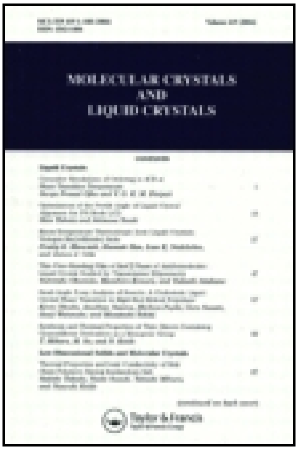

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The Gas of Long Rods as a Model for Lyotropic Liquid Crystals

J. P. Straley [a] [b]
[a] Department of Physics, University of Kentucky, Lexington, Ky., 40506
[b] Department of Chemistry, Cornell University, Ithaca, New York, U.S.A.

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The Gas of Long Rods as a Model for Lyotropic Liquid Crystals

J. P. STRALEY†

Department of Chemistry
Cornell University
Ithaca, New York, U.S.A.

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Abstract—The microscopic theories which have been proposed for lyotropic liquid crystals are studied, in particular in connection with the model gas of hard rods. For sufficiently long rods most theories are equivalent to that of Onsager; for shorter rods no theory seems to have a very good claim to accuracy. The theory of Flory is shown to be untrustworthy. A series of experimental tests is proposed which would allow determination of the coefficients of the Onsager expansion; available experimental data are reviewed.

1. Introduction

A liquid crystal is a phase of matter which is spontaneously anisotropic but lacks crystalline order. The anisotropy, which is readily detected in the optical properties of the substance, is due to the alignment of the component molecules. Several types of ordering are recognized; in what follows we shall restrict our attention to nematic liquid crystals, which exhibit birefringence and dichroism similar to that of uniaxial crystals.

This paper will discuss microscopic theories for lyotropic liquid crystals. The starting point for most of these is a gas (or suspension) of hard rod-like particles. In Sec. 2 are introduced the macroscopic and microscopic variables which will be used to describe the rod gas; Sec. 3 then assesses several methods that have been proposed to treat the liquid crystal transition of the gas of long rods and compares their predictions. The basic conclusions to be drawn are that (i) for long rods most theories effectively reduce to Onsager's

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† Supported by the National Science Foundation through a N.S.F. Postdoctoral Fellowship. Present Address: Department of Physics, University of Kentucky, Lexington, Ky. 40506.

result,(1) and (ii) for shorter rods none is very reliable. The limiting validity of Onsager's theory, which is of a mean-field character, rests on the smallness of the parameter D/L, where D is the diameter and L the length of the rods. In Sec. 4 a series of experiments is proposed which would determine the parameters of the Onsager expansion and thus give an experimental test of these theories. Finally in Sec. 5 the available data for two experimental systems are reviewed with the conclusion that, while the existing data are roughly consistent with the Onsager theory, they are not sufficient for a really critical test.

2. Order Parameter and Distribution Function

For the sake of simplicity of description, it will be assumed throughout that the orientation of a molecule is completely specified by a single vector, as in the case of particles having an axis of rotational symmetry. Then the degree of alignment of N molecules is measured by the order parameter

$$S = N^{-1} \sum_i \left(\tfrac{3}{2}\cos^2\theta_i - \tfrac{1}{2}\right), \tag{2.1}$$

where θ_i is the angle of inclination of the axis of the ith molecules with respect to the direction of preferred alignment. The order parameter can also be measured by

$$S^2 = N^{-2} \sum_{i,j} \left(\tfrac{3}{2}\cos^2\theta_{ij} - \tfrac{1}{2}\right), \tag{2.2}$$

where θ_{ij} is the angle between the axes of molecules i and j. This definition avoids the need to specify a direction of alignment, and will in general agree, in the thermodynamic limit, with that given above.

The dielectric tensor of the ordered material can be related to the dielectric properties of a single molecule by

$$\begin{aligned} \epsilon_\parallel &= \tfrac{1}{3}\epsilon_\parallel'(1+2S) + \tfrac{2}{3}\epsilon_\perp'(1-S) \\ \epsilon_\perp &= \tfrac{1}{3}\epsilon_\parallel'(1-S) + \tfrac{1}{3}\epsilon_\perp'(2+S) \end{aligned} \tag{2.3}$$

where $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants parallel and perpendicular to the direction of orientation, and $\epsilon_\parallel'$ and $\epsilon_\perp'$ are the dielectric constants parallel and perpendicular to the axis of a molecule.(2)

A more detailed description of the distribution of orientation than the order parameter can provide will frequently be necessary. We therefore define a distribution function $f(\Omega)$: if $\rho(\Omega)$ particles per unit volume have orientations in a solid angle $\Delta\Omega$ near Ω, let

$$\rho(\Omega) = \rho f(\Omega)\Delta\Omega, \tag{2.4}$$

where ρ is the total number density. Since all particles must have some orientation, there is a normalization condition

$$\int f(\Omega)\,\mathrm{d}\Omega = 1. \tag{2.5}$$

The physical system which f describes is a collection of particles, each of which can take on many orientations. The description suggests a second or ideal system in which each particle is constrained to maintain its orientation always, with the distribution of orientations being arranged to mimic the physical system. Every configuration of particles accessible to one system is accessible to the other and assigned the same probability; consequently they will have the same partition function and *equilibrium* thermodynamic properties. The advantage of the second system is that it allows us to discuss the properties of a system whose distribution function is constrained to take on a particular form, and to discuss the dependence of the thermodynamic functions on the distribution function in a meaningful way.

The order parameter may be defined in terms of f as

$$S = 2\pi \int P_2(\theta) f(\theta) \sin\theta\,\mathrm{d}\theta, \tag{2.6}$$

where $P_2(\theta)$ is the second Legendre function. If the distribution function is large only for small angles (giving a " prolate " distribution), the order parameter is positive; if on the contrary it is largest near $\theta = 90°$ (so that it is actually alignment perpendicular to a preferred axis that is occurring), the order parameter is negative. Thus the sign of S carries information about the nature of the ordering (in contrast to the magnetization of a ferromagnet, whose sign depends on nothing more than a point of view). Under this circumstance, the Landau theory of phase transitions⁽³⁾ predicts a first order phase transition between ordered and isotropic phases; experimentally the transitions seem to be first order but with rather small discontinuities.(4)

3. The Gas of Long Rods

Very few liquid crystalline materials can be characterized accurately as suspensions of long rods.(5) Nonetheless, the idealization is a useful starting point for a microscopic theory, since the forces assumed between the molecules are physically realistic and experimentally realizable, so that comparison with experiment will be possible. Furthermore, since the scale of the forces promoting alignment are determined by the dimensions of the rods, the introduction of unknown parameters is avoided.

