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Theory of Systems of Rodlike Particles: I. Athermal systems

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Theory of Systems of Rodlike Particles

I. Athermal systems

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An improved treatment of the lattice model proposed in 1956 is presented for a system of hard rods, with axial ratio x, dispersed in a diluent. Interparticle forces, apart from repulsions on contact, are deliberately ignored within the scope of the present paper. The equilibrium distribution of orientations of the rodlike particles in a phase with nematic order is derived and explicitly taken into account. Thermodynamic properties in the asymptotic limit of high degree of order reduce, approximately, to those obtained previously. Calculations carried out for equilibrium between anistropic (nematic) and isotropic phases yield $v_x'/v_x = 1.4653$ for the ratio of volume fractions in the respective phases in the limit $x \to \infty$. The product xv_x expressing the combined covolume of solute species in the isotropic phase at coexistence is 7.89 in the same limit. The calculated critical value of the axial ratio for coexistence of the two phases in the neat liquid is $x_{\text{crit}} = 6.417$. Results are compared with those of other theories. Those that rely on the virial expansion are subject to errors implicit in treating the solvent as a continuum.

INTRODUCTION

The structures of liquids are determined predominantly by the sizes and shapes of their constituent molecules. Intermolecular attractions generally have little effect on the spatial arrangements of the molecules in typical liquids.[1-5] Owing to the close packing prevailing at normal liquid densities and the short range of the intermolecular repulsions compared with the range of the forces of attraction (hydrogen bonded liquids excepted), it should suffice therefore to represent the molecules by "hard" bodies, of appropriate

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shape(s), whose only interactions are described by an insurmountable repulsive barrier upon contact one with another. Radial distribution functions for spherical molecules calculated on this basis are in good agreement with computer simulations and with experiments.[3–5]

It follows that thermodynamic properties of liquids can be formulated by first treating the configuration for a system of non-attracting hard particles and subsequently introducing the perturbing effects of the intermolecular energy.[3–5] For this purpose the energy may be represented by a mean field.[2,6] In a first approximation, the perturbation of the spatial configuration often can be ignored, in which case the configuration partition function reduces to the product of a combinatory, or "steric," factor and the Boltzmann exponential of the intermolecular energy.

These findings accruing principally from investigations of molecules of low asymmetry recommend a similar approach to the treatment of liquids and liquid crystalline phases consisting of rodlike particles and their solutions. Lattice methods are especially attractive for deduction of the combinatory part of the configuration partition function, *i.e.*, the "steric factor" which comprehends the spatial configurations that conform to the virtual requirement that overlaps be avoided. Such methods were adapted to systems consisting of rodlike particles a number of years ago and presented in a paper published in 1956.[7] Disorder in the orientation of the rods with respect to the preferred axis of the system was expressed by a parameter y determined by the projection of the rod of axial ratio x in a plane perpendicular to the preferred axis. Separation into two phases, one isotropic and the other nematic, was predicted above a critical axial ratio that depends on the concentration. The predictions of this theory have been found to be in approximate agreement with experiments on α-helical polypeptides[8–10] and other rodlike polymers.[11,12]

Modified versions of this treatment advanced subsequently by various authors[13–15] limit the orientations of the rods to the orthogonal axes of the usual cubic lattice. The continuous variation of the disorientation parameter y, allowed in the original model and treatment, is thus forfeited. Advantages of this conceptual simplification of the original formulation are not apparent. That it constitutes a substantial departure from actualities in such systems is obvious. Moreover, it leads to the prediction of an axial ratio x of about 3.5[14] or less[15] for onset of nematic character in a system unaffected by an intermolecular energy (*e.g.*, in the limit $1/T = 0$). That this value is much too small will be apparent from the analysis of experimental results presented in the following paper.[16]

Straley[17] has criticized the lattice theory as originally presented[7] on the grounds that, upon refinement, it leads to inconsistencies and that it fails to predict separation of an anisotropic phase even for long rods. These assertions are traceable to an incorrect rendition of the relationship of y to the angular disorientation of the rodlike particle, as will become apparent below.

We have carried out a more exacting treatment of systems containing hard rods, present either as a solute or as the sole constituent of the neat liquid, the original version of the lattice model[7] being employed for this purpose. As in the early study, the degree of disorder is allowed to vary continuously, with molecules of the system assuming a distribution of disorientations dependent upon the axial ratio x and the concentration. Only hard-core repulsions between molecules are taken into account; intermolecular attractions are deliberately ignored within the scope of the present paper. In the following paper[16] an orientation dependent energy is incorporated in the theory.

Derivation of primary relations

The lattice is subdivided into cubic cells of linear dimension equal to the diameter of the particles. Hence, each rod of axial ratio x is construed to consist of x segments, one segment being accommodated by a cell of the lattice. Adopting a customary simplification, we take the molecule of the solvent to be equal in size to a segment of the rod.

The preferred axis of a given domain is taken along one of the principal axes of the lattice. In order to conform to the requirements of the lattice consisting of a cubic array of sites, each rodlike molecule is represented by y sequences of x/y segments[7] as shown in Figure 1. The number y of sequences required for thus representing the molecule depends on the angle ψ of

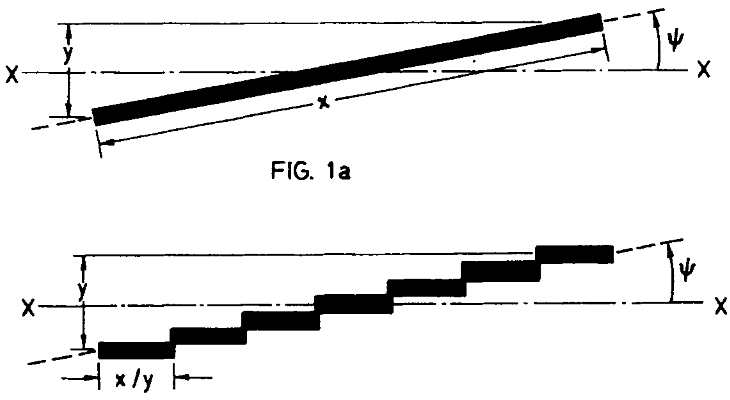

FIG. 1a

FIG. 1b

FIGURE 1 (a) Rodlike particle oriented at angle ψ to the preferred axis of the domain. (b) Its representations as y sequences, or submolecules, each parallel to the domain axis.

inclination of the rod to the preferred axis of the domain. Specification of the quantitative relation of y to the angle ψ is postponed for later consideration. It suffices for the present to observe that the value assigned to y is dictated by the dual requirements that each sequence be parallel to the preferred axis and that sequences occupy runs of sites in adjacent rows of the lattice.

