$$

Whence, the remainder integral is

$$R\{\phi'(x,5/2)\} = 1.354 \ {\rm Ei}(-m \ln x) \tag{8}$$

where Ei(t) is the exponential integral

$$\int_t^\infty (e^{-y}/y) \, dy$$

Similarly

$$\phi'(x,3/2) \simeq \sum_{k=2}^{m} kx^k(S_{\rm i}) + 1.354 \int_m^\infty x^k \, {\rm d}k$$

Whence

$$R\{\phi'(x,3/2) = 1.354x^m/(-\ln x) \tag{9}$$

and

$$\phi'(x1/2) \simeq \sum_{k=2}^{m} k^2x^k(S_{\rm i}) + 1.354 \int_m^\infty kx^k \, {\rm d}k$$

Whence

$$R\{\phi'(x,1/2)\} = 1.354\{x^m(-\ln x)\}\{m + 1/(-\ln x)\} \tag{10}$$

For values of x near unity, with which the correction terms are used, $-\ln x$ is closely equal to $1 - x$, or $1/D_{\rm c}$, the chain number-average molecular weight. Algorithm for computing the complementary error function is built into the PL/I compiler used for the program; the exponential integrals were found by using the IMSL Fortran Mathematical Library, as function MMDEI.

Appendix II. Comparison of Numerical Errors in the Ratio of Ring-Catenane Isomers

Examination of (1-7) and (1-9) allows computation of the number ratio of any size rings (n) to the isomeric ($i + j = n$) catenanes. This ratio is independent of x, ν, and b, i.e., invariant with respect to both the chain parameters and the degree of polymerization. The ratio is given by

$$Ca_{ij}/R_{i+j} = (C/B)[i + j + q(ij)^{1/2}]^{3/2}[(i + j)/ij]^{3/2} \tag{11}$$

For the case $i = j$, this reduces to

$$Ca_{ii}/R_{2i} = (C/B)(2 + q)^{3/2}2^{5/2}/i \tag{12}$$

and for the case where $i = j = 1$, i.e., the ratio of 1,1-catenanes to dimer rings

$$Ca_{11}/R_2 = (C/B)(2 + q)^{3/2}2^{5/2} = 2.6 \tag{13}$$

Dependence of x, ν, and b are absent from all three of these relations, all quantities therein except the size of the isomers being numerical. The degree of reaction (represented by x) cancels out while $i + j = n$, for any group of catenane isomers, compared to isomeric rings. The chain parameters ν and b cancel out for any group of rings and catenanes whatever, compared together, appearing in the same relation in both C and B.

Requirements that there be no sensible steric hindrance, and that the polymer combinations follow Gaussian statistics, however, remain. Any change from these conditions would cause different ratios for catenanes to rings. These relations hold for both the general and the chain-free systems, as they pertain only to the ring–catenane ratios.

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Induced Chain Rigidity, Splay Modulus, and Other Properties of Nematic Polymer Liquid Crystals

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ABSTRACT: We present a numerical analysis of the induced chain rigidity or global persistence length, the order parameter, the splay modulus, and other properties of a polymer nematic. The macromolecules are viewed as long slender wormlike cylinders interacting via hard-core repulsions in the second virial approximation. We calculate the orientational distribution function from the nonlinear integrodifferential equation first formulated by Khokhlov and Semenov. A bifurcation analysis of this equation is also given. Exact expressions for the susceptibility and the global persistence length are derived in terms of the distribution function. Analytical estimates of these quantities based on the usual methods are extremely poor approximations to those determined numerically. We also discuss the splay modulus which is directly related to the susceptibility and the global persistence length.

I. Introduction

The average dimension of an *isolated* wormlike chain is a well-known function of the persistence length P which in turn equals the chain bending constant divided by the temperature.[1,2] It is not widely appreciated that this relation is not universally valid since it is statistical in nature.

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For instance when a semiflexible chain is strongly constrained to align more or less in one direction only, the usual persistence length P is no longer a relevant scale. Scaling and other types of analyses show that a new *local* scale emerges which may be called a deflection length λ.[3,4] This determines the statistical properties of a strongly confined worm, e.g., its orientational free energy is proportional to the contour length divided by λ. In addition, there is also a second scale, the *global* persistence length g, which can be derived from λ by scaling arguments (see section II). As its name implies, it is g that is related to the average dimension of a confined chain. As we shall see, the global persistence length governs various important quantities of the polymer nematic like the splay modulus.

The nematically induced *global* rigidity of a stiff chain has been the center of attention for some time.[5-14] However, most of the theory has been rudimentary with regard to the nature of the nematic field. Khokhlov and Semenov[6] did give a precise formulation of the global persistence length using a self-consistent field theory within the second virial approximation. Here, we note that there are in fact systems for which these approximations should work very well.[4] Nevertheless, Khokhlov and Semenov's WKB calculation of g is erroneous because their equation is strongly nonlinear so that the WKB approximation is very poor.

This paper has several aims. We first show that scaling arguments can be used to understand the connection between the global persistence length g, the splay modulus K_1, and the deflection length λ (section II). Next, in order to set up a precise theory of these quantities, we start by surveying the Khokhlov–Semenov integrodifferential equation (section III). A bifurcation analysis of this is presented in section IV. We analyze the equation numerically (section V), study the properties of the nematic phase (section VI), and compare the numerical analysis with the leading order solution (the so-called Gaussian approximation). For the sake of completeness we calculate the values of the thermodynamic quantities at the isotropic–nematic transition (section VII). In section VIII we derive an exact formula for the global persistence length in terms of the orientational distribution function and calculate g numerically using the information of the previous sections. Finally, we discuss the implications of our results in section IX.

II. Qualitative Remarks

As we pointed out above, the deflection length λ is the scale of physical relevance in describing a strongly confined semiflexible chain. For a lyotropic nematic, λ is derived by qualitatively analyzing the correlation function $\langle \theta^2(|s-t|)\rangle$ for the angle $\theta(|s-t|)$ between two unit vectors tangential to the contour of the test chain at distances s and t from one end. For small enough $|s-t|$ the orientational correlations should be in accord with the central limit theorem, i.e., $\langle \theta^2(|s-t|)\rangle \approx |s-t|/P$ valid for a chain in dilute solution.[2] For larger distances the correlation function will eventually be restricted in view of the prevailing nematic order. Accordingly, we can identify a crossover distance $|s-t| = \lambda$ such that[3,4]

$$\langle \theta^2(|s-t| = \lambda)\rangle \approx \alpha^{-1} \qquad \text{(II.1)}$$

i.e.

$$\lambda = P/\alpha \qquad \text{(II.2)}$$

where the nematic order is specified by a parameter α ($\alpha \gg 1$; for a precise definition in terms of the orientational distribution function, see eq VI.5).

A typical configuration of a nematically confined chain is depicted in Figure 1. The nematic field exerted by the surrounding chains deflects the test chain toward the director, about once every deflection length λ. However, if the chain is long enough there is a nonnegligible probability of the formation of hairpin bends, also shown in Figure 1. Since we postulate that λ is the sole relevant scale, the contour length of such a sharp bend must be of order λ.

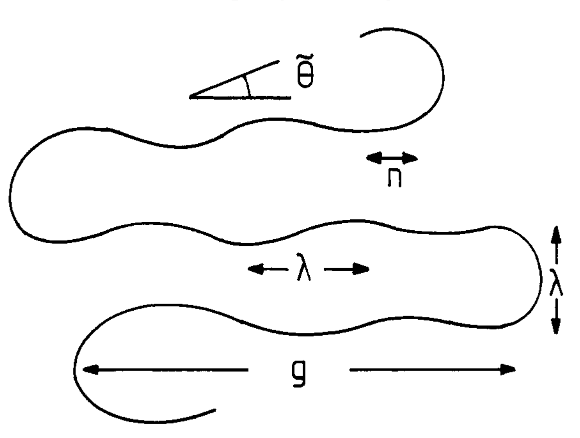

Figure 1. Typical configuration of a very long semiflexible chain in the nematic field exerted by the surrounding polymer segments. There are two scales discernible: the deflection length λ and the global persistence length g. The orientational restriction is $\tilde{\theta} = \alpha^{-1/2}$ and the director is denoted by n.

The chain in Figure 1 is basically a one-dimensional random walk with fluctuating step length, the mean-square of its extension R being given by a relation like

$$\langle R^2\rangle \approx Lg \qquad (L \gg g) \qquad \text{(II.3)}$$

Here L is the contour length and the other factor must be the global persistence length g, since g is proportional to an average step length. Thus, the distance between hairpin bends is also about g, on average.[32] Note that the U-turn bends or defects are actually distributed randomly along the chain contour. Hence, the statistical mechanical problem of calculating g boils down to an analysis of a one-dimensional gas of Lg^{-1} defects of concentration λg^{-1} (fluctuations in the step length can be disregarded).