It is far more efficient to pack pencils roughly parallel, rather than with random orientations. Of the total set of configurations that can be attained by a relatively dense gas of long hard rods, we might expect the preponderance to belong to configurations in which the axes are roughly aligned, since such arrangements allow greater freedom of motion. In this section we discuss several attempts to quantify this consideration into a more formal statistical mechanical statement.

The starting point is the analysis of Onsager(1); the principal contention of this section will be that Onsager's method is basically correct, and that alternate theories that have been proposed either are incorrect or do not differ substantially from it.

1. THE ONSAGER VIRIAL EXPANSION

The free energy for a collection of long rods can be expanded in a series in the distribution function as

$$\begin{aligned} F/NkT = {} & \mu_0 + \int f(\Omega) \ln f(\Omega)\, d\Omega + \ln \rho \\ & + \tfrac{1}{2}\rho \iint B(\Omega, \Omega') f(\Omega) f(\Omega')\, d\Omega\, d\Omega' \\ & + \tfrac{1}{3}\rho^2 \iiint C(\Omega, \Omega', \Omega'') f(\Omega) f(\Omega') f(\Omega'') \\ & \times d\Omega\, d\Omega'\, d\Omega'' + \ldots \end{aligned} \tag{3.1}$$

where $B(\Omega, \Omega')$ is the irreducible cluster integral which measures the volume from which a rod of orientation Ω is excluded by a rod of orientation Ω'; $C(\Omega, \Omega', \Omega'')$ is proportional to the number of configurations in which three rods of orientations $\Omega, \Omega', \Omega''$ are simultaneously overlapping each other.

In the limit that the rod length L is large compared to the diameter D the covolume $B(\Omega, \Omega')$ will clearly be much larger than the volume of a single rod but strongly dependent on the angle γ between the orientations Ω and Ω'; indeed in the limit of small angles $B(\gamma = 0) = 8v_0$, where v_0 is the volume of a rod. For the case of spherocylinders (right circular cylinders with hemispherical caps on the ends) the covolume has the form⁽⁶⁾

$$B(\gamma) = B_0 + B_1 |\sin \gamma|, \tag{3.2a}$$

with

$$B_0 = 2\pi LD^2 + \tfrac{4}{3}\pi D^3 \tag{3.2b}$$

and

$$B_1 = 2L^2D. \tag{3.2c}$$

The behavior of this function as well as that of some other examples (see Appendix 1) is shown in Fig. 1.

The ordering transition is brought about by the competition between the " orientational entropy "⁽⁷⁾

$$k^{-1}S_{\text{orient.}} = \int f(\Omega) \ln f(\Omega)\, d\Omega, \tag{3.3}$$

which is minimized by an isotropic distribution function, and the " entropy of packing "

$$k^{-1}S_{\text{pack.}} = \tfrac{1}{2}\rho \iint f(\Omega) f(\Omega') B(\Omega, \Omega')\, d\Omega\, d\Omega', \tag{3.4}$$

which is minimized by a perfectly ordered configuration. The latter term will become dominant when $\rho B(90°) \sim 1$, or equivalently $\rho L^2 D \sim 1$. For long rods this situation will occur for $\rho v_0 \ll 1$; (since $v_0 \sim D^2 L$); the transition is thus quite distinct from the crystalline ordering which presumably occurs for $v_0 \sim 1$.

The effect of the higher order terms in Eq. (3.1) must also be considered. These may be shown to be negligible by the following considerations: for example, the third virial coefficient $C(\Omega, \Omega', \Omega'')$ will be of order D^3L^3 if Ω, Ω' and Ω'' do not lie nearly in a common

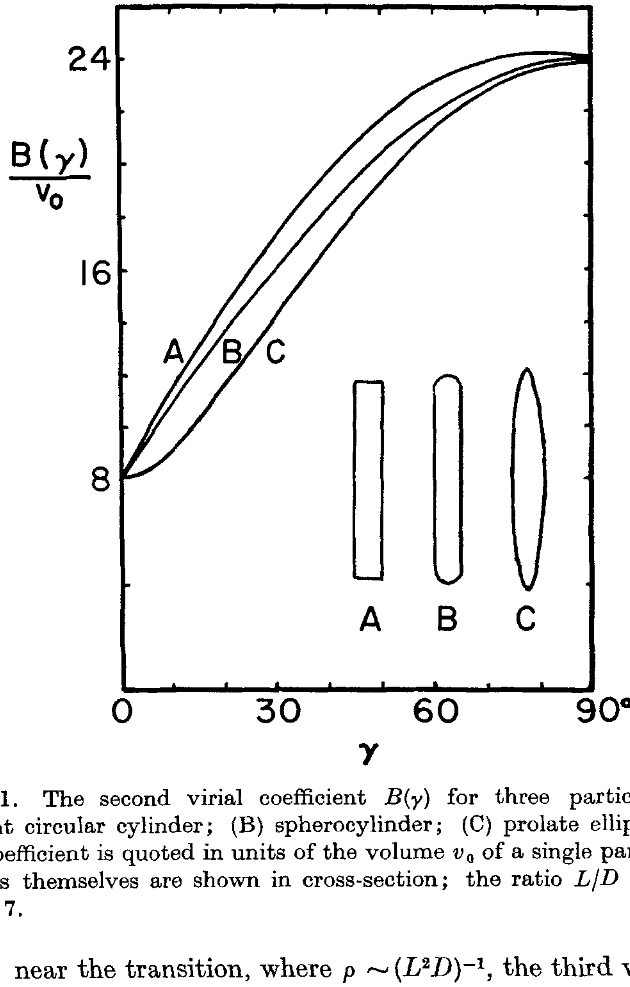

Figure 1. The second virial coefficient $B(\gamma)$ for three particle shapes: (A) right circular cylinder; (B) spherocylinder; (C) prolate ellipsoid. The virial coefficient is quoted in units of the volume v_0 of a single particle. The particles themselves are shown in cross-section; the ratio L/D is approximately 7.

plane; near the transition, where $\rho \sim (L^2D)^{-1}$, the third virial term will be of order

$$\rho^2C \sim (L^2D)^{-2}L^3D^3 \sim D/L, \tag{3.5}$$

and hence small in the limit of long rods. In the case where Ω, Ω', and Ω'' are nearly coplanar, ρ^2C is of order unity: but this case represents only a fraction D/L of all possible orientations of these rods and hence is also negligible.