The treatment depends on evaluation of the expected number ν_{j+1} of situations accessible to rodlike particle $j + 1$ after j particles have been assigned to the lattice subject to the condition that no segment may intrude on a lattice site occupied by another segment. Following the procedure introduced in the 1956 paper and employed recently[18] in another connection, we select a set of x lattice cells comprising y sequences arranged as required to accommodate the rodlike particle so represented. Evaluation of the expectation that this set of cells is vacant when j rods have been assigned previously to the lattice having n_0 cells constitutes the essential step. On the assumption that the sequences of segments occurring in a given row of cells parallel to the preferred axis are uncorrelated with those in adjacent rows, the expectation of vacancy at the site required for an initial segment of one of the y_{j+1} sequences of particle $j + 1$ is just the volume fraction $(n_0 - xj)/n_0$ of vacancies in the lattice containing j rods. Having established that one site is vacant, we require the conditional probability that the next one in the row also is vacant. On the further assumption that sequences in any given row are distributed at random, this conditional probability is given by the number fraction $(n_0 - xj)/(n_0 - xj + \sum_1^j y_i)$ of vacancies in the mixture of sequences and vacancies.[7] Hence, the required expectation that all cells of the set chosen for occupancy by the x segments of molecule $j + 1$ arranged in y_{j+1} sequences are vacant is

$$\nu_{j+1} n_0^{-1} = \left(\frac{n_0 - xj}{n_0}\right)^{y_{j+1}} \left(\frac{n_0 - xj}{n_0 - xj + \sum_{i=1}^{j} y_i}\right)^{x - y_{j+1}} \tag{1}$$

It follows that[7,18]

$$\nu_{j+1} = (n_0 - xj)^x \left(n_0 - xj + \sum_{i=1}^{j} y_i\right)^{-(x - y_{j+1})} n_0^{1 - y_{j+1}} \tag{2}$$

or, with negligible approximation,

$$\nu_{j+1} = \left\{\frac{(n_0 - xj)!}{[n_0 - x(j+1)]!}\right\} \left\{\frac{[n_0 - x(j+1) + \sum_{i=1}^{j+1} y_i]!}{[n_0 - xj + \sum_{i=1}^{j} y_i]!}\right\} n_0^{1 - y_{j+1}} \tag{2'}$$

The following development rests on Eq. (2), or Eq. (2′), derived by resort to the model consisting of sequences of segments aligned parallel to the preferred axis in the manner detailed above. Justification for this device rests on the patently plausible assertion that the expectancy of vacancies throughout the designated set of x lattice sites comprising y sequences should closely approximate the expectation that a given cylindrical volume chosen for occupation by the unbroken rod inclinded at the same angle ψ is empty, short-range order of the liquid being appropriately taken into account. The error incurred should be negligible for small values of y/x.[7,18] At larger disorientations y the procedure is less secure.[7] Hence, results thus deduced should be employed with some reservation at large disorientations; see below. Fortunately, the range in which $y/x \ll 1$ is of greatest interest.

In other respects, the formulation of Eq. (2) involves steps commonly employed in lattice statistics, which therefore entail no qualifications beyond those incident in general on the use of a lattice for evaluation of combinatory factors.

Inasmuch as we ignore the intermolecular energy in the present paper, it suffices to represent the configuration partition function Z_M for the mixture as the product of combinatory and orientational factors, Z_{comb} and Z_{orient}, respectively; *i.e.*,

$$Z_M = Z_{\text{comb}} Z_{\text{orient}} \tag{3}$$

The combinatory, or "steric," factor can be assembled from the v_j according to

$$Z_{\text{comb}} = \left(\frac{1}{n_x!}\right) \prod_{1}^{n_x} v_j \tag{4}$$

where n_x is the total number of rodlike particles, or solute molecules, in the system. The result obtained by substitution from Eq. (2') is [7,18]

$$Z_{\text{comb}} = \frac{(n_1 + \bar{y}n_x)!}{n_1!\,n_x!\,(n_1 + xn_x)^{n_x(\bar{y}-1)}} \tag{5}$$

where $n_1 = n_0 - xn_x$ is the number of vacancies, or of solvent molecules assumed to be monomeric ($x = 1$) in size; $\bar{y}$ is the average value of y given by

$$\bar{y} = n_x^{-1} \sum_y y n_{xy}$$

where n_{xy} is the number of solute molecules that assume the disorientation denoted by the index y; of course,

$$n_x = \sum_y n_{xy}.$$

The orientational factor in the partition function may be written

$$Z_{\text{orient}} = \prod_y \left(\frac{\sigma\omega_y n_x}{n_{xy}}\right)^{n_{xy}} \tag{6}$$

or

$$\ln Z_{\text{orient}} = \sum n_{xy} \ln\left[\left(\frac{n_x}{n_{xy}}\right)\omega_y\right] + n_x \ln \sigma \tag{6'}$$

where ω_y is the *a priori* probability, or fractional range of solid angle, for the interval of orientations associated with disorder index y, and σ is a constant.† By appropriate choice of σ the statistical weight $\sigma\omega_y$ for the state of perfect order ($y = 1$) may be made equal to unity. The value assigned to σ is otherwise of no importance.

