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Third Virial Coefficient for the Gas of Long Rods†

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Abstract—The Onsager theory for the liquid crystal phase transition of a gas of hard rods is known to be accurate if the rods are *long enough*. In order to quantify the necessary length, the first correction term (the third virial coefficient) to the Onsager theory is estimated numerically. On the basis of a study of the behavior of this function (for the cases $L/D = 10$, 20, 40, and 100), a model function which approximates its angular dependence is proposed. This is used to estimate the corrections to the predictions of the Onsager theory arising from the finite length of the rods, in both isotropic and ordered phases. It is concluded that the Onsager approximation is not quantitatively accurate for $L/D < 100$.

1. Introduction

The gas of long hard rods exhibits a phase transition whereby at sufficiently large density a spontaneous alignment of the rods occurs.[1] The phenomenon has been discussed as a model for liquid crystals,[2–6] of particular relevance to lyotropic systems such as Tobacco Mosaic Virus or poly (γ-benzyl-L-glutamate). Onsager[1] has given a discussion of the theory of this system, wherein it was shown that in the limit that the ratio of length L to diameter D is large the ordering can be accurately discussed by a form of molecular field theory. Although several alternative treatments of the rod gas have been given,[2–5] their predictions reduce to that of the Onsager theory in the large L/D limit,[6] and none has given a discussion of the equation, " How long must the rods be for the theory to have quantitative validity? " The present work attempts to resolve this

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question by estimating the lowest order (in D/L) correction to the Onsager theory.

The next section outlines the Onsager theory and delimits the problem to be discussed. The third section describes how the third virial coefficient for any given orientations of three rods can be calculated numerically, and also reports analytic results for certain special cases. The fourth section proposes a model function which seems to closely imitate the angular dependence of the third virial coefficient, and reports the isotropic average of this function. The fifth section explains how the weighted angular averages relevant to the ordered phase were calculated with the aid of an approximation described in the Appendix. The final section discusses the effect of the third virial term on the predictions of the Onsager theory, and compares the computed third virial coefficient with estimates for it implicit in other theories.

2. Onsager Theory

The Helmholtz free energy per particle for the rod gas can be given a low density expansion[1]

$$\begin{aligned} F/(NkT) = {} & \int f(\hat{\mathbf{n}}) \ln f(\hat{\mathbf{n}})\, d\hat{\mathbf{n}} + \ln \rho \\ & + \tfrac{1}{2}\rho \iint B(\hat{\mathbf{n}}, \hat{\mathbf{m}}) f(\hat{\mathbf{n}}) f(\hat{\mathbf{m}})\, d\hat{\mathbf{n}}\, d\hat{\mathbf{m}} \\ & + \tfrac{1}{3}\rho^2 \iiint C(\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}) f(\hat{\mathbf{n}}) f(\hat{\mathbf{m}}) f(\hat{\mathbf{l}})\, d\hat{\mathbf{n}}\, d\hat{\mathbf{m}}\, d\hat{\mathbf{l}} \\ & + \ldots . \end{aligned} \tag{1}$$

The coefficients of this expansion depend explicitly on the orientational distribution function $f(\hat{\mathbf{n}})$, which is the number of rods per unit volume per unit solid angle having orientation near $\hat{\mathbf{n}}$, and which obeys the normalization condition

$$\int f(\hat{\mathbf{n}})\, d\hat{\mathbf{n}} = 1. \tag{2}$$

For any fixed density ρ, the equilibrium phase is specified as being the form of $f(\hat{\mathbf{n}})$ which minimizes the Helmholtz free energy. The transition between phases is located by comparing the Gibbs free energies of phases having the same pressure.[7]

The functions B and C appearing in (1) are referred to here as the second and third (TVC) virial coefficients. For any axially symmetric rod they may be expressed as

$$B(\hat{\mathbf{m}}, \hat{\mathbf{n}}) = \int \Phi(\mathbf{q}, \mathbf{r}; \hat{\mathbf{m}}, \hat{\mathbf{n}})\, d\mathbf{q} \tag{3}$$

and

$$C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) = \tfrac{1}{2}\iint \Phi(\mathbf{p}, \mathbf{q}; \hat{\mathbf{l}}, \hat{\mathbf{m}})\, \Phi(\mathbf{q}, \mathbf{r}; \hat{\mathbf{m}}, \hat{\mathbf{n}})\, \Phi(\mathbf{r}, \mathbf{p}; \hat{\mathbf{n}}, \hat{\mathbf{l}})\, d\mathbf{p}\, d\mathbf{q} \tag{4}$$

where $\Phi(\mathbf{p}, \mathbf{q}; \hat{\mathbf{l}}, \hat{\mathbf{m}})$ is a function which is unity if a rod of orientation $\hat{\mathbf{l}}$ whose center is at $\mathbf{p}$ overlaps a rod of orientation $\hat{\mathbf{m}}$ whose center is at $\mathbf{q}$, and zero otherwise. The second virial coefficient can be interpreted as the volume from which a rod of orientation m is excluded by a rod of orientation $\hat{\mathbf{n}}$; the TVC is a measure of the number of positions that may be assumed by three rods of fixed orientations $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{n}}$ which are constrained each to overlap the other two, as shown in Fig. 1.