The free energy of the defect gas in units of temperature T is simply

$$\frac{\Delta F_{\text{def}}}{k_B T} \approx \frac{L}{g} \ln\left(\frac{\lambda}{g}\right) + \frac{LP}{g\lambda} \qquad \text{(II.4)}$$

One recognizes an ideal gas term and a bending energy per defect given by

$$U_{\text{bend}} = \frac{1}{2} P k_B T \int_0^{\lambda} \left(\frac{\partial \mathbf{v}}{\partial s}\right)^2 \mathrm{d}s \approx P k_B T/\lambda \qquad \text{(II.5)}$$

The inverse radius of curvature is $(\partial \mathbf{v}/\partial s)$, where $\mathbf{v}$ is the tangential unit vector at contour point s. Minimizing ΔF_{def} with respect to g yields

$$g \approx \lambda \exp(P/\lambda) \approx P\alpha^{-1} \exp(\alpha) \qquad \text{(II.6)}$$

If the chains interact via excluded-volume interactions, the parameter $\alpha \approx c^{2/3}$ where the dimensionless variable c is the number density ρ_p of persistence segments scaled by the excluded volume $(\pi/4)P^2D$ (P = persistence length, D = chain diameter)[3,4] (see section III). Hence, we have

$$g \approx Pc^{-2/3} \exp(c^{2/3}) \qquad \text{(II.7)}$$

Meyer[15] has shown that the splay modulus for nematic rigid rods is simply

$$K_1 \approx l^2 \rho_l k_B T \qquad \text{(II.8)}$$

if their length is l and their number density ρ_l. If $L \gg g$

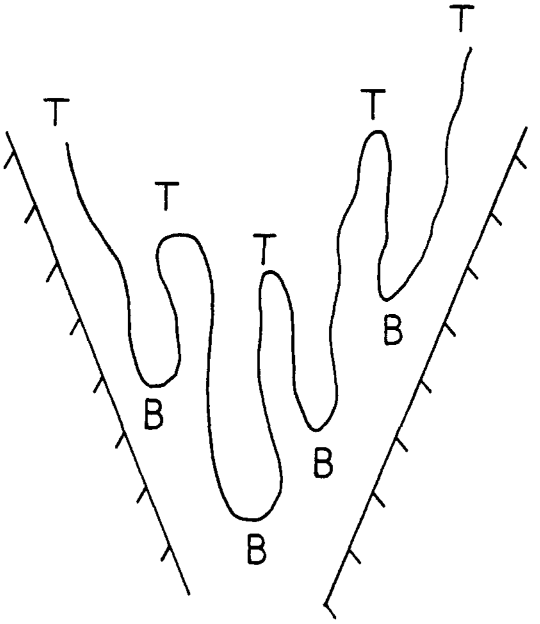

Figure 2. Chain of Figure 1 under splay. The entropy of top (T) and bottom (B) hairpinlike bends is important.

the solution of chains is effectively a solution of rods of length g because we want to count "end" defects (see Figure 2). In view of the identity $l\rho_l = P\rho_p = g\rho_g$ we obtain

$$K_1 \approx gP\rho_p k_B T$$

or

$$DK_1/k_BT \approx c^{1/3}\exp(c^{2/3}) \qquad \text{(II.9)}$$

A precise theory of g and K_1 is developed in sections VIII and IX.

III. Khokhlov–Semenov Integrodifferential Equation

Onsager's theory[16] on the formation of a nematic liquid crystal from a solution of long, slender molecules (length L, diameter D, persistence length P) is severely restricted by the requirement that the molecules have to be considered as completely rigid, thin rods ($P \gg L \gg D$). This is hardly ever fulfilled in nature. Khokhlov and Semenov[17] formulated a theory for very long, semiflexible molecules ($L \gg P \gg D$). Their expression for the free energy (here formulated as the free energy per persistence length segment, ΔF_p) as a functional of the orientational distribution function f can be written as

$$\Delta F_p/k_BT = cst + \sigma_p(f) + c\rho(f) \qquad \text{(III.1)}$$

where the dimensionless variables σ, c, and ρ are defined below.

Because, locally, the molecules can still be considered as almost fully rigid and rodlike, the second virial term $c\rho(f)$, which describes hard-core two-particle interactions (i.e., excluded-volume interactions), is identical with Onsager's, to a first approximation

$$\rho(f) \equiv \frac{4}{\pi}\int\int \sin\gamma\, f(\cos\theta)f(\cos\theta')\, d\Omega\, d\Omega' \qquad \text{(III.2)}$$

By convention γ is chosen in such a way that $\sin\gamma \geq 0$. For very long chains f is the same for every infinitesimal chain section and θ is the angle between it and the director. The distribution is normalized

$$\int f(\cos\theta)\, d\Omega = 1 \qquad \text{(III.3)}$$

The angle γ is that between two infinitesimal segments. If their orientations are described by polar angles (θ, ϕ) and (θ', ϕ') defined with respect to the director, then $\cos\gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi' - \phi)$. $d\Omega \equiv d\cos\theta\, d\phi$ implies an integration over the full solid angle. The dimensionless concentration c signifies the number of persistence length segments present in a volume $b_p = (\pi/4)P^2D$ (the isotropic excluded volume of two persistence length segments), i.e.

$$c \equiv \frac{\pi}{4}P^2D\frac{L}{P}\rho_L \qquad \text{(III.4)}$$

where ρ_L is the number density of the macromolecules.

Because of the semiflexibility of the chains, the expression[17] for the orientational entropy per persistence length is quite different from Onsager's for rods

$$\sigma_p(f) \equiv -\frac{1}{2}\int f^{1/2}(\cos\theta)\Delta f^{1/2}(\cos\theta)\, d\Omega \qquad \text{(III.5)}$$

with

$$\Delta \equiv \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} = \frac{\partial}{\partial\cos\theta}(1-\cos^2\theta)\frac{\partial}{\partial\cos\theta} \qquad \text{(III.6)}$$

i.e., the θ-dependent part of the Laplacian defined on a unit sphere. This expression is based on the wormlike chain model so it also takes into account the orientational fluctuations of a chain with respect to the director. The terms comprised in the constant, cst, are irrelevant to the rest of this article; it is important to note, however, that a translational entropy term which appears in Onsager's theory is negligible here because the persistence length segments are connected.

To find the distribution function $f(\cos\theta)$ we must minimize the free energy (III.1) with respect to arbitrary variations in f. This leads to an integrodifferential equation

$$-\frac{1}{2}\psi^{-1}(\cos\theta)\Delta\psi(\cos\theta) = E - \frac{8c}{\pi}\int \sin\gamma\, \psi^2(\cos\theta')\, d\Omega' \qquad \text{(III.7)}$$

where we plausibly define a "wave function"[4,17]

$$\psi(\cos\theta) \equiv f^{1/2}(\cos\theta) \qquad \text{(III.8)}$$

E is a Lagrange multiplier originating from the constraint eq III.3. Although eq III.7 apparently involves a two-dimensional integration, it becomes an integrodifferential equation in one variable $\cos\theta$ $(=x)$

$$-\frac{1}{2}\Delta\psi(x) = \left[E - 16c\int_{-1}^{1} S(x,x')\psi^2(x')\, dx'\right]\psi(x) \qquad \text{(III.9)}$$

when we introduce the kernel $S(x,x')$ defined by

$$S(x,x') \equiv \frac{1}{2\pi}\int_0^{2\pi} \sin\gamma\, d\phi' \qquad \text{(III.10)}$$

and

$$\Delta = \frac{\partial}{\partial x}(1-x^2)\frac{\partial}{\partial x}$$

from now on.

IV. Bifurcation Analysis

As can be easily verified, eq III.9 has an isotropic solution $\psi^i(x) = (4\pi)^{-1/2}$ for all values of c. Now the question arises whether an anisotropic solution is also feasible for certain values of c. Mathematically, we are dealing with a nonlinear operator equation with a variable parameter c. Thus, we turn to bifurcation theory which may tell us the concentration c^* at which a necessarily anisotropic solution branches off from the isotropic one. Kayser and Raveché[18] performed such an analysis on the integral equation for rigid rods, which has a different kind of nonlinearity though.

In our case we also need the Legendre expansion of the kernel $S(x,x')$ discussed in ref 18, obtained by making a Legendre expansion of $\sin \gamma$ in terms of $P_{2n}(\cos \gamma)$ ($n = 0, 1, 2, ...$), applying the addition theorem[19] and performing the ϕ'-integration in eq III.10:

$$S(x,x') = \sum_{n=0}^{\infty} d_{2n} P_{2n}(x) P_{2n}(x') \qquad \text{(IV.1)}$$

with $d_0 = \pi/4$, $d_2 = -5\pi/32$, and

$$d_{2n} = -\frac{\pi(4n + 1)(2n - 3)!!(2n - 1)!!}{2^{2n+2} n!(n + 1)!} \qquad n \geq 2 \qquad \text{(IV.2)}$$

Furthermore we should take into consideration that the Legendre polynomials are eigenfunctions of Δ

$$\Delta P_{2n}(x) = -2n(2n + 1) P_{2n}(x) \qquad \text{(IV.3)}$$

Using these properties we show heuristically in Appendix A that there is bifurcation at a scaled concentration $c^* = 6$ (as has been pointed out before[20]). Near this point at concentration

$$c = 6 + \nu \qquad \text{(IV.4)}$$

we argue that the integrodifferential equation has the following solution

$$\psi(x) = \frac{1}{(4\pi)^{1/2}} \left[1 - \frac{7}{18} \nu P_2(x) + \mathcal{O}(\nu^2) \right] \qquad \text{(IV.5)}$$

obtained by combining eq A.9, 10, and 15. Having thus ensured that the nematic state is feasible, we next turn to a numerical analysis of its properties.