Substitution of Eqs. (5) and (6) into Eq. (3), followed by introduction of Stirling's approximations for factorials gives[7,18]

$$-\ln Z_M = n_1 \ln v_1 + n_x \ln\left(\frac{v_x}{x}\right) - (n_1 + \bar{y}n_x)\ln\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right] + n_x(\bar{y} - 1) - \sum_y n_{xy} \ln\left[\left(\frac{n_x}{n_{xy}}\right)\omega_y\right] - n_x \ln \sigma \qquad (7)$$

where $v_1 \equiv n_1/(n_1 + xn_x)$ and $v_x \equiv xn_x/(n_1 + xn_x)$ are the volume fractions of the respective components.

For perfectly aligned rods $\bar{y} = y = 1$, and mixing is effectively one-dimensional. Equation (7) must then reduce to the ideal mixing law

$$-\ln Z_M = n_1 \ln\left(\frac{n_1}{n_1 + n_x}\right) + n_x \ln\left(\frac{n_x}{n_1 + n_x}\right) \qquad (8)$$

This requirement is fulfilled if we take

$$\sigma = \frac{1}{\omega_1} \qquad (9)$$

Consistent with this condition is the stipulation $\sigma = x^2$ adopted in previous papers.[7,18] Here we choose to retain σ as an arbitrary parameter.

At the opposite extreme of random disorder $n_{xy}/n_x = \omega_y$. Reduction of Eq. (7) in this case to the expression for a solution of disoriented polymer molecules, *i.e.*, to

$$-\ln Z_M = n_1 \ln v_1 + n_x \ln\left(\frac{v_x}{x}\right) + n_x(x - 1) - n_x \ln \sigma \qquad (10)$$

requires the substitution $\bar{y} = x$.

The system at equilibrium disorder

Equation (7) holds for any arbitrary distribution of orientations specified by the ratios n_{xy}/n_x for each value of y. The distribution at equilibrium is, of course, the one of particular interest. This distribution is implicit in Eqs. (1)

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† The quantity $\sigma\omega_y$ as here defined corresponds to ω_{xy} in Ref. 18.

and (2). Adaptation of Eq. (2) to the final mixture containing n_x solute particles yields

$$\nu_y = n_0\left\{\frac{(1 - v_x)}{[1 - v_x(1 - \bar{y}/x)]}\right\}^x\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right]^y \tag{11}$$

for the expected number of situations accessible to a particle whose disorder is specified by y. It follows that the fractional number of particles so oriented at equilibrium is of the form

$$\frac{n_{xy}}{n_x} = f_1^{-1}\omega_y \exp(-ay) \tag{12}$$

where

$$a = -\ln\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right] \tag{13}$$

and

$$f_1 = \sum_y \omega_y \exp(-ay) = \int_0^{y_{\max}} \omega_y \exp(-ay)\mathrm{d}y \tag{14}$$

Equation (12) may be derived alternatively[17] by variational methods applied to Eq. (7). The present procedure obviously is more direct.

Substitution of Eq. (12) in 6′ and 7 yields

$$\ln Z_{\text{orient}} = n_x[\ln(f_1\sigma) + a\bar{y}] \tag{15}$$

and[7,18]

$$-\ln Z_M = n_1 \ln v_1 + n_x \ln\left(\frac{v_x}{x}\right) - n_1 \ln\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right] + n_x(\bar{y} - 1) - n_x \ln(f_1\sigma) \tag{16}$$

It is to be understood that $\bar{y}$ must be assigned its equilibrium value in this equation and others that follow from it.

Chemical potentials and relations for phase equilibrium

The chemical potentials of the components are most easily derived from Eq. (7). Since

$$\left[\frac{\partial \ln Z_M}{\partial(n_{xy}/n_x)}\right]_{n_1, n_x} = 0$$

at equilibrium, the chemical potentials are given directly by the partial derivatives with respect to n_1 and n_x, respectively, *i.e.*,

$$\frac{\mu_1 - \mu_1^0}{RT} = -\left(\frac{\partial \ln Z_M}{\partial n_1}\right)_{n_x, \{n_{xy}/n_x\}_{eq}} \tag{17}$$

$$\frac{\mu_x - \mu_x^0}{RT} = -\left(\frac{\partial \ln Z_M}{\partial n_x}\right)_{n_1 \{n_{xy}/n_x\}_{eq}} \tag{18}$$

Application of these operations to Eq. (7) yields

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - v_x) + \frac{v_x(\bar{y} - 1)}{x} - \ln\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right] \tag{19}$$

and

$$\frac{\mu_x - \mu_x^0}{RT} = \ln\left(\frac{v_x}{x}\right) + (\bar{y} - 1)v_x - \ln(f_1\sigma) \tag{20}$$

the latter equation having been simplified by substitution of Eq. (12) for $n_{xy}/n_x\omega_y$ in the argument of the logarithm obtained by differentiating Eq. (7) with respect to n_x.

The corresponding expressions for the random solution, obtained from Eq. (10) for the unoriented mixture, are

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - v_x) + \left(1 - \frac{1}{x}\right)v_x \tag{21}$$

$$\frac{\mu_x - \mu_x}{RT} = \ln\left(\frac{v_x}{x}\right) + (x - 1)v_x - \ln \sigma \tag{22}$$

The conditions for biphasic equilibrium between isotropic and anisotropic (nematic) phases are

$$\left.\begin{aligned} \mu_1 &= \mu_1' \\ \mu_x &= \mu_x' \end{aligned}\right\} \tag{23}$$

the anisotropic phase being distinguished by a prime. Substitution from Eqs. (21) and (19) in the former of these conditions yields

$$\ln\left(\frac{1 - v_x'}{1 - v_x}\right) = \left(1 - \frac{1}{x}\right)v_x - \frac{(\bar{y} - 1)v_x'}{x} + \ln\left[1 - v_x'\left(1 - \frac{\bar{y}}{x}\right)\right] \tag{24}$$

where v_x and v_x' are the volume fractions in the isotropic and anisotropic phases, respectively. Substitution from Eqs. (22) and (20) in the latter of the Eqs. (23) gives

$$\ln\left(\frac{v_x'}{v_x}\right) = (x - 1)v_x - (\bar{y} - 1)v_x' + \ln f_1 \tag{25}$$

Combination of these two equations yields the alternative relationship

$$\ln(1 - v_x) - x^{-1}\ln v_x = \ln(1 - v'_x) - x^{-1}\ln v'_x - \ln\left[1 - v'_x\left(1 - \frac{\bar{y}}{x}\right)\right] + x^{-1}\ln f_1 \qquad (26)$$

which may be used to advantage in numerical calculations. Application of these equations to the calculation of phase equilibria requires evaluation of f_1 defined by Eq. (14). This, in turn, depends on the relationship of the *a priori* probability ω_y to y, which up to this point has not been specified. The functional connection between these and associated quantities is taken up in the following section.