The numerical magnitude of the third virial coefficient for long cylinders can be estimated, showing that this argument is literally valid only for L of the order of $100D$. However, the sign of this correction term is such that it only quantitatively affects the phase transition, and for qualitative consideration it may be neglected. For further details see Ref. 8.

The Onsager theory, then, basically consists of the argument that the series (3.1) can be truncated at the term linear in ρ and that the virial coefficient $B(\Omega, \Omega')$ can be approximated by that appropriate to a system of very long rods. The equilibrium distribution function is determined as being that normalized $f(\Omega)$ which minimizes the truncated form of (3.1) at constant density; upon equating the variational derivative to zero there results the integral equation

$$f(\Omega) = f_0 \exp\left[-\rho \int B(\Omega, \Omega') f(\Omega')\, \mathrm{d}\Omega'\right], \tag{3.6}$$

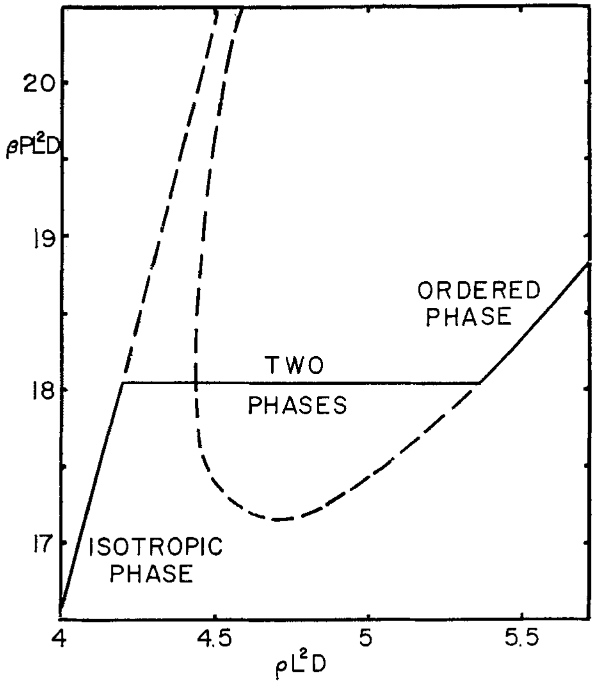

Figure 2. The equation of state for the Onsager model. At the liquid crystal transition, an anisotropic phase of density 5.3 $L^{-2}D^{-1}$ is in equilibrium with an isotropic phase of density 4.2 $L^{-2}D^{-1}$. The order parameter in the dense phase at the transition is $S = 0.78$.

where the constant f_0 must be chosen to guarantee the normalization condition (2.5). Since $B(\Omega, \Omega')$ depends only on the angle between Ω and Ω', the isotropic function is always a solution to (3.6).

Equation (3.6) with $B(\gamma)$ given by Eq. (3.2) has been solved numerically by Lasher.⁽⁹⁾ The resulting equation of state (for $L/D \sim \infty$) is shown in Fig. 2. There are two branches (isotropic and anisotropic distribution functions) which cross at a rather high pressure (not shown). The resulting curve is to be thought of as a peculiar Van der Waals loop, indicating a first order phase transition. The transition densities can be located by a Maxwell construction, but it is conceptually better to require that the chemical potentials and pressure of the phases be equal at the transition (as was done here). The value of the order parameter in the dense phase at the transition is $S = 0.78$. Of course S vanishes in the low density phase.

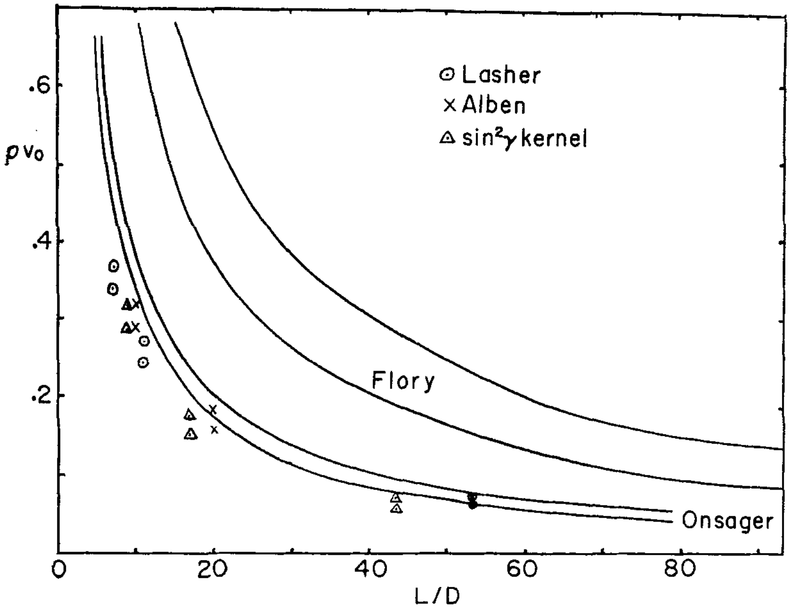

Figure 3. Predicted densities of the phases at the liquid crystal transition. The pairs of coexisting densities are given as functions of the ratio L/D for the theories of Flory, Onsager, Alben and Lasher. Likewise are shown the coexisting densities predicted by an approximation to the Onsager integral equation in which $|\sin\gamma|$ is replaced by $\sin^2\gamma$. Only occasional pairs of points for the latter three cases are shown.

This numerical analysis can be carried out for various finite L/D ratios; the resulting transition densities are shown in Fig. 3.

The integral equation (3.6) can also be solved analytically for the case⁽¹⁰⁾

$$B(\gamma) = B_0 + B_1 \sin^2 \gamma. \tag{3.7}$$

This might be a more appropriate form for the case of rod-like particles interacting through some continuous force field, or for hard prolate ellipsoids⁽¹⁰⁾ (for which the angle-dependent second virial coefficient is parabolic near $\gamma = 0$, as shown in Fig. 2). It has also been used as an approximation to the form (3.2). I have calculated the transition densities predicted by this " approximation ";⁽¹¹⁾ they are also shown in Fig. 3. These transition densities are 20% smaller than those found previously; more significantly, the order parameter at the transition is considerably lower, namely $S = 0.6$ (in place of $S = 0.78$).