V. Numerical Procedure

We now want to find a numerical solution of eq III.9. We have found it expedient to expand $\psi(x)$ in Legendre polynomials

$$\psi(x) = \frac{1}{(4\pi)^{1/2}} \sum_{n=0}^{\infty} a_{2n} P_{2n}(x) \qquad \text{(V.1)}$$

Because of the inversion symmetry of the nematic liquid crystal we retain the even polynomials only. Substituting (V.1) in eq III.9 and using eq IV.1–3 result in

$$\sum_{n=0}^{\infty} n(2n + 1) a_{2n} P_{2n}(x) = \left[E - \frac{8c}{\pi} \sum_{k,l,m=0}^{\infty} d_{2k} a_{2l} a_{2m} I_{2k,2l,2m} P_{2k}(x) \right] \sum_{n=0}^{\infty} a_{2n} P_{2n}(x) \qquad \text{(V.2)}$$

Here $I_{k,l,m}$ represents the following integral

$$I_{k,l,m} \equiv \frac{1}{2} \int_{-1}^{1} P_k(x) P_l(x) P_m(x) \, \mathrm{d}x \qquad \text{(V.3)}$$

and is explicitly given by[21]

$$I_{k,l,m} = \frac{(k + l - m)!(k - l + m)!(-k + l + m)!}{(k + l + m + l)!} \times \left[\frac{\left(\frac{k + l + m}{2}\right)!}{\left(\frac{k + l - m}{2}\right)! \left(\frac{k - l + m}{2}\right)! \left(\frac{-k + l + m}{2}\right)!} \right]^2 \qquad \text{(V.4)}$$

provided $(k + l + m)$ is even and $(k + l - m)$, $(k - l + m)$, and $(-k + l + m)$ are never negative. In all other cases $I_{k,l,m} = 0$.

We now multiply (V.2) by $P_{2j}(x)$ and integrate over x, using (V.3) and the orthogonality of Legendre polynomials.[19,21] This yields

$$\frac{j(2j + 1)}{(4j + 1)} a_{2j} = \frac{E}{(4j + 1)} a_{2j} - \frac{8c}{\pi} \sum_{k,l,m,n=0}^{\infty} d_{2k} a_{2l} a_{2m} a_{2n} I_{2k,2l,2m} I_{2k,2n,2j} \qquad \text{(V.5)}$$

In this way the nonlinear integrodifferential equation (III.9) has been transformed into an infinite set of nonlinear algebraic equations with as many unknown variables a_{2n}. Because E is unknown as well, we need an extra relation which follows from the normalization (III.3)

$$\sum_{n=0}^{\infty} \frac{a_{2n}^2}{(4n + 1)} = 1 \qquad \text{(V.6)}$$

We now solve eq V.5,6 numerically by iteration, truncating the expansions at P_{2q}. Equation V.6 is rearranged as

$$a_0^{(i)} = \left[1 - \sum_{n=1}^{q} \frac{a_{2n}^{(i)^2}}{(4n + 1)} \right]^{1/2} \qquad \text{(V.7)}$$

Equation V.5 gives for $j = 0$

$$E^{(i)} = \frac{8c}{a_0^{(i)} \pi} \sum_{k,l,m=0}^{q} \frac{d_{2k} a_{2k}^{(i)} a_{2l}^{(i)} a_{2m}^{(i)}}{(4k + 1)} I_{2k,2l,2m} \qquad \text{(V.8)}$$

where we have used the identity

$$I_{2k,2n,0} = \frac{1}{(4k + 1)} \delta_{kn} \qquad \text{(V.9)}$$

Finally, eq V.5 yields for $1 \leq j \leq q$

$$a_{2j}^{(i')} = \frac{4j + 1}{j(2j + 1)} \left[\frac{E^{(i)}}{(4j + 1)} a_{2j}^{(i)} - \frac{8c}{\pi} \sum_{k,l,m,n=0}^{q} d_{2k} a_{2l}^{(i)} a_{2m}^{(i)} a_{2n}^{(i)} I_{2k,2l,2m} I_{2k,2n,2j} \right] \qquad \text{(V.10)}$$

The label (i) indicates the number of iterations made thus far.

For concentrations $c \lesssim 6$ the set of coefficients $a_{2j}^{(i')}$ obtained from eq V.10 may be taken as the new set

$$a_{2j}^{(i+1)} = a_{2j}^{(i')} \qquad \text{(V.11a)}$$

However, for higher concentrations this scheme turns out to be unstable. This problem is circumvented by tempering the change in the coefficients as for instance in the following way

$$a_{2j}^{(i+1)} = \frac{1}{c - 4} a_{2j}^{(i')} + \frac{c - 5}{c - 4} a_{2j}^{(i)} \qquad \text{(V.11b)}$$

We thus find a solution by choosing a set of starting values $a_{2j}^{(0)}$ ($1 \leq j \leq q$) and applying the above iteration scheme till the coefficients have converged to within chosen bounds. We then ascertain that the use of coefficients beyond q has a negligible effect.

Below a (scaled) concentration of 5.19 this iteration procedure yields only the isotropic solution, ψ^i ($a_0 = 1$, $a_2 = a_4 = ... = 0$). Between $c = 5.19$ and $c = 6$, however—depending on the choice of $a_{2j}^{(0)}$—another solution is found, ψ^+ (with all $a_{2n} > 0$). Both the anisotropic and isotropic solutions are stable with respect to our iteration procedure, i.e., when one of the coefficients is altered slightly the original solution is regained after iterating. Above the bifurcation point this is no longer true for the isotropic solution: a small perturbation does not die away. A small perturbation like $a_2^{(0)} = \epsilon$, $a_4^{(0)} = a_6^{(0)} = ... = 0$ with $\epsilon > 0$ iterates to the anisotropic solution, ψ^+. If $\epsilon < 0$ the iteration leads to a different kind of solution, ψ^-, with

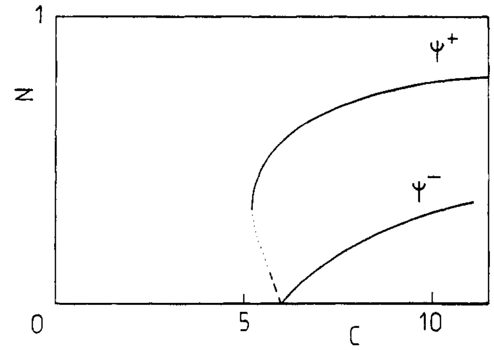

Figure 3. Bifurcation diagram of the function $N = N[\psi] \equiv (1 - a_0{}^2)^{1/2}$ versus the concentration c. Solid curves denote the numerical solutions, the dashed line comes from the bifurcation analysis whereas the dotted line is extrapolated. The lower solid curve represents the physically unrealizable state given by ψ^-.

coefficients of alternating sign ($a_{4n} > 0$ and $a_{4n+2} < 0$). Choosing a random set of coefficients always results in one of the two anisotropic solutions ψ^+ and ψ^- if $c > 6$.

The combination of these results with those from the bifurcation analysis provides us with a clear picture of the stability diagram. For concentrations $c = 6 + \nu$ ($|\nu| \ll 1$) we expect a solution given by (IV.5). Our numerical solution ψ^- does indeed have $a_2 = -0.3888 ... \nu$ if ν is small enough and positive (coefficients higher than a_2 are negligible). For $\nu < 0$ the same kind of solution applies although it is unstable with respect to our iteration procedure. To illustrate the analysis graphically we plot a measure of the anisotropy of $\psi(x)$, viz., $N \equiv (1 - a_0)^{1/2}$, against c in Figure 3. This figure is similar to Figure 1 of ref 18 which deals with the distribution function for entirely stiff rods (note that N is never greater than unity whereas the unbounded norm $\|(4\pi f - 1)\|$ in L_2 is used in ref 18).

Finally we elaborate some examples of our numerical procedure, focusing on ρ to estimate the degree of convergence. First we consider $c = 6$, in which case (V.11a) can be used. Starting with $a_2{}^{(0)} = 1$, $a_4{}^{(0)} = ... = a_{20}{}^{(0)} = 0$, we find that the relative change per step in ρ is 1×10^{-6} after 20 iteration steps. The relative difference between the present value of ρ and the fully converged one (see the next section) is also about 1×10^{-6}. After 28 steps the relative change has decreased to 1×10^{-8} with a relative error of 5×10^{-9}. Thus for this concentration the procedure converges very fast. Taking all polynomials up to P_{40} into account gives the same values of the relevant properties. For $c = 20$ the numerical scheme converges much more slowly, mainly because we are forced to use (V.11b). After 200 steps the relative change in ρ is 1×10^{-6} and the relative error 2×10^{-5}. These values are 1×10^{-8} and 2×10^{-7}, respectively, after 300 steps. Even here the difference between an expansion up to the fortieth degree and one up to the twentieth appears only in the tenth decimal for ρ and σ. We did not go beyond P_{40} in the expansion. This set an upper limit of about 50 for the concentration c.