Relationship of the disorder parameter to spatial orientation

Exact treatment of the model. Consider the cross section of the cubic lattice transverse to the preferred axis shown in Figure 2. The transverse axes are labeled Y_1 and Y_2, respectively. As in Figure 1, ψ denotes the azimuthal angle between the axis of the rod, represented by a heavy line in Figure 2, and the domain axis; φ is the angle of rotation about the domain axis. Representation

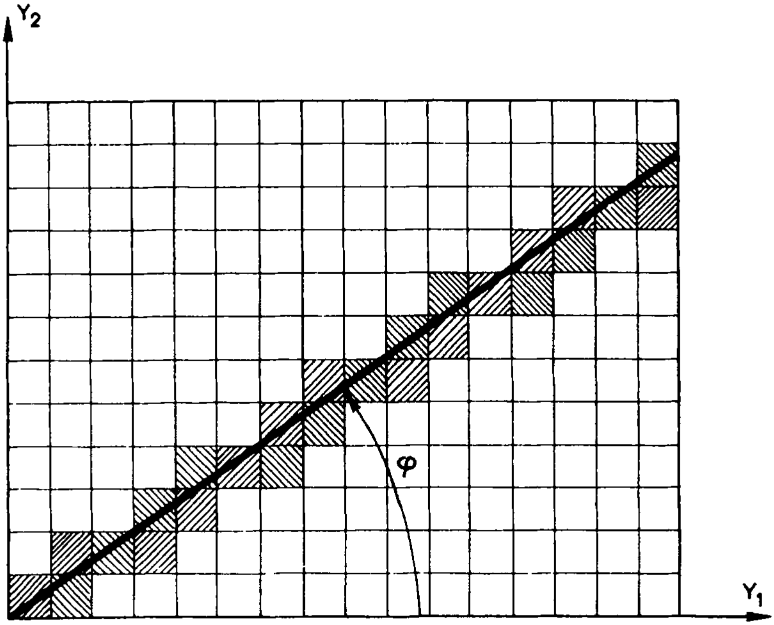

FIGURE 2 The model projected in a plane perpendicular to the domain axis (X).

of the rod by sequences occupying adjacent rows of the lattice, with each row parallel to the preferred axis, requires placement of sequences in the rows with shaded transverse sections in Figure 2. It will be apparent that the number of such sequences must equal the sum of the magnitudes of the components y_1 and y_2 of the length of the rod, measured by x, on the axes Y_1 and Y_2. For a given angle ψ, therefore,

$$y = |y_1| + |y_2| = x \sin \psi(|\cos \varphi| + |\sin \varphi|)$$

Averaging over φ, we obtain

$$y = \left(\frac{4}{\pi}\right) x \sin \psi \tag{27}$$

It follows from Eq. (27) that

$$\omega_y = \sin \psi \left(\frac{\mathrm{d}\psi}{\mathrm{d}y}\right) = \left(\frac{\pi}{4}\right) x^{-1} \tan \psi \tag{28}$$

$$= \left(\frac{\pi}{4}\right)^2 y x^{-2} \left[1 - \left(\frac{\pi}{4}\right)^2 \left(\frac{y}{x}\right)^2\right]^{-1/2} \tag{29}$$

Hence, according to Eq. (12)

$$\frac{n_{xy}}{n_x} = \left(\frac{\pi}{4}\right)^2 f_1^{-1} y x^{-2} \left[1 - \left(\frac{\pi}{4}\right)^2 \left(\frac{y}{x}\right)^2\right]^{-1/2} \exp(-ay) \tag{30}$$

or

$$n_{x\psi}\, \mathrm{d}\psi = n_x f_1^{-1} \sin \psi \exp(-\alpha \sin \psi) \mathrm{d}\psi \tag{31}$$

where

$$\alpha = \left(\frac{4}{\pi}\right) a x = -\left(\frac{4}{\pi}\right) x \ln\left[1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right] \tag{32}$$

and, from Eq. (14),

$$f_1 = \int_0^{\pi/2} \sin \psi \exp(-\alpha \sin \psi) \mathrm{d}\psi \tag{33}$$

The average of $\sin \psi$ is given by

$$\langle \sin \psi \rangle = \frac{f_2}{f_1} \tag{34}$$

where

$$f_2 = \int_0^{\pi/2} \sin^2 \psi \exp(-\alpha \sin \psi) \mathrm{d}\psi \tag{35}$$

Hence,

$$\bar{y} = \left(\frac{4}{\pi}\right) x \frac{f_2}{f_1} \tag{36}$$

Substitution of Eq. (36) in Eqs. (19) and (20) implements evaluation of the chemical potentials, the integrals f_1 and f_2 being furnished by Eqs. (33) and (35), respectively. Substitution of Eq. (33) in Eqs. (15) and (16) completes requirements for evaluation of Z_{orient} and of Z_M (apart from the arbitrary constant σ), and hence of the free energy of mixing.

For random orientation of the rods, attained by letting $\alpha = 0$, Eqs. (33) and (35) yield $f_1 = 1$ and $f_2 = \pi/4$. Hence

$$\bar{y} = \left(\frac{4}{\pi}\right) x \langle \sin \psi \rangle = x \tag{37}$$

and Eq. (16) reduces to Eq. (10) as required.