2. Theory of Flory

Flory⁽¹²⁾ has provided a theory of the ordering transition based on a probabilistic argument for the construction of the partition function. This technique is interesting and has been reapplied with some modifications to this problem by other workers.⁽⁷,¹³⁾ The analysis presented here, however, will show that the quantitative predictions of the theory are in error, and that Flory's form for the partition function of a gas of long rods displays unsatisfactory and non-physical behavior.

Flory's calculation is based on a lattice model. A rod inclined at angle θ_i to the preferred axis is represented by a group of $x (x = L/D)$ adjoining sites, subdivided into $y_i = x \, |\sin \theta_i|$ parallel rodlets. (Strictly speaking we should use $1 + y_i$ pieces, since there will be one piece for the perfectly oriented rod. This correction causes the replacement $y \rightarrow y+1$ throughout but does not materially affect either Flory's conclusions or the considerations presented here.) By estimating the probability that an additional rod can be added to a set already present, Flory obtains for the partition function the expression

$$Q = (n - xn_2 + yn_2)! \, [(n - xn_2)! \, n^{(y-1)n_2} \prod_k n_k!]^{-1}, \tag{3.8}$$

where n is the total number of sites in the lattice, n_2 is the number of rods, n_k is the number of particles having orientation in $\Delta\Omega_k$ (the product is taken over all angles), and y is a parameter measuring the degree of orientational disorder, defined by

$$y = \langle y_i \rangle = x \int f(\theta)\,|\sin\theta|\,\mathrm{d}\Omega. \tag{3.9}$$

The values of y range from 0 for the perfectly ordered system, to $\frac{1}{4}\pi x$ for the isotropic distribution.

Taking the logarithm we find the free energy to be

$$\begin{aligned} F/NkT = & \int f(\Omega)\ln f(\Omega)\,\mathrm{d}\Omega + \ln\rho - 1 + y \\ & + (\rho^{-1} - x)\ln(1 - x\rho) - (\rho^{-1} + y - x)\ln(1 + y\rho - x\rho), \end{aligned} \tag{3.10}$$

where the particle density (measured in units of particle/lattice site) $\rho = n_2/n$ has been introduced; the first two terms come from Stirling's approximation

$$\ln \prod_k n_k! \simeq \prod_k n_k \ln n_k - n_2 \tag{3.11}$$

and the definition (2.4) of the distribution function f. This result resembles the Onsager form for the free energy in that it expresses F as the free energy of an ideal gas of non-interfering rods plus correction terms which vanish in the limit that the density is vanishingly small.

In his treatment, Flory now introduces an approximation to eliminate the first term. This is based upon the behavior of his form for the partition function in the limit that the rods are almost perfectly aligned. In the present notation Flory's approximation [his Eq. (6)] becomes

$$\int f(\Omega)\ln f(\Omega)\,\mathrm{d}\Omega \simeq -2\ln y; \tag{3.12}$$

upon making this replacement the free energy (3.10) becomes a function of just the density ρ and the parameter y. The equilibrium state of given density if found by choosing y to minimize this function. There results the relation

$$\rho = (x - y)^{-1}[1 - \exp(-2y^{-1})]. \tag{3.13}$$

The behavior of this function is illustrated in Fig. 4. There is a minimum density for which this equation can be solved; Flory

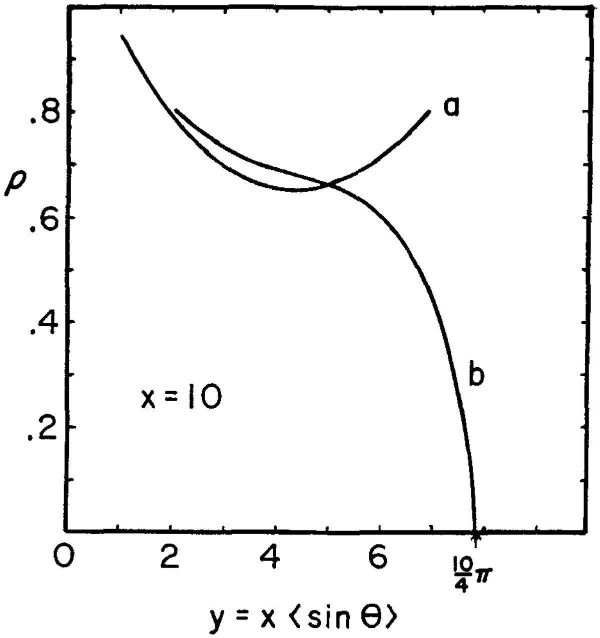

Figure 4. Relationship between the density ρ and the disorder parameter y in the liquid crystalline phase as given by the Flory equation of state. The results of both (a) Flory's approximate treatment, and (b) the numerical integration of equations (3.9) and (3.14) are shown.

compared the chemical potentials and pressure of the isotropic phase with those for an anisotropic phase described by Eq. (3.13) to locate the position of the liquid crystal transition; the resulting transition densities are shown in Fig. 3.

Flory's approximation (3.12) can, however, be avoided: by means of the calculus of variations it can be shown that the free energy (3.11) will be minimized at constant density by a distribution satisfying

$$f(\theta) = C\exp[\,|\sin\theta|\ln(1+(y-x)\rho)], \qquad (3.14)$$

where the constant C is determined by the normalization condition on f. In contrast with the Onsager result, this distribution cannot be isotropic except at vanishing density: in other words, the isotropic function is *not* in general an extreme of Flory's approximation for the free energy. The form (3.14) for the distribution function substituted in Eq. (3.9) gives an integral equation for y; the solution of this equation is also shown in Fig. 4. For small y (highly oriented rods) the two curves come together; Flory's approximation is accurate here. In the opposite limit, however, we see that the approximation breaks down; in particular for *every* density there is an anisotropic distribution which is a local extremum of the free energy (3.10).