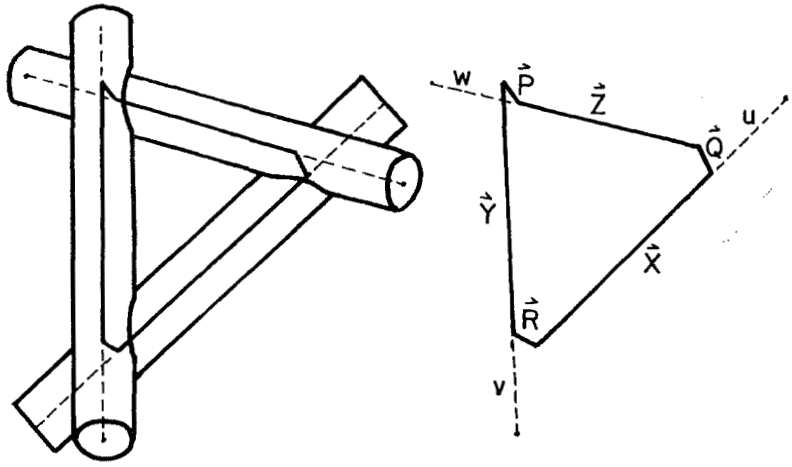

Figure 1. Three rods each overlapping the other two. The vectors **x**, **y**, **z** lie along the axes of the rods $(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}})$; **p**, **q**, **r** are the shared normals which measure the minimum distance between rod axes. The quantities u, v, w measure the distance between an arbitrarily chosen rod end and the foot of the nearer shared normal.

Onsager evaluated the second virial coefficient exactly for right circular cylinders, and for cylinders with spherical caps. In the limit that L/D is large, both may be represented by

$$B(\hat{\mathbf{m}}, \hat{\mathbf{n}}) = 2L^2D\,|\sin\gamma\,|, \tag{5}$$

where γ is the angle between $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$. He further argued that in

this same limit the higher virial coefficients can be ignored. With these approximations the equation of state (1) predicts a phase transition near the density

$$\rho_c \sim 5L^{-2}D^{-1}. \tag{6}$$

The second virial coefficient for finite length rods differs from (5) both in that the angular dependence may be slightly different, and in that it has a part of order D^2L independent of angle. The nature and effect of these aspects of the second virial coefficient have been discussed elsewhere[2,6] showing that a phase transition occurs for rods of any length in the Onsager approximation, and that the relation (6) always holds (with only a 10% variation as L/D ranges from 10 to infinity). While it is necessary to use an accurate representation of the second virial coefficient in an actual calculation, it is sufficient for the present purposes to use the form (5).

3. Third Virial Coefficient

For the present purposes the evaluation of the TVC does not have to be particularly accurate, provided that adequate precautions are taken to ensure that significant features of the function are not overlooked. This is so both because the accurate form of the TVC depends on the details of rod shape, and because to the extent that the third virial term is of any consequence to the expansion (1), the higher order terms should be considered also. Finally since the integrations of Eqs. (1) and (3) will be done numerically, there are rather restrictive practical limitations on the degree of accuracy which can be achieved.

Figure 1 is a representation of three cylindrical rods overlapping each other. This figure also introduces a coordinate system which is useful in describing such a configuration. The vectors $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ lie along the axes of the cylinders; $\mathbf{p}$, $\mathbf{q}$, and $\mathbf{r}$ are the normals shared by pairs of the axes (so that $\mathbf{p}$ is perpendicular to $\mathbf{x}$ and $\mathbf{y}$) and represent the smallest distances between the cylinder axes. These vectors are related by

$$\mathbf{x}+\mathbf{y}+\mathbf{z}+\mathbf{p}+\mathbf{q}+\mathbf{r}=0. \tag{7}$$

Finally u, v, and w are the distances between one end of a cylinder and the closer of the feet of the shared normals.