VI. Properties of the Nematic Phase

Before we determine the properties of the nematic phase we first show to which anisotropic solution it corresponds. It is useful to focus on the order parameter

$$S \equiv 2\pi \int_{-1}^{1} P_2(x) f(x)\, \mathrm{d}x = \sum_{m,n=0}^{\infty} a_{2m} a_{2n} I_{2m,2n,2} \qquad \text{(VI.1)}$$

for the two solutions ψ^+ and ψ^- as a function of c (shown in Figure 4). The function ψ^+ has a positive order parameter and has maxima for $x = \pm 1$ ($\theta = 0$ or π). By contrast ψ^- has a negative order parameter, its only maximum being located at $x = 0$ ($\theta = \pi/2$) so the molecules are more or less perpendicular to the director (note that in the plane perpendicular to the director the molecules are randomly oriented because we presuppose uniaxial symmetry). In order to assess the feasibility of ψ^+ and ψ^- we study the free energy $\sigma_p(f) + c\rho(f)$. From (III.3, 5, 7, and 8) we derive

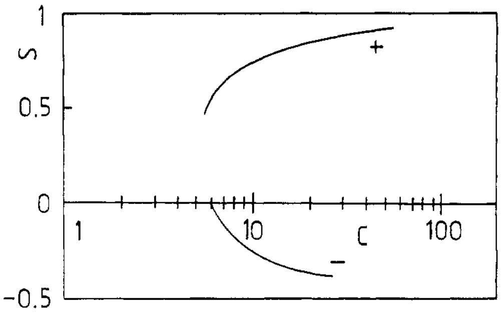

Figure 4. Order parameters S of the two states ψ^+ (+) and ψ^- (−) versus the concentration c (on a logarithmic scale).

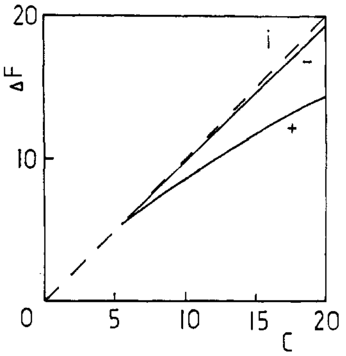

Figure 5. Free energy ΔF of the isotropic (i) and the two nematic states (+ and −) versus the concentration.

$$\sigma_p(f) = E - 2c\rho(f) \qquad \text{(VI.2)}$$

and from (III.2 and 10) and (IV.1)

$$\rho(f) = \frac{4}{\pi}\sum_{k=0}^{\infty} d_{2k}\Big[\sum_{l,m=0}^{\infty} a_{2l} a_{2m} I_{2k,2l,2m}\Big]^2 \qquad \text{(VI.3)}$$

The free energy $\sigma_p(f) + c\rho(f)$ as a function of c is given in Figure 5. We see that the ψ^- state has a slightly lower free energy than the isotropic one but never lower than that pertaining to the ψ^+ state. The ψ^- state is physically irrelevant so we discard ψ^- altogether (note that it could be of use in more complex systems, e.g., mixtures of chains and plates).

Before giving the numerical values we recall some previous analytical results. We use integrodifferential equation (III.9) implicity by choosing a trial function with a variational parameter (or parameters), calculating σ_p and ρ and minimizing the resulting expression for the free energy (III.1) with respect to the parameter(s). Khokhlov and Semenov[17] chose the Onsager trial function[16]

$$f(\alpha) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha \cos\theta)}{\sinh(\alpha)} \qquad \text{(VI.4)}$$

A simpler form of this trial function,[4] the so-called Gaussian function, gives exact leading terms

$$f(\alpha) = \frac{\alpha}{4\pi} \exp\left(-\frac{1}{2}\alpha\theta^2\right) \qquad 0 \le \theta < \pi/2$$

$$f(\alpha) = \frac{\alpha}{4\pi} \exp\left[-\frac{1}{2}\alpha(\pi - \theta)^2\right] \qquad \pi/2 < \theta \le \pi \qquad \text{(VI.5)}$$

Table I
Numerical Values of the Order Parameter S, the Orientational Entropy σ_p, and the Excluded-Volume Parameter ρ for Different Concentrations[a]

c	S	σ_p	ρ	$[(1-S)-(1-S_G)]/(1-S)$, %	$(\sigma_p-\sigma_{p,G})/\sigma_p$, %	$(\rho-\rho_G)/\rho$, %
6	0.5448	1.030	0.8104	27	−119	7.3
8	0.6785	1.789	0.6996	15	−53	2.4
10	0.7358	2.313	0.6410	10	−37	1.1
12	0.7711	2.758	0.6003	8.4	−30	0.64
15	0.8062	3.356	0.5557	6.8	−24	0.36
20	0.8424	4.253	0.5040	5.4	−18	0.18
25	0.8654	5.069	0.4675	4.6	−15	0.10
30	0.8815	5.829	0.4398	4.0	−13	0.07
40	0.9029	7.230	0.3994	3.3	−10	0.03
50	0.9167	8.517	0.3706	2.8	−9	−0.02

[a] Further, the relative difference between the numerical values and the Gaussian approximations, viz., $1 - S_G \sim 3/\alpha$, $\sigma_{p,G} \sim \alpha/4$, and $\rho_G \sim 4\pi^{-1/2}\alpha^{-1/2}$ as a function of the concentration $c \sim {}^1/_8\pi^{1/2}\alpha^{3/2}$.

This is borne out by inspection of eq III.9. To leading order the free energy is calculated by making an asymptotic expansion of σ_p and ρ for large α by using eq VI.5

$$\sigma_p(\alpha) \sim \alpha/4 \tag{VI.6}$$

$$\rho(\alpha) \sim 4/(\pi\alpha)^{1/2} \tag{VI.7}$$

Minimizing the resulting expression for ΔF_p with respect to α leads to the relation

$$\alpha \sim 4c^{2/3}/\pi^{1/3} \tag{VI.8}$$

A similar asymptotic expression for the order parameter can be found from the definition eq VI.1

$$S(\alpha) \sim 1 - 3/\alpha \tag{VI.9}$$

In Table I we give σ_p, ρ, and S for different values of c and the relative difference compared with the leading terms of the analytical theory (note that it is better to focus on $1 - S$ rather than S itself). We discern that $\sigma_p(\alpha)$ is not as good an approximation to the respective numerical values as $\rho(\alpha)$ and $S(\alpha)$ although the error term decreases nicely with increasing concentration. The Gaussian approximation of the excluded-volume term ρ works very well over the whole range of concentrations, though the error term changes sign at $c \approx 50$.

VII. Isotropic–Nematic Phase Transition

To determine the isotropic–nematic phase transition we need to know the osmotic pressure (for a solution of volume V consisting of N macromolecules and a solvent of chemical potential μ_0)

$$\Pi = -\left.\frac{\partial \Delta F}{\partial V}\right|_{N,\mu_0,T} = \frac{k_B T}{b_p} c^2 \rho \tag{VII.1}$$

and the chemical potential

$$\mu = -\left.\frac{\partial \Delta F}{\partial N}\right|_{V,\mu_0,T} = \mathrm{cst} + \frac{L}{P} k_B T[\sigma_p + 2c\rho] \tag{VII.2}$$

At the phase transition the isotropic phase with concentration c_i, $\rho = 1$ and $\sigma_p = 0$ coexists with an anisotropic phase with concentration c_a, $\rho = \rho_a$ and $\sigma_p = \sigma_{p,a}$ at the same osmotic pressure and chemical potential. This leads to the coexistence equations

$$c_i^2 = c_a^2 \rho_a \tag{VII.3}$$

$$2c_i = \sigma_{p,a} + 2c_a\rho_a \tag{VII.4}$$

Table II
Legendre Coefficients a_{2n} of the Function ψ at the I-N Transition

a_0	0.878 153 980	a_{12}	$4.615\,98 \times 10^{-6}$
a_2	1.059 364 19	a_{14}	$2.503\,42 \times 10^{-7}$
a_4	$1.982\,5233 \times 10^{-1}$	a_{16}	$1.312\,3 \times 10^{-8}$
a_6	$1.903\,6052 \times 10^{-2}$	a_{18}	6.688×10^{-10}
a_8	$1.337\,754 \times 10^{-3}$	a_{20}	3.33×10^{-11}
a_{10}	$8.142\,318 \times 10^{-5}$		

For the numerical calculation it is convenient to combine these two equations with eq VI.2, whence it follows that

$$c_a = E/2\rho_a^{1/2} \tag{VII.5}$$

In order to analyze the phase transition numerically we pose an initial estimate of c_a and calculate the distribution function, E, and ρ_a according to section V and eq VI.3. Then a revised estimate of c_a is obtained by substituting E and ρ_a into the right-hand side of eq VII.5. We repeat this procedure until c_a does not change any more, eventually obtaining the following (scaled) quantities at the transition

$$c_i = 5.1236 \qquad c_a = 5.5094 \qquad S = 0.461\,65$$
$$\sigma_{p,a} = 0.717\,61 \qquad \rho_a = 0.864\,84 \qquad \Pi = 26.25\frac{k_B T}{b_p}$$
$$\mu = cst + 10.25\frac{L}{p}k_B T \tag{VII.6}$$

The expansion coefficients of the square root of the distribution function in the anisotropic phase are given in Table II (cf. eq V.1). We also establish that the free energy of the anisotropic phase is $0.027k_BT$ per persistence length lower than the corresponding isotropic of the same concentration.