We now have shown that the isotropic distribution never gives a local minimum of Flory's free energy, and that an anisotropic distribution which minimizes the free energy exists: these facts taken together strongly suggest that the anisotropic phase is always the more stable (has the lower free energy) at all densities; explicit calculations confirm this expectation (Fig. 5). Thus the Flory approximation for the partition function implies that any suspension of anisotropic objects, however dilute, will exhibit spontaneous ordering. This

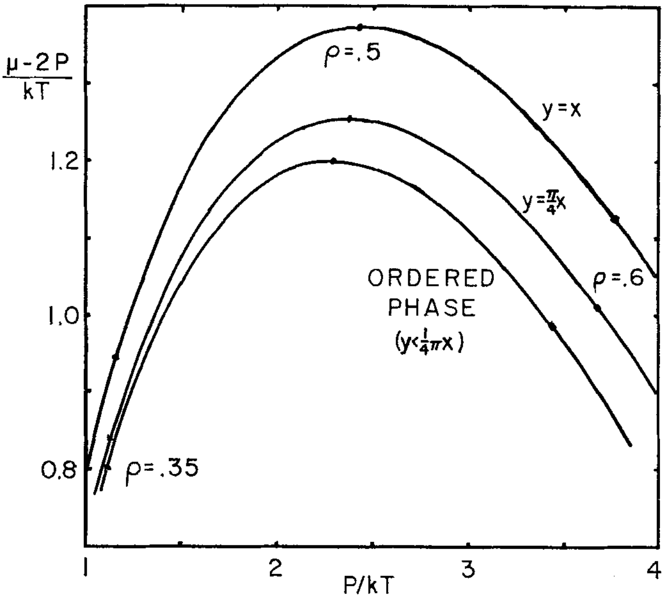

Figure 5. Relative stability of the various phases according to the Flory equation of state. The stable phase should have minimum chemical potential at fixed pressure. Here is plotted $\mu - 2P$ (for graphical clarity) showing that the oriented phase is always stable with respect to the " phases " $x = y$ and $y = \frac{1}{4}\pi x$.

must certainly be incorrect at sufficiently low densities. The origin of this nonphysical behavior can probably be traced to the failure to retain the overall spherical symmetry of the interacting gas. The definition of Flory disorder parameter requires the prior specification of a preferred axis, and an equivalent definition independent of the direction of alignment apparently cannot be given. Treatments which violate the spherical symmetry in effect introduce an ordering field; under such circumstances there will be "induced" order at all densities and (as for a ferromagnet in the presence of an external magnetic field) the phase transition will in general fail to occur altogether.(14)

3. Other Theories

The equation of state for a gas of hard spherocylinders in the Onsager approximation is given by

$$P/kT = \rho + \tfrac{1}{2}\rho^2(8v_0 + 2L^2D\langle\langle|\sin\gamma|\rangle\rangle), \qquad (3.15)$$

where

$$\langle\langle B(\Omega,\Omega')\rangle\rangle = \iint f(\Omega)f(\Omega')B(\Omega,\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega'. \qquad (3.16)$$

Several other equations of state have been proposed for this problem.

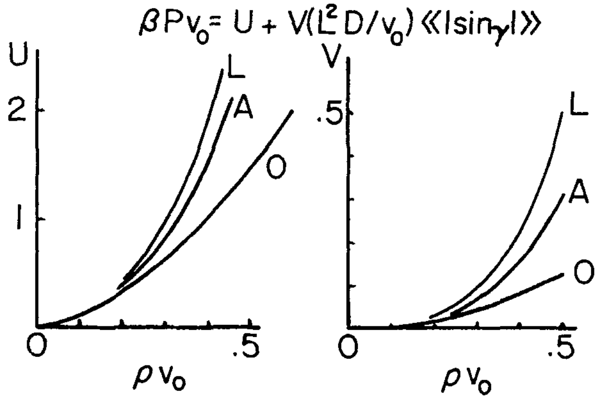

Figure 6. The equation of state for Onsager, Lasher and Alben theories. The function U is the part independent of the angular distribution; V gives the density dependence of the terms proportional to (L^2D/v_0) $\langle\langle|\sin\gamma|\rangle\rangle$ All theories are asymptotically the same in the small density limit; the Lasher and Alben theories have divergences at $\rho v_0 = 1$.

Cotter and Martire⁽¹⁵⁾ and Lasher⁽⁹⁾ have proposed modifications of the scaled-particle method.⁽¹⁶⁾ Lasher gives the equation of state

$$P/kT = (1-\rho v_0)^{-2}[\rho + 2\rho^2 v_0 + \rho^2 L^2 D \langle\langle |\sin\gamma| \rangle\rangle]. \qquad (3.17)$$

This form agrees with Onsager's (3.15) in the limit of small densities (Fig. 6); however, the singular behavior near $\rho v_0 = 1$ prevents a close approach to close-packing density: in this respect the Lasher equation of state is more realistic than that of Onsager. It should be noted that an arbitrary assumption eliminated a more singular term $(1-\rho v_0)^{-3}$, so that the Lasher equation of state does *not* reduce to the equation of state for hard spheres in the limit of vanishing axial ratios (as would clearly be desirable). Alben⁽⁷⁾ has reworked the Flory method of construction of the partition function and finds the equation of state

$$\begin{aligned} Pv_0/kT = & -\ln(1-\rho v_0) + [\rho(1-\rho v_0)^{-1} + v_0^{-1}\ln(1-\rho v_0)] \\ & \times (7v_0 + 2L^2 D \langle\langle |\sin\gamma| \rangle\rangle). \end{aligned} \qquad (3.18)$$

This result shares with the scaled particle approach the features that it approaches the Onsager approximation in the limit of low densities, and that it is singular near close-packing density (Fig. 6); however, the singularity is milder than that found by the scaled particle arguments.

In Fig. 3 are shown the densities of the phases at the liquid crystal transition predicted by the Onsager, Lasher and Alben equations of state. For longer rods ($L/D > 20$) these theories are in close agreement, evidently supporting the contention that the Onsager approximation is adequate to deal with this limit. In the case of short rods the discrepancies become significant. The corrections indicated by the Lasher and Alben theories are in the direction that consideration of the problems posed by the approach to close packing would imply; however, they probably cannot be taken too seriously: neither method reduces to the (approximate) equation of state for hard spheres in the $L \to 0$ limit, and neither seems to consider any more complicated angular correlations than are already present in the Onsager model. The distribution function in each theory is determined as a solution to the integral equation (3.6) with the density ρ replaced by some function of ρ, as if the third virial coefficient of Eq. (3.1) could be expressed

$$C(\Omega, \Omega', \Omega'') = \text{const.}\,[B(\Omega, \Omega') + B(\Omega', \Omega'') + B(\Omega'', \Omega)]. \tag{3.19}$$

The true angular dependence of the higher virial coefficients is somewhat more complex than this⁽⁸⁾; and the estimated magnitude of the third virial coefficient is considerably larger than the coefficients of the ρ^3 term of the expansions of (3.17) and (3.18). The question of the correctness of the various theories for the case of short hard spherocylinders is somewhat academic; as Fig. 1 demonstrates, the second virial coefficients for short objects is considerably shape-dependent; the resultant uncertainty makes comparison of theory and experiment rather difficult.