In what follows the definition of an overlapping configuration is taken to be

$$|\mathbf{p}|, |\mathbf{q}|, |\mathbf{r}| < D, \qquad |\mathbf{x}|, |\mathbf{y}|, |\mathbf{z}| < L \tag{8}$$
$$0 < u < L - |\mathbf{x}|, \; 0 < v < L - |\mathbf{y}|, \; 0 < w < L - |\mathbf{z}|,$$

so that the axis of a given cylinder must at some points lie within D of the axes of the other two cylinders, and the points of closest approach must lie within the cylinder. This definition is not quite in accord with the geometrical properties of real cylinders: there are discrepancies in cases where a point of closest approach is on the extended axis of a cylinder just beyond its physical end. Since only the rod ends are involved, the error is unimportant for long rods and represents a higher-order shape-dependent part of the TVC.

Except for a few degenerate cases, the specification of the directions $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, $\hat{\mathbf{n}}$, the quantities u, v, w and any three of the amplitudes x, y, z, p, q, r determines the configuration uniquely. For example, with p, q, and r taken as independent variables, x, y, and z are determined by (7), which can be solved to give

$$\begin{aligned} x &= p\left(\frac{\alpha\beta-\gamma}{\lambda\epsilon}\right) + q\left(\frac{\mu}{\epsilon}\right) + r\left(\frac{\beta\gamma-\alpha}{\gamma\epsilon}\right) \\ y &= p\left(\frac{\alpha\gamma-\beta}{\lambda\epsilon}\right) + q\left(\frac{\beta\gamma-\alpha}{\mu\epsilon}\right) + r\left(\frac{\nu}{\epsilon}\right) \\ z &= p\left(\frac{\lambda}{\epsilon}\right) + q\left(\frac{\alpha\beta-\gamma}{\mu\epsilon}\right) + r\left(\frac{\alpha\gamma-\beta}{\nu\epsilon}\right) \end{aligned} \tag{9}$$

where $\alpha = \hat{\mathbf{l}}\cdot\hat{\mathbf{m}}$, $\beta = \hat{\mathbf{m}}\cdot\hat{\mathbf{n}}$, $\gamma = \hat{\mathbf{n}}\cdot\hat{\mathbf{l}}$ are the cosines of the angles between cylinder axes; λ, μ, and ν are the absolute values of the corresponding sines; and

$$\epsilon = \hat{\mathbf{l}}\cdot(\hat{\mathbf{m}}\times\hat{\mathbf{n}}) = \pm[1-\alpha^2-\beta^2-\gamma^2+2\alpha\beta\gamma]^{1/2} \tag{10}$$

is the volume of the parallelopiped whose edges are $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{n}}$. This relation can be used in cases where $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{n}}$ are not coplanar ($\epsilon \neq 0$).

In terms of these coordinates the integral (4) becomes

$$C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) = \tfrac{1}{2}\iiint \mathrm{d}p\,\mathrm{d}q\,\mathrm{d}r\,\epsilon^{-1}(L-|x|)(L-|y|)(L-|z|), \tag{11}$$

where the integrals over u, v, and w have already been done; the limits of the integration on p, q, and r are given by (8); and the

factor ϵ^{-1} comes from the transformation to the (p, q, r) coordinate system. In the cases where ϵ is not small (the rods do not even approximately lie in a common plane), x, y, and z are never much larger than D (according to (9)), and (11) may be approximately evaluated

$$C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) \sim 4\epsilon^{-1}D^3(L-D)^3 \tag{12}$$

or

$$L^{-4}D^{-2}C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) \sim 4\epsilon^{-1}(1-D/L)^3D/L.$$

This approximation implies that the TVC for non-planar configurations becomes small for large L/D.

With a different coordinate system using x, p, and r as independent variables, the TVC for *planar* configurations can also be evaluated. The result is

$$L^{-4}D^{-2}C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) = 3\mu\nu\left[1 - \frac{\lambda+\mu+\nu}{2\lambda} + \frac{\lambda\mu+\mu\nu+\nu\lambda}{3\lambda^2} - \frac{\mu\nu}{4\lambda^2}\right] \tag{13}$$

for the case that λ is the largest of the absolute values of the sines of the angles between the rods. This expression is independent of the ratio D/L, which would seem to imply that the TVC can never be neglected; however, we shall see shortly that the region of solid angle to which this result is applicable decreases as D/L so that the contribution to the angular integrations of Eq. (1) does indeed become asymptotically small.

The TVC can also be evaluated analytically for the special case of parallel rods. The result is

$$L^{-4}D^{-2}C = 8.68(D/L)^2 \tag{14}$$

where the numerical coefficient contains the third virial coefficient for the hard disk gas.[9] The coefficient is quite small for long rods.