Let us compare our numerical results with those[4] obtained by using the Onsager trial function (VI.4)

$$\begin{gathered} c_i = 5.409 \qquad c_a = 6.197 \qquad S = 0.610 \\ \sigma_{p,a} = 1.376 \qquad \rho_a = 0.762 \end{gathered} \tag{VII.7}$$

we see that eq VI.4 affords reasonable qualitative insight although it exaggerates the degree of anisotropy. The relative gap in concentration between the two phases as calculated numerically is much smaller than the one for entirely stiff rods (for the numerical versions of Onsager's theory see ref 21, 22)

$$\left.\frac{c_a - c_i}{c_i}\right|_{\mathrm{flex}} = 0.075 \qquad \left.\frac{c_a - c_i}{c_i}\right|_{\mathrm{rod}} = 0.274 \tag{VII.8}$$

The same applies to the order parameter

$$S_{\mathrm{flex}} = 0.4617 \qquad S_{\mathrm{rod}} = 0.792 \tag{VII.9}$$

VIII. Global Persistence Length

As argued in section II the conformation of a nematically confined worm is essentially a one-dimensional random walk in the z direction (parallel to the director). Hence, if the contour length L is much larger than the global persistence length g, the mean-square extension of a test chain defines g in the usual way

$$\langle R_z^2 \rangle \equiv 2Lg \tag{VIII.1}$$

We show below that this definition is consistent with the one valid for dilute solutions. It is generally recognized that the dimension of a polymer chain is connected with its susceptibility in analogy with other problems in statistical mechanics relating moments to correlation functions. Khokhlov and Semenov[6] stated the following relation without proof (for the sake of completeness we derive it in Appendix B)

$$\langle R_z^2\rangle_0 = LP\chi_0 \qquad \text{(VIII.2)}$$

with

$$\chi_0 \equiv \left.\frac{\partial\langle P_1\rangle}{\partial u}\right|_{u=0} = \frac{2g}{P} \qquad \text{(VIII.3)}$$

where the average is calculated for the nematic in an external field of the dipole type parallel to the director, i.e., an external free energy per persistence segment ΔF_{ext} is added to eq III.1

$$\frac{\Delta F_{\text{ext}}}{k_{\text{B}}T} = -u\int \cos\theta\, f(\cos\theta)\; \mathrm{d}\Omega = -u\langle P_1\rangle \qquad \text{(VIII.4)}$$

If a worm of length P were to be straightened out into a rod pointing in the z direction, its (dipole) energy would be $\pm uk_{\text{B}}T$, depending on its orientation.

In the remainder of this section, we focus on the dimensionless susceptibility χ_0 instead of g in view of eq VIII.3. Upon minimizing the total free energy consisting of the sum of eq III.1 and VIII.4 we get a more complex form of the original integrodifferential equation

$$-\frac{1}{2}\psi^{-1}(x)\Delta\psi(x) = E - 16c\int_{-1}^{1} S(x,x')\psi^2(x')\; \mathrm{d}x' + ux \qquad \text{(VIII.5)}$$

To determine χ_0 we must solve (VIII.5) for small u. Therefore we attempt a regular expansion in the small parameter u

$$\psi(x) = \psi_0(x) + u\psi_1(x) + \mathcal{O}(u^2) \qquad \text{(VIII.6)}$$

where $\psi_0(x)$ is the solution of (VIII.5) for $u = 0$, which is symmetric in x. Because the applied field ux is antisymmetric, the first-order function $\psi_1(x)$ will be likewise. Using this property in expression (A.1), we see that

$$E = E_0 + \mathcal{O}(u^2) \qquad \text{(VIII.7)}$$

Substituting these expansions in eq VIII.5 we find after retaining terms linear in u

$$\psi_0\Delta\psi_1 - \psi_1\Delta\psi_0 = -2x\psi_0^2 \qquad \text{(VIII.8)}$$

It can be proved that a term originating from the integral vanishes as a consequence of the antisymmetry of ψ_1.

We expect $\psi_1(x)$ to resemble $\psi_0(x)$ in some way, which motivates the substitution

$$\psi_1(x) = h(x)\psi_0(x) \qquad \text{(VIII.9)}$$

in eq VIII.8. This gives a surprisingly simple differential equation for $h'(x)$

$$h''(x) + \left[2(\ln\psi_0)' - \frac{2x}{1-x^2}\right]h'(x) = -\frac{2x}{1-x^2} \qquad \text{(VIII.10)}$$

It can be solved by standard analysis so that

$$\psi_1(x) = \psi_0(x)\int_0^x \frac{1}{(1-y^2)\psi_0^2(y)}\left[\int_y^1 2z\psi_0^2(z)\; \mathrm{d}z\right] \mathrm{d}y \qquad \text{(VIII.11)}$$

where we have used the boundary condition $\psi_1(0) = 0$ and the fact that $\psi_1'(\pm1)$ is finite.

To linear order in u we have

$$\langle P_1\rangle = 4\pi u\int_{-1}^{1} x\psi_0(x)\psi_1(x)\; \mathrm{d}x + \mathcal{O}(u^2) \qquad \text{(VIII.12)}$$

Applying the definition of the susceptibility in zero field (VIII.3) and using expression VIII.11 for $\psi_1(x)$ we get an exact expression for χ_0 in terms of $\psi_0(x)$ after interchanging the order of the integrations

$$\chi_0 = 4\pi\int_0^1 \frac{1}{(1-y^2)\psi_0^2(y)}\left[\int_y^1 2x\psi_0^2(x)\; \mathrm{d}x\right]^2 \mathrm{d}y \qquad \text{(VIII.13)}$$

Table III
Numerical Values of the Susceptibility χ_0 as a Function of the Scaled Concentration c[a]

c	χ_0	c	χ_0
5.5094	6.506	13	1.3484×10^3
6	11.99	15	3.948×10^3
7	29.51	18	1.791×10^4
8	62.28	20	4.642×10^4
9	1.2334×10^2	25	4.299×10^5
10	2.333×10^2	35	2.28×10^7
11	4.281×10^2	50	3.9×10^9
12	7.670×10^2		

[a] The lowest value of c represents the nematic at the I–N transition.

Note that $\chi_0 = {}^2/_3$ for the isotropic distribution, which is consistent with the usual expression for $\langle R_z^2\rangle_0$ (see eq VIII.2).

Let us survey several seemingly plausible approximations to the susceptibility. The distribution is quite sharply peaked at $\theta = 0$ and $\theta = \pi$. Hence, we can replace the term $\int_y^1 xf(x)\,\mathrm{d}x$ in the integrand of eq VIII.13 by $\int_0^1 xf(x)\,\mathrm{d}x$, at least if we focus on the leading behavior of χ_0 only. Next, in view of the known asymptotic behavior of f toward the Gaussian $(4\pi)^{-1}\alpha\exp(\alpha(x-1))$ as x tends to unity, we attain an even more straightforward expression for the susceptibility, valid for higher scaled concentrations c[25]

$$\chi_0 \sim \pi^{-1}\int_0^{1-\epsilon} [(1-x^2)f(x)]^{-1}\; \mathrm{d}x \qquad \text{(VIII.14)}$$

It is not so easy to simplify eq VIII.14 further because we need to know more than merely the asymptotic behavior of f. Indeed, it is evident that a large contribution to χ_0 arises from the value of f near $x = 0$. It turns out that a reliable estimate of χ_0 can be given only if we know f accurately in an appreciable range of x extending from zero. This necessitates analyzing eq III.9 globally which no one has succeeded in doing until now. A qualitative estimate can of course be obtained by the use of a trial function like eq VI.4. In that case, eq VIII.14 yields

$$\chi_0 \sim \pi\alpha^{-2}\exp(\alpha) \qquad (\alpha \gg 1) \qquad \text{(VIII.15)}$$

which should be compared with eq II.6 ($\chi_0 = 2g/P$). It is also of interest to derive ψ_1 within the same approximation

$$\psi_1(x) \sim \psi_0(x)[\alpha^{-2}\exp(\alpha)\arctan(\sinh(\alpha x))] \qquad \text{(VIII.16)}$$

Accordingly, ψ_1 is essentially an antisymmetric version of ψ_0 multiplied by a large factor, except near $x = 0$.

The susceptibility is rigorously obtained by integrating eq VIII.13 numerically with the aid of the distribution derived in section V. The resulting χ_0 values are collected in Table III. We have checked these by another much more roundabout method because the numerical analysis of the markedly varying f is somewhat delicate. First, we solve eq VIII.5 by the usual Legendre expansion of ψ and the kernel, not forgetting to incorporate the odd polynomials in ψ which arise because the symmetry is broken by the external dipole field. The iteration procedure is analogous to the one discussed in section V. Finally, the susceptibility is calculated from eq VIII.3 by determining $\langle P_1\rangle$ for minute values of u. In the long run, this extremely

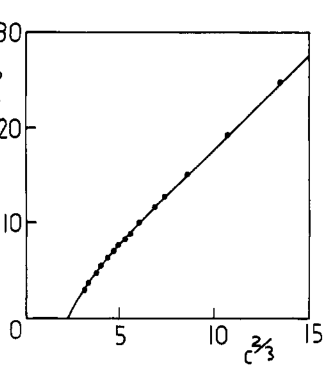

Figure 6. Plot of $\ln(c^{2/3}\chi_0)$ versus $c^{2/3}$ obtained by a least-squares fit of $c^{2/3}\ln(c^{2/3}\chi_0)$ versus $k_{11}c^{4/3} + k_{12}c^{2/3} + k_{13}$ together with the numerical data.

slowly converging scheme yields the same values for χ_0 as before.