Thus, reviewing the various equations of state that have been proposed for suspensions of rodlike objects we reach the conclusion that to the extent that they are seriously credible, they all reduce to the expression given by Onsager, and predict closely similar phase transition densities.

4. Experimental Determination of the Virial Coefficients

In this section we will show how the Onsager virial expansion can be used to interpret a number of experiments with asymmetric molecules or longer objects. It will be shown generally that certain averages of the virial coefficients can be determined by these experiments, thus allowing us to judge the validity of the assumption that the higher-order virial coefficients can be neglected, and giving a check on the assumed form for the second virial coefficients.

1. OSMOTIC PRESSURE OF ISOTROPIC PHASE

A good experimental realization of a gas of long rods is a suspension of a rod-like virus or rigid polymeric chains in some solvent; for this system the free energy we have been discussing becomes the excess free energy over that of the solvent, and the pressure becomes the osmotic pressure.

Measurement of the osmotic pressure in the isotropic phase permits determination of the coefficients of the virial expansion

$$\pi/kT = \rho + \tfrac{1}{2}B_0\rho^2 + \tfrac{2}{3}C_0\rho^3 + \dots, \tag{4.1}$$

which are related to the coefficients introduced in Eq. (3.1):

$$B_0 = (4\pi)^{-2}\iint B(\Omega, \Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega' \tag{4.2}$$

and

$$C_0 = (4\pi)^{-3}\iiint C(\Omega, \Omega', \Omega'')\,\mathrm{d}\Omega\,\mathrm{d}\Omega'\,\mathrm{d}\Omega''.$$

The Onsager theory would assume that C_0 is negligible; it also implies that the ratio $\pi/\rho kT$ which approaches unity for dilute suspension should be greater than 4 near the liquid crystal transition.

The osmotic pressure can be determined by a number of methods,⁽¹⁷⁾ which I will not presume to review here. In connection with subsequent comments, it will be noted that the derivative of the osmotic pressure with respect to concentration can be inferred from the vertical concentration gradient in a gravitational or centrifugal field

$$\partial\pi/\partial\rho = w\rho\left[\frac{\partial\rho}{\partial z}\right]^{-1}, \tag{4.3}$$

where w is an effective gravitational force acting on a particle (corrected for buoyancy); and from the scattering of light by disordered suspensions, in which the turbidity is given by⁽¹⁸⁾

$$\tau = \rho HkT[\partial\pi/\partial\rho]^{-1}, \tag{4.4}$$

where H is a constant related to the indices of refraction of solvent and suspension.⁽¹⁹⁾

2. FIELD-INDUCED ORIENTATION

As will be shown below, the second-moment average

$$B_2 = (4\pi)^{-2}\iint P_2(\Omega)B(\Omega, \Omega')P_2(\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega' \tag{4.5}$$

can be measured by consideration of the birefringence or dichroism introduced by an electric or magnetic field. The effect of such an ordering field is to induce alignment of the particles, even in very dilute suspensions. If the effect of the particle interaction is such as to induce spontaneous orientation at high concentration, then it should cooperate with the ordering field, giving rise to an enhancement of the field-induced birefringence as the concentration is increased.

In the presence of an ordering field the free energy in the Onsager approximation is

$$F/NkT = \int f(\Omega)\ln f(\Omega)\,\mathrm{d}\Omega + \ln\rho + \tfrac{1}{2}\rho\iint B(\Omega,\Omega')$$
$$\times f(\Omega)f(\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega' - \mathscr{T}\int f(\theta)P_2(\theta)2\pi\sin\theta\,\mathrm{d}\theta, \quad (4.6)$$

where $\mathscr{T}$ is the ratio of the energy gained by aligning a particle and the thermal energy kT. It is assumed here that the particles lack a permanent magnetic or electric dipole moment. The theory for the alternate case is readily developed along the lines given here. In the weak field limit we may assume

$$f(\theta) = (4\pi)^{-1}[1+aP_2(\theta)], \quad (4.7)$$

where a is much less than unity. The distribution function minimizing the free energy is that for which

$$a = \mathscr{T}(1+5\rho B_2)^{-1}; \quad (4.8)$$

the order parameter in the presence of the field is $S = \frac{1}{5}a$ and the birefringence per particle is proportional to this. For those cases where the Onsager theory predicts a liquid crystal transformation B_2 is negative; hence the induced birefringence increases with concentration; near the liquid crystal transition the birefringence should be five times as large as the low concentration behavior would imply.

3. Behavior of the Ordered Phase

The spontaneous birefringence of the liquid crystalline phase is also a quantity of interest, since it indicates the behavior of the order parameter. To know the magnitude of the order parameter it is necessary to have an estimate of the dielectric anisotropy of a single particle. The concentration dependence of the order parameter predicted by the Onsager theory is shown in Fig. 7; in this figure the concentration has been normalized with respect to the concentration of the ordered phase at the transition in order to make the point that the form of the angle-dependent second virial coefficient $B(\gamma)$ can have significant effect.

The osmotic pressure of the ordered phase is also of interest. It should behave qualitatively as shown in Fig. 2, but the detailed behavior has some sensitivity to the precise form of the angular dependence of the second virial coefficient. Measurement of this quantity, in particular in conjunction with a determination of the order parameter, might permit some judgement on the form of $B(\gamma)$.