Equation (11) was evaluated numerically by dividing the cube $|p|, |q|, |r| < D$ into N^3 small cubes (N ranging from 10 to 30), and, for each small cube with coordinates (p_i, q_i, r_i), evaluating x_i, y_i, z_i and the integrand of (11). If x_i, y_i, and z_i passed the condition (8), the integrand was accumulated with weight N^{-3}; otherwise, it was discarded. This procedure seemed to be accurate for most cases; however, for nearly coplanar configurations the rejection rate proved to be quite high, and so a second evaluation based on the $(\mathbf{x}, \mathbf{p}, \mathbf{r})$

coordinate system was introduced. For those configurations where both evaluations could be used, they agreed to a few percent.

Some results of this numerical study are given in Fig. 2. Most of the data given refers to a configuration in which the first rod is perpendicular to the second ($\lambda = 1$), and the third makes equal angles with the first two ($\mu = \nu$). The angle θ is arcsin (ϵ). In the limit $\theta = 0$, the TVC takes on the value given by Eq. (13), which is independent of D/L. For most θ, the TVC has a value close to the $\theta = 90°$ limit given in (12). Figure 2 also shows for one case what happens if the third rod remains perpendicular to the first two, and the angle between these is varied.

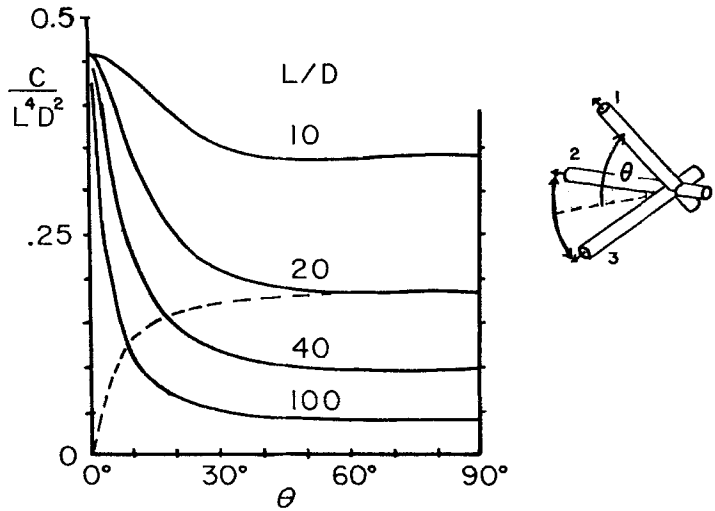

Figure 2. Third virial coefficient for a class of orientations. The solid lines refer to cases where rod 2 is perpendicular to rod 3, and rod 1 makes equal angles to rods 2 and 3; the dashed line is the case with rod 1 perpendicular to rods 2 and 3 and a varying angle between 2 and 3.

4. Approximate Analytical Form

The numerical calculation of the previous section required about one second per configuration. This is fast enough that many configurations and L/D ratios could be examined, but much too slow to allow the angular integrations of Eq. (1) to be done directly. Therefore it was necessary to devise a function of the variables μ, ν, λ which

summarizes the results of the numerical studies and can be evaluated rapidly. The form chosen was

$$L^{-4}D^{-2}C(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) = UZ(V/U), \tag{15}$$

where

$$U = 4D\lambda\mu\nu L^{-1}\epsilon^{-1}, \tag{16}$$

V is the function given in Eq. (13), and

$$Z(x) = \frac{x + x^2}{1 + 0.8x + 1.1x^2}. \tag{17}$$

This form was in particular chosen for the fact that it reproduces the limits of mutually perpendicular and nearly coplanar configurations correctly; however, the form seems to be correct to within 10% for all configurations and L/D ratios; and furthermore slightly exaggerates the peaks and valleys, so that any crucial dependence on these features will not be overlooked.

In the isotropic phase the coefficient of the ρ^2 term of Eq. (1) is just the angular average of the TVC. The integrations involve six independent angular variables, but for reasons of symmetry three of these can be done analytically. The remaining three angular integrations were done numerically, again by dividing the domain of integration into N^3 subdivisions. Care was taken that the peak of the TVC for nearly coplanar configurations did not fall between the points sampled by the grid; in fact, a version of Simpson's method was employed which approximates the integral of this peak by the integral of a parabolic surface which roughly fits the peak: this method slightly overestimates the contribution of the peak. The values obtained for the average TVC are plotted as the right-hand edge of Fig. 3. The values of the isotropic average TVC are given to good approximation by the value $4(L - D)^3D^3$ which obtains for the case of mutually perpendicular rods, Eq. (12), thus showing that the coplanar peaking of the TVC is indeed restricted to a small set of configurations.