Inspired by the qualitative expressions eq II.6 and VIII.15 we have made least-squares fits of the numerical χ_0 versus the concentration according to

$$\chi_0 = c^{-2n/3}\exp(k_{n1}c^{2/3} + k_{n2} + k_{n3}c^{-2/3}) \qquad n = 1, 2 \tag{VIII.17}$$

In order to accommodate all values of c, we have included a higher order term proportional to k_{n3}. This term is present since we know f can be expanded as

$$f \sim \frac{\alpha}{4\pi}\exp\left(-\frac{1}{2}\alpha\theta^2\right)[1 + d_1\theta^2 + d_2\theta^4 + ...] \tag{VIII.18}$$

The deviation of eq VIII.17 from the numerical data of Table III never exceeds about 2% for both values of n except for $c = 5.51$. Nevertheless, the physically motivated derivation of eq II.6 is a better starting point than that leading to eq VIII.15. For this reason and for the sake of definiteness we shall insist on setting n equal to unity in order to ease the comparison of qualitative theory with our numerical analysis. We emphasize that the numerical values of χ_0 are described by some function $\exp[c^{2/3}m(c)]$ where $m(c)$ is slowly varying and unknown, so that the approximation eq VIII.17 with $n = 1$ is merely convenient and probably not imperative. The quality of the fit is shown in Figure 6; the constants are $k_{11} = 1.824$, $k_{12} = 0.705$, and $k_{13} = -10.18$. Using the asymptotic relation $\alpha \sim 4\pi^{-1/3}c^{2/3}$ we rewrite eq VIII.17 as follows[31]

$$\chi_0 = 5.53\alpha^{-1}\exp(0.668\alpha - 27.8\alpha^{-1}) \tag{VIII.19}$$

IX. Discussion

The main analytical result of this paper is eq VIII.13, the susceptibility χ_0 or equivalently the global persistence length $g = {}^1/_2P\chi_0$ (eq VIII.3) expressed in terms of the distribution function $f(x) = f(\cos\theta) = \psi_0{}^2(\cos\theta)$. It may come as a surprise that eq VIII.13 is valid not only for excluded-volume interactions (ρ given by eq III.2) but for any interaction like

$$\rho_K(f) = \int\int K(|\sin\gamma|)f(\cos\theta)f(\cos\theta')\,d\Omega\,d\Omega' \tag{IX.1}$$

where the kernel K is quite general although it must of course allow for the existence of a state of uniaxial symmetry. In fact, if we minimize the total free energy of the system with $\rho_K(f)$ instead of $\rho(f)$ and in the presence of a slight dipolar field, we regain eq VIII.8 on using $\psi \approx \psi_0 + u\psi_1$. Again, the cross term

$$\int_{-1}^{1}\int_{-1}^{1}\int_{0}^{2\pi} K(|\sin\gamma(\theta,\theta',\phi)|)\times \psi_0(\cos\theta)\psi_1(\cos\theta')\,d(\cos\theta)\,d(\cos\theta')\,d\phi = 0 \tag{IX.2}$$

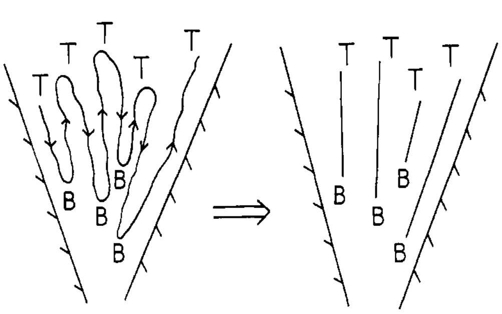

Figure 7. Splayed nematic chain and its representation by effective rods. Chain sections pointing downward are deleted.

since the integrand is antisymmetric under the transformation $(\theta,\theta',\phi) \rightarrow (\pi-\theta,\theta',\pi+\phi)$. Realistic examples of K include those pertaining to electrostatic and van der Waals interactions. We hope to come back to this topic in future contributions.

We have seen that the global persistence length is dominated by the behavior of f or ψ^2 near the equatorial region $x = 0$ or $\theta = {}^1/_2\pi$. This behavior is not well-known analytically so it is hard to deduce a reasonably accurate expression for χ_0 or g.

For a quantitative comparison of the computer results with analytical theory, we rewrite eq VIII.19 in terms of the global persistence length

$$g = 2.77P\alpha^{-1}\exp(0.688\alpha - 27.8\alpha^{-1}) \tag{IX.3}$$

Qualitatively speaking, this is in agreement with the scaling analysis of section II for $\alpha \gg 1$. However, it is stressed again that the α^{-1} factor is not very meaningful. As we saw in the previous section the numerical data could have been rationalized just as easily by a different power law like α^{-2} instead of α^{-1}. Furthermore the bending energy of a hairpin may involve a term logarithmically dependent on α that would be neglected altogether in a scaling analysis. Of greater import is the predicted magnitude of χ_0 and g. At the I-N transition the global persistence length equals $3.25P$, whereas eq II.6 yields about $100P$ and eq VIII.15 about $50P$ (we have employed the value of $\alpha = 6.5$ given in ref 4). In practice the analytical estimates are useless. In fact, stiff polymers with contour lengths longer than about $10P$ are very difficult to deal with experimentally so that our predictions differ markedly from previous theories. The hopelessness of determining χ_0 by leading order approximations is in marked contrast with the success of calculating several other properties of the nematic state (see section VI).

The qualitative relation between g and the splay modulus K_1 discussed in section II can be made precise. Let us recall Meyer's result[15] for K_1 for a nematic solution of rods of length l and density ρ_l

$$K_1 = {}^1\!/_4 l^2\rho_l k_B T \tag{IX.4}$$

Equation IX.4 is derived by assessing the inhomogeneity in the distribution of the top and bottom ends in a splayed nematic. When extending this expression to the case of semiflexible chains, we should bear in mind the following points. To an excellent approximation, a nematic chain is a random walk along the director (when $\alpha \gg 1$); its statistical segment length A is twice the global persistence length. It is well-known that the distribution of each step follows a Gaussian of zero mean and mean square equal to $A^2 = 4g^2$. Figure 7 shows that in calculating the splay modulus we are to account for steps going in one direction only. Steps in the reverse direction are in effect redundant when we need specify merely the top and bottom ends of the effective rods of varying lengths l. It is readily shown that $\langle l \rangle = (2/\pi)^{1/2} g$ via the Gaussian distribution. Accordingly, we have

$$K_1 = \tfrac{1}{4}(2/\pi)^{1/2} g l \rho_l k_B T$$
$$= \tfrac{1}{8}(2/\pi)^{1/2} \chi_0 P^2 \rho_p k_B T \qquad (L \gg g) \qquad \text{(IX.5)}$$

$$K_1 = \tfrac{1}{4} L^2 \rho_L K_B T \qquad (L \ll g) \qquad \text{(IX.6)}$$

As usual the index pertaining to the number density implies that we count the number of respective "segments". We rewrite eq IX.5 and IX.6 with the help of the relation $c = (\pi/4) P^2 D \rho_p$

$$K_1 = (2\pi^3)^{-1/2} \chi_0 c (k_B T/D)$$
$$= 0.257 c^{1/3} \exp(1.824 c^{2/3} - 10.18 c^{-2/3})(k_B T/D) \qquad (L \gg g) \qquad \text{(IX.7)}$$

$$K_1 = \pi^{-1}(L/P) c (k_B T/D) \qquad (L \ll g) \qquad \text{(IX.8)}$$

Equations IX.7 and IX.8 should be compared with the elastic moduli stemming from the excluded-volume effect[26,27]

splay $\quad K_{1,\mathrm{ex}} = 3K_2$

twist $\quad K_2 \approx c^{1/3}(k_B T/D) \qquad (L \gg \lambda) \qquad$ (IX.9)

bend $\quad K_3 \approx c(k_B T/D) \qquad (L \gg \lambda)$

The splay modulus arising from the nonuniform distributions of "top" and "bottom" hairpins clearly overwhelms that caused by the excluded-volume effect: $K_1 \gg K_{1,\mathrm{ex}}$. In general K_1 is also greater than K_2. In practice, contour lengths are quite short (i.e., $L \ll g$ and $L = \mathcal{O}(P)$) so that K_3 and K_1 are often of the same order of magnitude.

As is evident in the previous sections a fair part of our analysis is based on the work of Khokhlov and Semenov.[6,17,20] They were the first to formulate eq VIII.5 and attempt its approximate solution. In their first method[6] they used a trial function akin to the usual ones showing that it led to an expression similar to eq II.6 so this procedure is closely related to the scaling analysis of section II. However, they rejected their first approach in favor of an analysis[6] inspired by Landau and Lifshitz's elegant treatment of quantum mechanical tunneling through a barrier.[21] Unfortunately, this analogy breaks down for two reasons. Equation VIII.5 is strongly nonlinear so it is neither possible to employ a WKB approximation nor to consider an eigenfunction expansion of ψ in terms of a self-consistent field containing ψ itself. Comparison of our exact solution for the susceptibility (eq VIII.13) to their χ_0 bears out the disastrous effect of using methods devised for linear equations on highly nonlinear ones. Grosberg and Zhestkov[26] used the χ_0 of Khokhlov and Semenov[6] to calculate K_1 which explains why it is not in accord with eq IX.7.