Obviously, values of y for some of the rods must exceed the average for the random distribution, given by x according to Eq. (37). The foregoing derivation aside, values of $y > x$ must occur if the mixing partition function is to reduce to Eq. (10) for random spatial orientations of the rods, for this requires $\bar{y} = x$. Returning to the derivation of Eq. (27), one may observe that for any value of ψ in the range $\pi/4 < \psi < \pi/2$ the parameter y exceeds x over a portion of the range of φ. At $\psi = \pi/2$ and $\varphi = \pi/4$, y reaches its upper bound, $y_{\max} = \sqrt{2}x$.

A number of sequences $y > x$ is difficult to reconcile with the lattice scheme as set forth above. The number of volume fraction factors in Eqs. (1) and (2) then exceeds the number of segments, identified above with the axial ratio x. Moreover, the number fraction factor occurs as its inverse raised to the power $y - x$. Partial resolution of these inconsistencies may be achieved by distortion of the simple cubic lattice rendering it anisotropic. Whatever the errors arising from the deficiencies of the conventional lattice, they are peculiar to orientations at large angles from the preferred direction. For systems at equilibrium the incidence of such orientations is very low. Hence, effects of probable inaccuracy of the theory at high disorientations should be very small.

Equations (32, 33, 35 and 36) yield solutions $\bar{y}/x$ only for volume fractions v_x greater than a limiting value. This value depends on x. At concentrations exceeding this limit the chemical potentials display characteristics indicative of phase separation, *i.e.*, they exhibit extrema with concentration. These features are illustrated by calculations below.

Straley's rendition. If one ignores the deployment of sequences in principal lattice planes (see Figure 2), contrary to a primary requisite of the lattice model, then the relation

$$y = x \sin \psi \tag{38}$$

adopted by Straley[17] suggests itself. It would follow that

$$\omega_y = x^{-1} \tan \psi \tag{39}$$

$$\frac{n_{xy}}{n_x} = f_1^{-1} y x^{-2} \left(1 - \frac{y^2}{x^2}\right)^{-1/2} \exp(-ay) \tag{40}$$

$$\alpha = ax \tag{41}$$

and

$$\bar{y} = x\frac{f_2}{f_1} \tag{42}$$

Equations (38–42) would then replace Eqs. (27, 28, 30, 32 and 36), respectively; Eqs. (33–35) obviously hold without revision.

The equations above that follow from adoption of Eq. (38) yield

$$\bar{y} = \left(\frac{\pi}{4}\right)x \tag{43}$$

for the isotropic system, *i.e.*, when $\alpha = a = 0$. The orientation partition function obviously is maximized at this point ($\alpha = 0$), but Z_{comb} reaches its extremum—a minimum—at $\bar{y} = x$, and not at $\bar{y} = (\pi/4)x$, as will be apparent from Eq. (7) if the last two terms, representing $-\ln Z_{\text{orient}}$, are deleted. Consequently, neither $\bar{y} = (\pi/4)x$ nor $\bar{y} = x$ minimizes the total free energy. Also, substitution of Eq. (43) and $f_1 = 1$ in Eq. (16) (or in Eq. (7) with $n_{xy}/n_x = \omega_y$, as follows from Eq. (12) with $a = 0$) does not yield the required relation, Eq. (10), for a random isotropic phase.

Returning to the partition function given by Eq. (16) with Eq. (42) substituted therein, we find, in agreement with Straley, that for rods of sufficient length (*e.g.*, for $x > 10$) the free energy exhibits a minimum at a value of $\bar{y} < x$ for any finite concentration. Thus, a finite degree of order is indicated regardless of the dilution. Moreover, the chemical potentials are monotonic with concentration. Hence, the system is predicted to remain homogeneous, without separating into two phases.

These "nonphysical" deductions led Straley[17] to condemn the model and theory as being "untrustworthy." Rather, the difficulty originates in Eq. (38) for the number of sequences into which the rod is resolved as a function of the angle of inclination. This relationship is not consistent with the model; it yields a partition function that fails to reduce to Eq. (10) for a random mixture, and is responsible for the other physically untenable results cited.

The asymptotic approximation. For values of $\alpha \gg \pi/2$, the integrals f_1 and f_2 may be developed in reciprocal powers of α as follows

$$f_1 = \frac{1}{\alpha^2} + \frac{3}{\alpha^4} + \cdots \tag{44}$$

$$f_2 = \frac{2}{\alpha^3} + \frac{12}{\alpha^5} + \cdots \tag{45}$$

Hence, from Eqs. (36) and (32)

$$\begin{aligned}\bar{y} &= \left(\frac{8x}{\pi}\right)(\alpha^{-1} + 3\alpha^{-3} + \cdots)\\ &= \left(\frac{2}{a}\right)\left(1 + \frac{3\pi^2}{16a^2x^2} + \cdots\right)\end{aligned} \tag{46}$$

and, from Eq. (15) in conjunction with Eqs. (32) and (46),

$$n_x^{-1} \ln Z_{\text{orient}} = \left[2 \ln \bar{y} + \left(\frac{3}{4}\right)\left(\frac{\pi\bar{y}}{4x}\right)^2 + \cdots\right] + \ln\left(\frac{\sigma}{x^2}\right) + C \tag{47}$$

where

$$C = 2 \ln\left(\frac{\pi e}{8}\right) \tag{48}$$

Omission of terms of higher orders in α^{-1}, or in $\bar{y}/x$, reduces these equations to

$$f_1 = \alpha^{-2} = \left(\frac{\pi}{4ax}\right)^2 \tag{49}$$

and

$$\bar{y} = \frac{2}{a} = -\frac{2}{\ln[1 - v_x(1 - \bar{y}/x)]} \tag{50}$$

Hence,

$$f_1 = \left(\frac{\pi\bar{y}}{8x}\right)^2 \tag{51}$$

Substitution of these relationships in Eqs. (15) and (16) yields

$$\ln Z_{\text{orient}} = n_x\left[2 \ln \bar{y} + \ln\left(\frac{\sigma}{x^2}\right) + C\right] \tag{52}$$

$$-\ln Z_M = n_1 \ln v_1 + n_x \ln\left(\frac{v_x}{x}\right) + \frac{2n_1}{\bar{y}} + n_x\left[\bar{y} + 1 - 2\ln\bar{y} - \ln\left(\frac{\sigma}{x^2}\right) - C\right] \tag{53}$$