In this section we have outlined three types of study which would provide a semi-phenomenological characterization of an experimental system sufficient to predict the densities of the phases at the liquid crystal transition. If such a characterization would prove

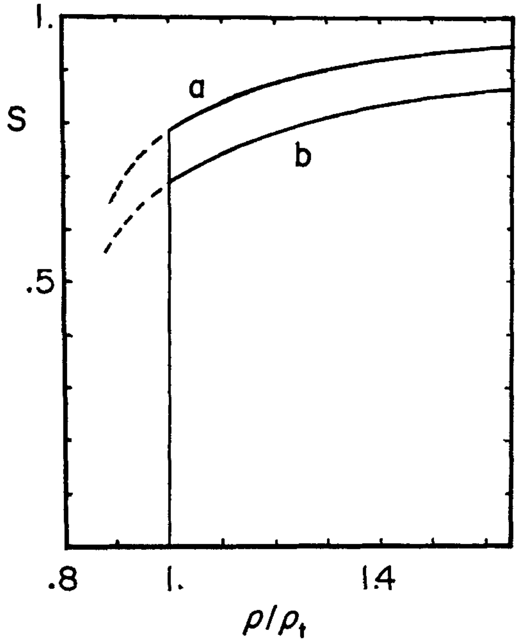

Figure 7. Concentration dependence of the order parameter S in the ordered phase. Two different forms for the angle-dependent virial coefficient are considered: (a) $B(\gamma) \sim |\sin\gamma|$; (b) $B(\gamma) \sim \sin^2\gamma$. The densities are normalized with respect to the density ρ_t of the ordered phase at the transition.

consistent it would, of course, provide an invaluable check on the parent theory.

5. Comparison with Experiment

There are a number of systems which approximate a suspension of long rods. In this section the available experimental data will be compared with the theoretical predictions.

A. VIRUSES

A number of virus suspensions form liquid crystals.(20) The best studied system is the Tobacco Virus. The TMV is a 2800 Å × 150 Å cylindrical rod(21) of molecular weight 4×10^7, composed of a nearly optically isotropic medium with index of refraction(22) 1.56. Suspensions in pure water form a liquid crystalline phase in concentrations above 2 weight percent(23,24); however, small concentrations of a salt can considerably reduce or destroy the tendency to align.(25)

The transition densities predicted by the Onsager theory for hard rods of these dimensions are an order of magnitude greater than those experimentally observed; the salt effect suggests, however, that electrostatic forces are important in the suspension so that TMV cannot be regarded as hard rods of the dimensions observed under the electron microscope. Onsager in fact intended that, in the estimation of the second virial coefficient, some effective range of force, rather than the particle dimensions themselves, be chosen. This alters the theoretical predictions in the right direction to give agreement with experiment, but no hard rod of reasonable dimensions seems to account for the smallness of the transition densities. This situation is summarized in Fig. 8, which compares the theoretical curves with the experimental points, entered both as the 2800 Å × 150 Å rod and as a spherocylinder having three times this radius (this value chosen consistent with the density of virus close-packed from pure water suspension(24)).

The birefringence of the TMV liquid crystal has been frequently observed but no quantitative details seem to have been published. As Fig. 6 emphasizes, the behavior of the order parameter is related to the form of the angular dependent part of the viral coefficient.

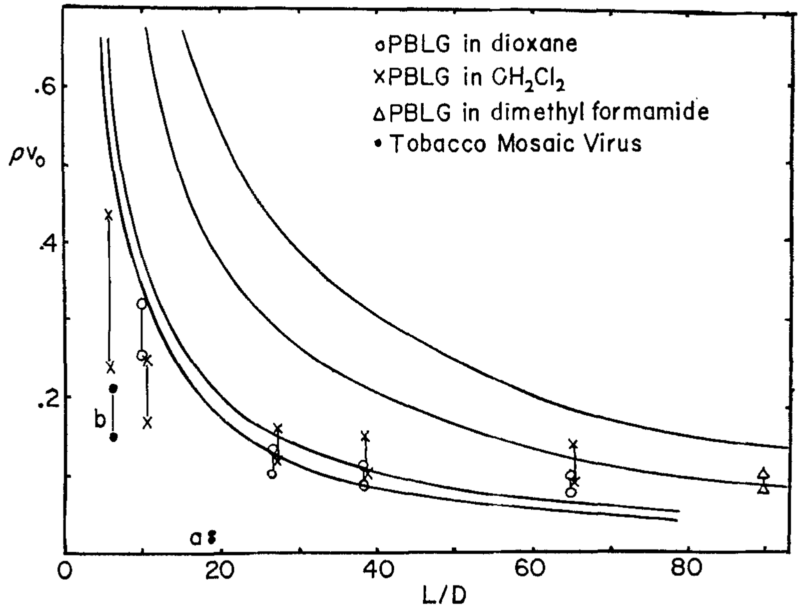

Figure 8. Comparison of theory and experiment. The theoretical curves are the same as those shown in Fig. 3. Experimental points are represented as connected pairs, of which the upper is the minimum density of the liquid-crystalline phase and the lower is the density of the isotropic phase in equilibrium with it. TMV is represented twice: (a) as a 150 Å × 2800 Å rod; (b) as a 500 Å × 2800 Å rod.

Direct osmotic pressure measurements are not feasible for TMV (all suspensions are necessarily less than 10^{-6} molar). The presence of the vertical concentration gradient has been reported only incidentally(24); it is apparently small but measurable. Measurements of the light scattering properties of virus suspensions over a range of concentrations have been performed by Oster(24); his results for the " compressibility " $(\partial\pi/\partial\rho)$ indicate that the second virial coefficient for TMV in a buffer is half again as large as that for 2800 Å × 150 Å spherocylinders; and in pure water the second virial coefficient is seven times as large as the spherocylinder estimate, and there is evidence that the third virial coefficient is not negligible.(26)

Several studies of the electric birefringence and dichroism of TMV have been performed(27,28); however, insufficient data on the concentration dependence of the susceptibility of the suspension to an ordering field have been presented to permit a determination of B_2. The work of Allen and Van Holde(28) is of particular interest, however, since it suggests that at pH below 8.0 dimerization of the virus particles occurs.

The principal conclusion of this brief survey of experimental information relevant to the TMV liquid crystal has to be that more experiments need to be done. There is a preliminary indication that the interparticle interactions are not characterized very well as long hard rods.

B. POLY (γ-BENZYL-L-GLUTAMATE)

The synthetic polypeptide PBLG can exist as an alpha-helix in a range of solvents; the light scattering properties of solutions in chloroform plus 5% dimethyl formamide indicate that the helices interact as long rods 20 Å in diameter,(29) to be compared with the 15 Å molecular dimension. Thus at least for this solvent system the range-of-force problem is not encountered; however, in other solvents (benzene, dioxane, pure chloroform) the viscosity is anomalously larger,(29) indicating intermolecular association; and in some solvents (dichloroacetic acid) the helices do not form at all.