Many analyses like that of ref 13 are based on replacing the self-consistent field U_{scf} in eq B.2 by $aP_2(\cos\theta)$ with a a constant. This replacement is ad hoc for several reasons. First, the nematic potential is much too strong to be described by an expansion valid for very weak order (order parameter $S \lesssim 0.1$). Second, the coupling of the environment to the test chain is utterly neglected. Furthermore, although the use of $U_{\mathrm{scf}} \cong aP_2(\cos\theta)$ leads to reasonably tractable equations,[28] the complete self-consistent eq VIII.5 can be solved exactly! Admittedly, the theory presented here is of the mean-field type but it is pointed out below that the influence of director fluctuations is negligible.

de Gennes[10] also presented an analysis for the global persistence length deriving

$$g = l \exp(\epsilon_h / k_B T) \qquad \text{(IX.10)}$$

This treatment was meant for a chain wriggling in a nematic "matrix", l and ϵ_h being defined in terms of rather vaguely defined parameters B and Q $(=Q_0)$: $l = (B/Q_0)^{1/2}$ and $\epsilon_h = 2(BQ_0)^{1/2}$. However, de Gennes' configurational free energy (his eq 4) turns out to be equivalent to that valid for a very long chain with excluded-volume interactions (see eq VIII.19 of ref 4) provided we identify Q_0 and B as follows: $Q_0 \rightarrow k_B T \alpha^2/4P$, $B \rightarrow P k_B T$. Hence we have $l = 2\lambda$ and $\epsilon_h = \alpha k_B T$ so that eq IX.10 scales as eq II.6. This equivalence is another example of the variety of ways of analyzing confined semiflexible chains.[4] Again, eq IX.10 overestimates eq VIII.15 by more than an order of magnitude at the very least, so this type of theory is of very little use in predicting the outcome of experiments.

The appendix to ref 10 proves useful in elucidating the import of director fluctuations. They cause a renormalization of the original Q_0 $(=\alpha^2 k_B T/4P$ in our case, with neglect of fluctuations) to an effective one given by $Q_{\mathrm{eff}}^{-1} = Q_0^{-1} + Q_1^{-1}$. An analysis of the effect of a configuration of a test chain on the surrounding nematic shows that $Q_1 = K/\ln (qD)^{-1}$ when the wavevector of the chain undulation is of magnitude q. The hybrid modulus K is some complicated function of K_1, K_2, K_3 (eq IX.7-9). We may set $q \cong \lambda^{-1} \cong \alpha/P$ in our case, so that

$$Q_1/Q_0 \cong PD^{-1}\alpha^{-3/2}\exp(m\alpha) \qquad (L \gg g) \quad \text{splay}$$
$$Q_1/Q_0 \cong PD^{-1}\alpha^{-3/2}(L\alpha/P) \qquad (L \ll g) \quad \text{splay}$$
$$Q_1/Q_0 \cong PD^{-1}\alpha^{-3/2} \qquad \text{twist}$$
$$Q_1/Q_0 \cong PD^{-1}\alpha^{-1/2} \qquad \text{bend} \qquad \text{(IX.11)}$$

if we consider each pure deformation separately. Our analysis holds in the second virial approximation, i.e., $D/\lambda \ll \alpha^{-1/2}$ or $P/D \gg \alpha^{3/2}$. Accordingly Q_1/Q_0 is much larger than unity so Q_0 need not be renormalized, thus justifying the neglect of fluctuations.

We have not been able to find any experimental data with which we can compare our theory. In general the lyotropic polymers used are too short. There is an interesting useful Monte Carlo simulation of the global stiffening of a semiflexible chain as it enters the nematic phase.[8] Khalatur et al. have determined the ratio of the respective mean-square extensions $\langle R^2 \rangle$ in the nematic and isotropic phases. From its value of 1.13 we can calculate $g \cong 1.5P$ on employing the usual formula for $\langle R^2 \rangle$ as a function of the contour length ($L \cong 1.34P$)[8] and persistence length. Because the contour length is still rather short, we cannot use c_a (eq VII.6). Now it stands to reason that g and S are very well correlated. Thus we use Khalatur's estimate for the order parameter $S = 0.37 \pm 0.05$,[8] from which we determine numerically $c_a = 5.26 \pm 0.06$ and $\chi_0 = 3.8 \pm 1$ or $g = (1.9 \pm 0.5)P$. Hence, this Monte Carlo result agrees reasonably well with theory although the comparison must be viewed as tentative for now.

Finally we discuss the experimental implications of our results. The numerical calculations of sections V and VI can be used for sufficiently stiff polymers ($P/D \gg \alpha^{3/2}$) that are long enough ($L \gg \lambda$) provided dispersion forces are very weak. The conditions for the validity of the quantities pertaining to the isotropic–nematic transition (section VII) are somewhat more stringent ($L \gg P$). The Gaussian approximation works much better than expected. Accordingly, previous work on the moduli,[26,27] the pitch of cholesterics,[29] and the surface tension[30] ought to have a reasonably wide range of validity. The calculation of these quantities for arbitrary contour lengths is in general very tedious even in the Gaussian approximation. The

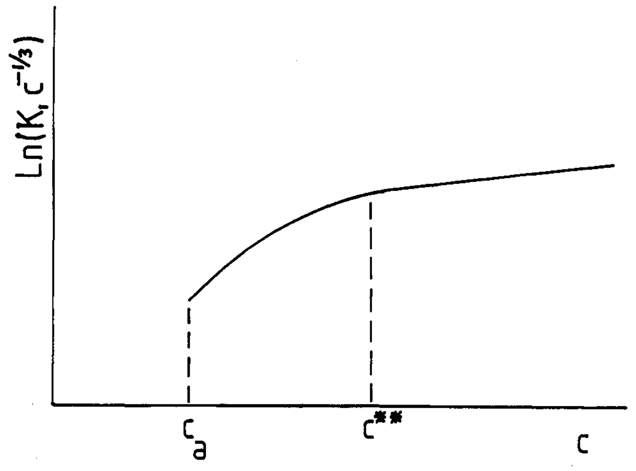

Figure 8. Plot of the logarithm of the splay modulus K_1 times $c^{-1/3}$ versus the concentration c when the chain contour L is appreciably longer than the global persistence length g at the I–N transition c_a. Note that $g \approx L$ at $c \approx c^{**}$ where c^{**} denotes a crossover concentration.

only useful result that has been attained is for the order parameter[4]

$$S \sim 1 - 3/\alpha(L) \qquad \text{(IX.12)}$$

with $\alpha(L)$ implicitly given by

$$\alpha^{1/2}[1 + (L\alpha/6P)(1 + \tfrac{1}{2}\tanh(\alpha L/5P))] = 2\pi^{-1/2}(Lc/P) \qquad \text{(IX.13)}$$

No experimental assessment of this expression has been published. Numerical work for all contour lengths is sorely needed especially of the variables at the phase transition.

The dependence of the global persistence length g on the concentration is spectacular so it should be readily discernible under the right circumstances. Table III shows that g has a lower bound equal to $3.25P$. If one wants to test the theory of induced rigidity, one should choose chains with a contour length larger than $3.25P$ and measure the splay modulus at and just above the isotropic–nematic transition. As the concentration increases, K_1 should increase very rapidly until it saturates when g has reached the contour length (Figure 8).

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Appendix A

We perform a bifurcation analysis of eq III.9. First we must find an expression for the Lagrange multiplier E in terms of $\psi(x)$. We divide eq III.9 by $\psi(x)$ and integrate over x, using the normalization condition (III.3), the kernel expansion (IV.1), and the orthogonality properties of Legendre polynomials. In this way we obtain

$$E = 2c - \tfrac{1}{4}\int_{-1}^{1}\psi^{-1}(x')\Delta\psi(x')\,\mathrm{d}x' \qquad \text{(A.1)}$$

Defining the operator

$$F(\psi,c) \equiv \tfrac{1}{2}\Delta\psi(x) - \tfrac{1}{4}\psi(x)\int_{-1}^{1}\psi^{-1}(x')\Delta\psi(x')\,\mathrm{d}x' + 2c\psi(x)\left[1 - 8\int_{-1}^{1}S(x,x')\psi^{2}(x')\,\mathrm{d}x'\right] \qquad \text{(A.2)}$$

we are posed with the problem of solving the operator equation

$$F(\psi,c) = 0 \qquad \text{(A.3)}$$

The bifurcation analysis determines the concentration c^* at which a new solution branches off from the isotropic one

$$\psi^{i}(x) = 1/(4\pi)^{1/2} \qquad \text{(A.4)}$$

From now on we follow the line of reasoning of ref 24 to determine the bifurcation point. Accordingly we look for nontrivial solutions $\phi(x)$ and the corresponding concentrations c^* of the branching equation

$$D_1F(1/(4\pi)^{1/2},c^*)\phi = 0 \qquad \text{(A.5)}$$

where we introduce an appropriate Banach space and take the Frêchet derivative $D_1F(1/(4\pi)^{1/2},c)$ of operator (A.2) with respect to ψ at the "point" $1/(4\pi)^{1/2}$ in this Banach space.[33] In this case

$$D_1F(1/(4\pi)^{1/2},c)\phi(x) = \tfrac{1}{2}\Delta\phi(x) - \tfrac{1}{4}\int_{-1}^{1}\Delta\phi(x')\,\mathrm{d}x' - \frac{8c}{\pi}\int_{-1}^{1}S(x,x')\phi(x')\,\mathrm{d}x' \qquad \text{(A.6)}$$