The chemical potentials (see Eqs. (19) and (20), expressed in this asymptotic approximation can be written

$$\frac{(\mu_1 - \mu_1^0)}{RT} = \ln(1 - v_x) + \frac{v_x(\bar{y} - 1)}{x} + \frac{2}{\bar{y}} \tag{54}$$

$$\frac{(\mu_x - \mu_x^0)}{RT} = \ln\left(\frac{v_x}{x}\right) + v_x(\bar{y} - 1) + 2(1 - \ln\bar{y}) - \ln\left(\frac{\sigma}{x^2}\right) - C \tag{55}$$

Equations (24) and (25) for phase equilibrium become

$$\ln\left(\frac{1 - v_x'}{1 - v_x}\right) = \left(1 - \frac{1}{x}\right)v_x - \frac{(\bar{y} - 1)v_x'}{x} - \frac{2}{\bar{y}} \tag{56}$$

and

$$\ln\left(\frac{v_x'}{v_x}\right) = (x - 1)v_x - (\bar{y} - 1)v_x' - 2\left[1 - \ln\left(\frac{\bar{y}}{x}\right)\right] + C \tag{57}$$

The 1956 approximation. This approximation was formulated[7] on the premise that the form of the distribution n_{xy}/n_x should be of minor importance. Hence, a uniform ("square-well") distribution over ψ was assumed for $0 \leq \psi < \psi'$. The connection between $\bar{y}$ and the solid angle within $\psi < \psi'$ was so adjusted to assure that $\bar{y} = x$ in the limit of complete disorder, and, hence, that the thermodynamic relations reduce to Eq. (10) and its consequents in this limit. The expressions obtained in this approximation correspond to Eqs. (52) and (53) with the small constant $C(=0.1306)$ set equal to zero; Eqs. (50) and (54) apply in this approximation as well as in the one above. Further simplification was achieved in the 1956 formulation by making the inconsequential stipulation that $\sigma = x^2$. Thus, the orientation partition function was expressed as

$$Z_{\text{orient}} = \bar{y}^{2n_x} \tag{58}$$

in that treatment.

Numerical calculations

Solvent chemical potentials for solutions containing rods of axial ratio $x = 20$ are plotted against the volume fraction v_x of solute in Figure 3. The solid line

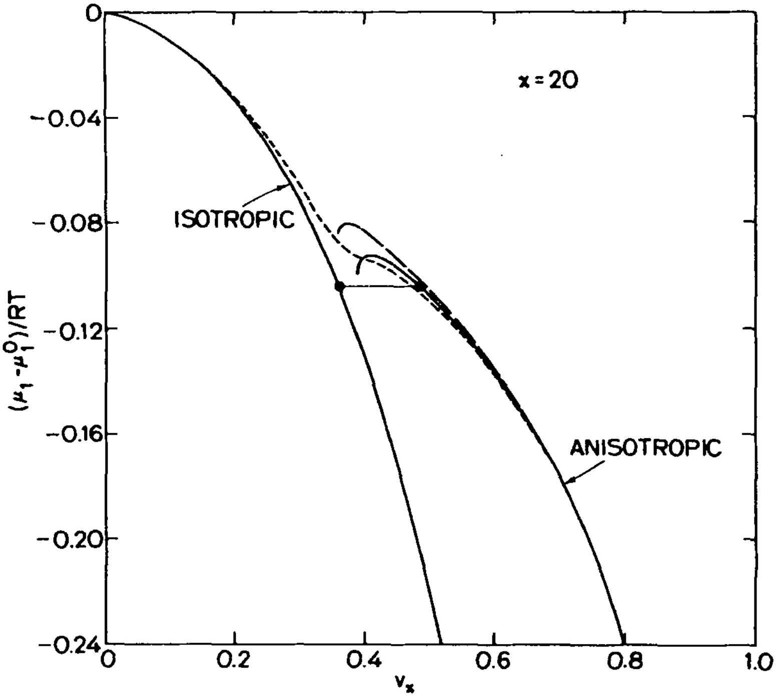

FIGURE 3 The chemical potential of the solvent plotted against the volume fraction v_x for $x = 20$. The solid curve labeled "isotropic" was calculated according to Eq. (21) for an unordered polymer solution. The curves to the right refer to the anisotropic phase; the solid curve was calculated according to Eq. 19 with $\bar{y}$ given by Eq. (36) ("exact" treatment) and the dashed curve according to Eq. (54) ("asymptotic" or "1956" approximation). The short-dashed curve, calculated according to Eqs. (19) and (42), follows from Straley's treatment.[17]

on the left was calculated for isotropic mixtures according to Eq. (21). The solid line on the right was calculated for anisotropic mixtures according to Eq. (19) with $\bar{y}$ furnished by Eq. (36); the integrals f_1 and f_2 appearing in the latter equation were evaluated numerically. The long dashed line was calculated according to Eq. (54) representing the asymptotic approximation (and the 1956 approximation as well). This line and the solid one representing the "exact" results according to the theory without approximation are terminated at the concentrations below which Eqs. (32, 33, 35 and 36) do not yield solutions $\bar{y}/x$; at concentrations below this limit the mixing free energy is monotonic with the degree of disorder.

The two points shown in Figure 3 denote the conjugate phases in equilibrium. They are therefore joined by a tie-line. The tie-line calculated in the asymptotic approximation (long dashed curve) lies slightly below the one shown; *cf. seq.*

The short dashed line included in Figure 3 was calculated according to Eq. (19) using Straley's relation, Eq. (42), instead of Eq. (36) for evaluation of $\bar{y}$. This line is asymptotic to the curve for isotropic mixtures, Eq. (21) at low concentrations and to that for anisotropic mixtures at high concentrations. It is continuous and monotonic. Hence, homogeneity is predicted for all concentrations. The reasons for this behavior have been cited above.