Liquid crystalline phases have been observed for PBLG and some other polymers in a number of solvents(30,31); the available data are summarized in Fig. 8. For $20 < L/D < 50$ (the rod length is variable, depending on the method of preparation), the locus of transition points is in rough agreement with the Onsager theory, although the density jump at the transition is appreciably larger than expected. The effect of changing the solvent is pleasingly small, suggesting that the interparticle forces are short ranged. The behavior for very long rods is anomalous, however: all theories would have the phase transition densities decrease as D/L, yet the experiments indicate that the volume fraction must always be above 10% for the ordered phase to form. The explanation may be that alpha-helices of these dimensions are not stiff and straight. This contention is not in conflict with the conclusion of Doty, Bradbury, and Holtzer(29) that PBLG is a straight rod for $L/D \lesssim 150$: their conclusion is based on measures of the mean square length of the polymer, which would not be affected greatly by an ability of the rod to assume a bowed shape (whereas our conception of the entropy of packing would be considerably altered).

The PBLG liquid crystal has strong optical rotary properties which indicate that it is a cholesteric phase, in which the direction of alignment varies periodically through the medium: the phase resembles a nematic liquid crystal which has been twisted. The forces giving rise to the twist arise from the helix itself [mixtures of poly (γ-benzyl-*D*-glutamate) and PBLG form an untwisted (nematic) structure(32)] and represent a very small perturbation on the local structure: the direction of alignment undergoes one full rotation over a distance of 10^{-3} cm, several thousand times the average interparticle distance.(30) Thus the application of the Onsager theory to this system is warranted.

The synthetic polypeptides obviously present a good system for study of a suspension of long rods which form a liquid crystal. Unfortunately, insufficient information is available at the present time to allow us to check the consistency of the Onsager theory.

6. Conclusion

This work has studied the various theoretical discussions of the model system of a gas of hard rods, and tested the suitability of these theories to describe some systems of lyotropic liquid crystals. The Onsager theory is known to be accurate for sufficiently long rods; we have seen that the Lasher and Alben theories agree with the Onsager theory in this limit. The Flory theory does not agree with these theories, and apparently is not to be trusted.

The available experimental data for systems which approximate suspensions of long rods have been reviewed. The measured phase separation curves are only in qualitative agreement with the Onsager theory. It has been shown above that in such a system the coefficients of the Onsager expansion can be determined by a series of three experimental measures: (1) the concentration dependence of the osmotic pressure, which determines the angular average of all the virial coefficients; (2) the density dependence of the field-induced birefringence, which determines the degree of angular dependence of the second virial coefficient; and (3) the birefringence of the ordered phase, which provides indirect evidence of the nature of the angular dependence of the second virial coefficient. A complete set of experiments for a suitable system would be very useful since it would point out the extent to which the higher-order corrections are important and would permit us to separate these effects from those arising from interparticle forces other than the hard rod interaction. The first two experiments are sufficient to determine the concentration at which ordering should occur, and hence it might be useful to study a system which ought to order but apparently does not, such as poly (*n*-butyl isocyanate).(33)

Real systems are not composed of hard rods; the experimentally measured virial coefficients would contain contributions from the Van der Waals and Coulomb forces. Theoretical consideration of the nature and effect of these forces would be useful here and of undoubted value to the general theory of ionic suspensions.

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Appendix I

SECOND VIRIAL COEFFICIENT

The purpose of this appendix is to collect together the expressions for the angle-dependent second virial coefficient for particles of various oblong shapes. Onsager(1) has given two cases:

$$\text{Spherocylinder:}\quad B(\gamma) = \tfrac{4}{3}\pi D^3 + 2\pi L D^2 + 2L^2 D\,|\sin\gamma|$$

$$\text{Cylinder:}\quad B(\gamma) = (2L^2D + \tfrac{1}{2}\pi D^3)\,|\sin\gamma| + \{\tfrac{1}{2}\pi(1 + |\cos\gamma|) + 2E(\sin\gamma)\}LD^2$$

Isihara(10) has given a general formula for the virial coefficient for hard objects which in the case of prolate ellipsoids of revolution becomes

$$B(\gamma) = \tfrac{8}{3}\pi a^2 b + 2a^2 b(1-\epsilon^2)\int_0^{2\pi} d\beta \int_0^{\pi} d\alpha \sin\alpha\,\frac{(1-\epsilon^2\sin^2\alpha)^{1/2}}{(1-\epsilon^2\sin^2\theta)^2},$$

where a and b are the minor and major axes respectively, ϵ is the eccentricity, and θ is related to γ, α, and β by

$$\cos\theta = \cos\gamma\cos\alpha + \sin\gamma\sin\alpha\cos\beta.$$

For the special case $\gamma = 0$, the vertical coefficient and its derivatives are readily evaluated:

$$B(0) = \tfrac{32}{3}\pi a^2 b$$

$$\mathrm{d}B/\mathrm{d}\gamma = 0$$

$$\mathrm{d}^2B/\mathrm{d}\gamma^2 = \tfrac{1}{5}\frac{\epsilon^4}{1-\epsilon^2}B(0)$$

The expression can be reduced to a single integral after a change in variables, giving

$$\begin{aligned} B(\gamma) = {} & \tfrac{8}{3}\pi a^2 b + 2a^2 b(1-\epsilon^2)^{1/2}\left\{\int_0^{\pi} \mathrm{d}u\,\frac{A^2}{B^2}\frac{1}{B^2 - C^2}\right. \\ & + \int_0^{\pi/2} \mathrm{d}u\,\frac{A^2}{B^3 C}\tanh^{-1}\left(\frac{C}{B}\right) \\ & \left. + \int_0^{\pi/2} \mathrm{d}u\,\frac{B^2}{A^3 C}\tan^{-1}\left(\frac{C}{A}\right)\right\}, \end{aligned}$$

where $A = [1 - \epsilon^2\sin^2(u + \tfrac{1}{2}\gamma)]^{1/2}$, $B = [1 - \epsilon^2\sin^2(u - \tfrac{1}{2}\gamma)]^{1/2}$, and $C = [\epsilon^2\sin\gamma\sin 2u]^{1/2}$. This expression was evaluated numerically to generate Fig. 1.

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