In view of the kernel expansion (IV.1) and the fact that the Legendre polynomials are eigenfunctions of Δ, we easily verify that the even polynomials, $P_{2n}(x)$, are nontrivial solutions of (A.5) at the respective concentrations

$$c^* = 2^{2n-2}n(2n+1)\frac{n!(n+1)!}{(2n-3)!!(2n-1)!!} \qquad \text{(A.7)}$$

The normalized eigenfunction with the required symmetry for a nematic phase is $(5/2)^{1/2}P_2(x)$, which has the simple eigenvalue

$$c^* = 6 \qquad \text{(A.8)}$$

Equation A.5 is a necessary though not sufficient condition for branching. Nevertheless, a formal modification[33] of section 3 of ref 24 does show that there is a bifurcation point at this concentration and justifies the use of Taylor expansions in a small parameter μ around it

$$\psi(x) = \frac{1}{(4\pi)^{1/2}} + \mu(5/2)^{1/2}P_2(x) + \mathcal{O}(\mu^2) \qquad \text{(A.9)}$$

$$c = 6 + \mu c_1 + \mathcal{O}(\mu^2) \qquad \text{(A.10)}$$

Reference 24 gives the following relation for c_1

$$\langle D_1D_2F(1/(4\pi)^{1/2},6)((5/2)^{1/2}P_2,1),(5/2)^{1/2}P_2\rangle c_1 + (1/2!)\langle D_1^{\,2}F(1/(4\pi)^{1/2},6)((5/2)^{1/2}P_2,(5/2)^{1/2}P_2),(5/2)^{1/2}P_2\rangle = 0 \qquad \text{(A.11)}$$

which is in fact the term linear in μ obtained by substituting the expansions in eq A.3 and taking an inner product with $(5/2)^{1/2}P_2(x)$

$$\langle\psi,(5/2)^{1/2}P_2\rangle \equiv \int_{-1}^{1}\psi(x)(5/2)^{1/2}P_2(x)\,\mathrm{d}x \qquad \text{(A.12)}$$

The second Frêchet derivatives are given by

$$D_1D_2F(1/(4\pi)^{1/2},c^*)(\phi,d) = -\frac{8d}{\pi}\int_{-1}^{1}S(x,x')\phi(x')\,\mathrm{d}x' \qquad \text{(A.13)}$$

and

$$D_1^{\,2}F(1/(4\pi)^{1/2},c^*)(\phi,\phi) = \pi^{1/2}\int_{-1}^{1}\phi(x')\Delta\phi(x')\,\mathrm{d}x' - \pi^{1/2}\phi(x)\int_{-1}^{1}\Delta\phi(x')\,\mathrm{d}x' - \frac{16c^*}{\pi^{1/2}}\int_{-1}^{1}S(x,x')\phi^{2}(x')\,\mathrm{d}x' - \frac{32c^*}{\pi^{1/2}}\phi(x)\int_{-1}^{1}S(x,x')\phi(x')\,\mathrm{d}x' \qquad \text{(A.14)}$$

Using (A.11-14) we find

$$c_1 = -\frac{90}{7}\left(\frac{2\pi}{5}\right)^{1/2} \qquad \text{(A.15)}$$

In principle it is possible to determine the higher order terms in (A.9) and (A.10) analogously.

Appendix B

We derive the Khokhlov–Semenov theorem used in section VIII, often referring to the formalism of section VIII of the review by one of us[4] and its references. We start with the partition function of a wormlike chain (with tangential unit end vectors fixed) written as a *formal* functional integration over all possible conformations

$$Z(\mathbf{v}_1,\mathbf{v}_2,L) = \int_{\mathbf{v}(0)=\mathbf{v}_1}^{\mathbf{v}(L)=\mathbf{v}_2} \exp\left[-\frac{1}{2}P\int_0^L \dot{\mathbf{v}}^2(s)\,\mathrm{d}s - \int_0^L \frac{U_{\mathrm{scf}}}{k_{\mathrm{B}}T}\,\mathrm{d}s + \frac{u}{P}\mathbf{e}_z\cdot\int_0^L \mathbf{v}(s)\,\mathrm{d}s\right]\mathcal{D}[\mathbf{v}(s)] \quad \text{(B.1)}$$

where $\mathbf{v}(s)$ is the unit tangent vector of the chain at point s, the first term in the exponent is the bending energy, the second term represents the potential energy of the chain in the nematic field (which is a self-consistent field of excluded-volume type), and the third gives the potential energy as a result of the external dipolar field. The integrand of (B.1) may be considered an unnormalized probability function for the conformations with fixed orientations of the end vectors $\mathbf{v}_1$ and $\mathbf{v}_2$.

Equation B.1 *formally* corresponds to the differential equation[4,17,23]

$$\frac{\partial Z(\mathbf{v}_1,\mathbf{v},l)}{\partial l} = \frac{1}{2P}\Delta_{\mathbf{v}} Z(\mathbf{v}_1,\mathbf{v},l) - \frac{U_{\mathrm{scf}}}{k_{\mathrm{B}}T}Z(\mathbf{v}_1,\mathbf{v},l) + \frac{u}{P}\mathbf{e}_z\cdot\mathbf{v}Z(\mathbf{v}_1,\mathbf{v},l) \quad \text{(B.2)}$$

When we now follow section VIII.d of ref 4 we find for the free energy per persistence length as a result of the external field

$$\Delta F_{\mathrm{ext}}/k_{\mathrm{B}}T = -u\int \cos\theta\, f(\cos\theta)\,\mathrm{d}\Omega = -u\langle P_1\rangle \quad \text{(B.3)}$$

Because we can write $f(\mathbf{v}) = f(\cos\theta)$ as[4]

$$f(\mathbf{v}) = \frac{\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2 \int_0^L \mathrm{d}l\, Z(\mathbf{v}_1,\mathbf{v},l)Z(\mathbf{v},\mathbf{v}_2,L-l)}{L\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2\, Z(\mathbf{v}_1,\mathbf{v}_2,L)} \quad \text{(B.4)}$$

$\langle P_1\rangle$ in eq B.3 can be rewritten as

$$\langle P_1\rangle = \frac{\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2 \int_0^L \mathrm{d}l \int \mathrm{d}\mathbf{v}\, [(\mathbf{e}_z\cdot\mathbf{v})Z(\mathbf{v}_1,\mathbf{v},l)Z(\mathbf{v},\mathbf{v}_2,L-l)]}{L\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2\, Z(\mathbf{v}_1,\mathbf{v}_2,L)} \quad \text{(B.5)}$$

Substituting (B.1) into eq B.5 and combining the functional integrations with the integration over $\mathbf{v}$ give

$$\langle P_1\rangle = \left[\int \left[L^{-1}\int_0^L \mathbf{e}_z\cdot\mathbf{v}(\mathrm{t})\,\mathrm{d}t\right] \times \exp\left[-\frac{1}{2}P\int_0^L \dot{\mathbf{v}}^2(s)\,\mathrm{d}s - \int_0^L \frac{U_{\mathrm{scf}}}{k_{\mathrm{B}}T}\,\mathrm{d}s + \frac{u}{P}\mathbf{e}_z\cdot\int_0^L \mathbf{v}(s)\,\mathrm{d}s\right]\mathcal{D}[\mathbf{v}(s)]\right] \Big/ \left[\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2\, Z(\mathbf{v}_1,\mathbf{v}_2,L)\right] \quad \text{(B.6)}$$

where the functional integration now takes place without restrictions. The susceptibility χ_0 is readily derived from this expression for $\langle P_1\rangle$

$$\chi_0 = \left.\frac{\partial\langle P_1\rangle}{\partial u}\right|_{u=0} = \frac{1}{LP}\left[\int \left[\int_0^L \mathbf{e}_z\cdot\mathbf{v}(t)\,\mathrm{d}t\right]^2 \exp\left[-\frac{1}{2}P\int_0^L \dot{\mathbf{v}}^2(s)\,\mathrm{d}s - \int_0^L \frac{U_{\mathrm{scf}}}{k_{\mathrm{B}}T}\,\mathrm{d}s\right]\mathcal{D}[\mathbf{v}(s)]\right] \Big/ \left[\int \mathrm{d}\mathbf{v}_1 \int \mathrm{d}\mathbf{v}_2\, Z(\mathbf{v}_1,\mathbf{v}_2,L)\right] \quad \text{(B.7)}$$

which shows that

$$\chi_0 = \frac{1}{LP}\langle R_z{}^2\rangle_0 \quad \text{(B.8)}$$

as we set out to prove.

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(31) Equation VIII.19 is a numerical relation between the susceptibility and the Gaussian parameter α. Thus, it is merely illustrative and convenient but not asymptotic.
(32) Thus, there are about L/g steps of average length g. The fluctuation in the step length is of order g, and the distribution is Gaussian.
(33) Our terminology is deliberately vague since our reasoning lacks any rigor. For a complete proof one must choose a Banach space like L_2 (or perhaps L_4), but the usual theorems do not apply since Δ is an unbounded operator. Rearrangement of eq A.3 with the help of a suitable Green function does lead to an equation involving only compact and bounded operators. But we have been unable to prove the compactness of the total operator, which is needed to apply standard theorems.[24]