Similar calculations for other axial ratios x present features resembling closely those exhibited in Figure 3 for $x = 20$. As x is increased the maximum in the curve for the anisotropic mixtures, and its terminus also, are displaced to lower v_x and to higher $(\mu_1 - \mu_1^0)/RT$. Apart from these alterations, the characteristics shown in Figure 3 are replicated.

Compositions of coexisting phases are shown in Figure 4 as functions of the axial ratio. The latter quantity is plotted on a logarithmic ordinate scale; the

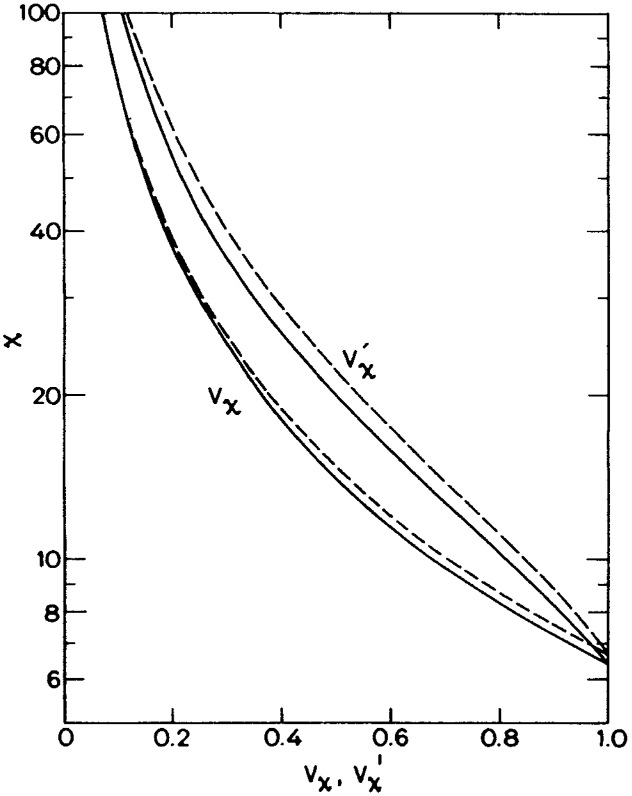

FIGURE 4 Volume fractions v_x (lower curves) and v_x' (upper curves) in the isotropic and anisotropic phases, respectively, coexisting at equilibrium as functions of the axial ratio x (log scale). Solid curves were calculated according to the exact treatment. Dashed curves represent the 1956 approximation.[7]

volume fractions v_x and v'_x in the conjugate phases are scaled linearly on the abscissa. The lower solid and dashed curves represent compositions v_x of isotropic phases; the upper curves show v'_x for the coexisting anisotropic phases. The solid curves present "exact" calculations carried out according to Eqs. (24) and (25) (or 26), $\bar{y}$ being given by Eq. (36) with f_1 and f_2 evaluated by numerical integrations of Eqs. (33) and (35). Dashed lines represent calculations carried out according to the 1956 approximation using Eqs. (56) and (57) with $C = 0$. Calculations in the asymptotic approximation, *i.e.*, according to Eqs. (56) and (57) with retention of C in the latter equation, yield curves falling between the two sets shown in Figure 4, but somewhat closer to the solid ("exact") curves. The approximations have only a small effect on the calculated phase equilibria.

The degree of disorder expressed as $\bar{y}/x$, in the anisotropic phase at biphasic equilibrium is plotted in Figure 5 against x using a logarithmic scale. These calculations were carried out in conjunction with those shown in Figure 4. Results obtained in both of the approximations are included for comparison with the results of the "exact" calculations. The termini of the curves on the left refer to limits $v_x = v'_x = 1$, *i.e.*, to neat liquids. The curves approach asymptotes as x increases. The change of $\bar{y}/x$ with x is small.

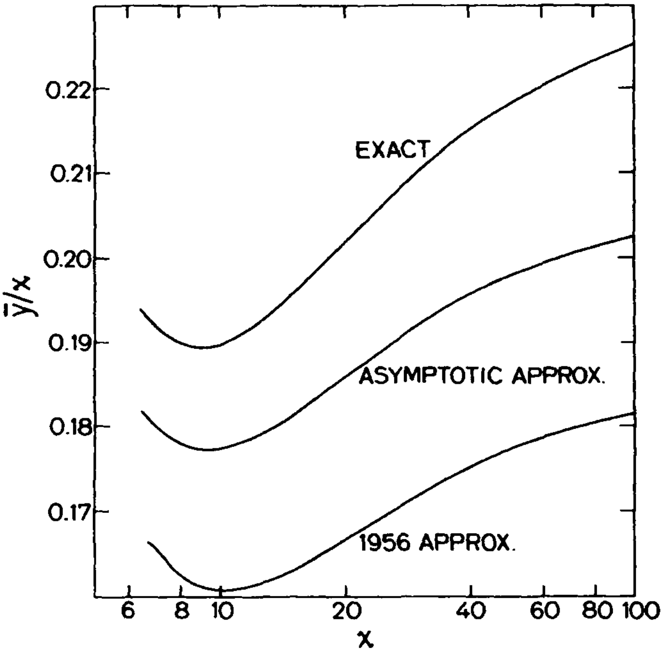

FIGURE 5 Disorder ratio $\bar{y}/x$ plotted against x (log scale) according to the exact treatment and the two approximations.

Numerical quantities characterizing biphasic equilibria in systems comprising hard rods are summarized in Table I. Results of calculations carried out employing the exact treatment, the asymptotic approximation and the 1956 approximation are compared.

The first four rows of Table I pertain to the neat liquid having the axial ratio x_{crit} required for coexistence of two phases. The quantities $\bar{y}_{\text{crit}}$ and, alternatively, $(\bar{y}/x)_{\text{crit}}$ afford measures of the degree of disorder in the anisotropic phase. The conventional order parameter, $(3\langle\cos^2\psi\rangle - 1)/2$, is recorded in the fourth row of the table. The refinement achieved by the exact theory is reflected in a somewhat lower value of x_{crit} and a larger value of $(\bar{y}/x)_{\text{crit}}$.

TABLE I

Summary of calculations on biphasic equilibria

	Exact treatment	Asymptotic approx.	1956 approx.
Neat liquids			
x_{crit}	6.4166	6.4517	6.7018
$\bar{y}_{\text{crit}}$	1.24445	1.17342	1.11527
$(\bar{y}/x)_{\text{crit}}$	0.19394	0.18188	0.16641
$(3 < \cos^2\psi > - 1)/2$	0.9473	0.9541	
Athermal solutions			
v_x for $x = 20$	0.36417	0.36615	0.37909
v'_x for $x = 20$	0.49785	0.51101	0.54131
$\bar{y}$ for $x = 20$	4.0394	3.7184	3.3347
$\bar{y}/x$ for $x = 20$	0.20198	0.18592	0.16673
$\bar{y}/x$ lim $x \to \infty$	0.23242	0.20780	0.18636
xv_x for $x = 20$	7.2835	7.3229	7.5818
xv_x lim $x \to \infty$	7.8937	7.9593	8.2834
v'_x/v_x for $x = 20$	1.3671	1.3956	1.4279
v'_x/v_x lim $x \to \infty$	1.4653	1.5264	1.5923

An axial ratio $x = 20$ has been selected for illustration of the composition and order in systems containing a diluent, as presented in the lower portion of the table. The volume fractions v_x and v'_2 decrease and the disorder parameter $\bar{y}$ increases with the axial ratio. The ratios $\bar{y}/x$ and v'_x/v_x and the product xv_x (and xv'_x also), however, undergo little change with x throughout the range from $x = x_{\text{crit}}$ (neat liquid) to $x = \infty$. The values of these quantities in the limit $x \to \infty$ are included.

Comparison of the second column of figures with the first in Table I shows the asymptotic approximation to yield values close to those of the exact theory. The 1956 approximation, which differs from the asymptotic approximation through the replacement of $C = 0.1306$ by zero, is inferior to the asymptotic approximation, but the error it entails is small. These numerical results corroborate the comparisons shown in Figures 3–5.

The most significant alterations occur in the ratios $\bar{y}/x$ and v_x'/v_x. In the limit $x \to \infty$ the disorder ratio $(\bar{y}/x)_{x\to\infty}$ is increased from 0.1864 in the 1956 approximation to 0.2324 according to the exact treatment. The composition ratio $(v_x'/v_x)_{x\to\infty}$ is decreased from 1.5923 (1956 approximation) to 1.4653 (exact).

Resort to the asymptotic approximation greatly simplifies applications of the theory and, hence, enhances its range of application. This approximation can be employed with the same facility as the 1956 treatment, but with significantly improved accuracy. The 1956 approximation nevertheless is acceptable for most purposes. We have confirmed that recent calculations[20] on polydisperse systems carried out according to the 1956 approximation are not significantly vitiated on this account.

It is perhaps worth noting that the revised values of the ratio v_x'/v_x given in the second column of Table I are closer to Onsager's estimate, 1.343, than are the results of previous calculations carried out according to the 1956 approximation[7] (see the last two entries in the fourth column of Table I). However, our value of $(xv_x)_{x\to\infty} = 7.894$ is more than twice Onsager's result 3.34, for the equivalent quantity. The concentration v_x at incipient separation of the anisotropic phase according to the Onsager theory, therefore, is less than half the value we obtain for a given axial ratio. The disparity between our value for $(xv_x')_{x\to\infty} = \lim_{x\to\infty}[(xv_x)(v_x'/v_x)] = 11.57$ and his estimate, 4.486, is even greater.

Onsager[19] employed well known cluster expansion methods for evaluation of coefficients in the virial series. In the face of the complexities inherent in this procedure, he terminated the expansion at the binary cluster term. While he succeeded in demonstrating that solutions of highly asymmetric rodlike particles should separate into two phases, one isotropic and the other nematic and of only slightly higher concentration, numerical results obtained on this basis must be regarded as approximate.[7,21] The inadequacy of the truncated virial expansion is evident from the fact that at coexistence the combined covolume of all particles exceeds the total volume by the factor 3.34 (see above) according to Onsager's calculations.† Our calculations lead to an even larger figure for this ratio, given by xv_x (Table I), which actually

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† The covolume (equal to half the excluded volume) of a particle averaged over all orientations and expressed in present notation is $x^2 V_1$ according to Zimm[22] and Onsager.[19] Here V_1 is the molecular volume of a segment. The number density being v_x/xV_1, it follows that the combined covolume of all particles per unit volume of an isotropic phase is xv_x.

increases toward its asymptote as the system, maintained at coexistence, is rendered more dilute by increasing x; *i.e.*, as $v_x \rightarrow 0$ when $x \rightarrow \infty$. Satisfactory convergence of the virial expansion is questionable under these circumstances even with inclusion of those additional terms in the series that might conceivably be evaluated.

Errors arising from treatment of the liquid as a continuum, as is implicit in application of the cluster expansion procedure to liquid mixtures, poses a source of error probably more serious than truncation of the virial series at its binary term. It is plainly evident that the second virial coefficient thus deduced will generally be too large, although to a degree that may depend on the size of the solvent relative to the diameter of the rod, or of a fibrillar solute of other geometry. For mixtures of spherical molecules of comparable size, for example, the second virial coefficient calculated from the cluster integral (as if the solvent were a continuum) is too great by a factor of eight. For a mixture of polymer chains with a low molecular dilent the former value is excessive by a factor of about two.[19,22] The error arising from failure to take into account the short-range order in the liquid probably is mainly responsible for the lower value of xv_2 at coexistence, and hence of the lower threshold concentration for phase separation, according to the Onsager treatment.[19]

In the following paper[16] we show that the critical axial ratio $x = 6.417$ for coexistence of isotropic and nematic phases as calculated here is supported by experimental results bearing on the value of this quantity in the "athermal" limit, *i.e.*, in the limit $1/T \rightarrow 0$.

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