We are thus brought to the conclusion that the nearly coplanar configurations do not make a major contribution to the averages of the TVC (and consequently to the thermodynamic functions neither), even though the TVC is itself large for such configurations. The general long rod gas is thus distinct from the restricted orientation

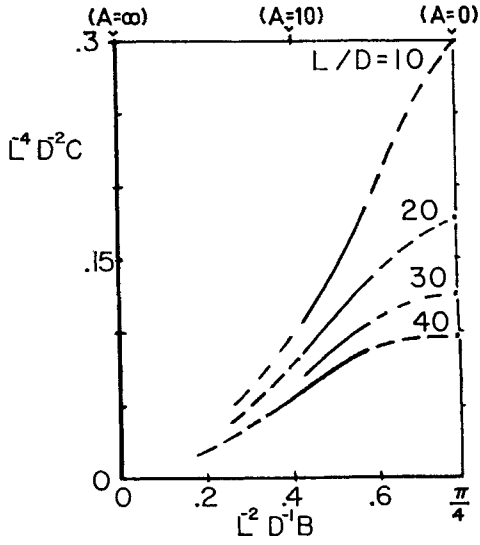

Figure 3. Weighted averages of the third virial coefficient.

model which Zwanzig[8] has proposed, for which the coplanar configurations are quite important. The Zwanzig model is not useful for discussion of real liquid crystals.[9]

5. Weighted Angular Averages

To appreciate the effect of the TVC on the ordered phase and on the position of the transition itself it is necessary to evaluate the angular integrations of Eq. (1) with a variety of distribution functions. In order to handle this problem some simplifications were made. First it was assumed that the distribution function depends only on the polar angle θ and can be written

$$f(\theta) = f_0 \exp(-A \sin^2\theta) \tag{18}$$

where A is a parameter and f_0 is determined by the normalization condition (2). Although the distribution function found in studies using just the second virial coefficient does not have this simple form, it is a sharply peaked function of not too dissimilar form. By studying the angular average of the TVC weighted with the distribution function (18) we hope to probe the sensitivity of the TVC term to the degree of ordering.

The evaluation of this weighted average involves integrations over four independent angles. It was not deemed practical to divide the domain into N^4 parts (the computation would be quite time-consuming unless N were small) and so a technique specific for large A was devised which allows approximate analytical evaluation of one of the integrals. The integration to be done may be written

$$C = \iiint f(\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{l}}) f(\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{m}}) f(\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{n}})\, C(\hat{\mathbf{l}} \cdot \hat{\mathbf{m}}, \hat{\mathbf{m}} \cdot \hat{\mathbf{n}}, \hat{\mathbf{n}} \cdot \hat{\mathbf{l}})\, \mathrm{d}\hat{\mathbf{l}}\, \mathrm{d}\hat{\mathbf{m}}\, \mathrm{d}\hat{\mathbf{n}}, \quad (19)$$

where $\hat{\mathbf{n}}_0$ is the direction of the preferred axis, and the fact that the TVC depends only on the angles between the rods has been explicitly indicated. Now it is observed that since the result is independent of $\hat{\mathbf{n}}_0$, the integral may also be written

$$C = \iiint C(\hat{\mathbf{l}} \cdot \hat{\mathbf{m}}, \hat{\mathbf{m}} \cdot \hat{\mathbf{n}}, \hat{\mathbf{n}} \cdot \hat{\mathbf{l}})\, H(\hat{\mathbf{l}} \cdot \hat{\mathbf{m}}, \hat{\mathbf{m}} \cdot \hat{\mathbf{n}}, \hat{\mathbf{n}} \cdot \hat{\mathbf{l}})\, \mathrm{d}\hat{\mathbf{l}}\, \mathrm{d}\hat{\mathbf{m}}\, \mathrm{d}\hat{\mathbf{n}}, \quad (20)$$

where

$$H = (4\pi)^{-1} \int f(\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{l}}) f(\hat{\mathbf{n}}_0 \cdot \mathbf{m}) f(\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{n}})\, \mathrm{d}\hat{\mathbf{n}}_0. \quad (21)$$

For reasons of symmetry this kernel can depend only on the angles between the rods, and thus if H were known in a closed form, only three numerical integrations over an angle would be required to evaluate Eq. (20). In the Appendix an approximate evaluation of H is outlined which is appropriate for $A \geqslant 6$. With this form for H the angular integrations were performed as before; the results are shown in Fig. 3 and Table 1. In Fig. 3 the average TVC is plotted

TABLE 1 Weighted Averages ($L^{-4}D^{-2}C$)

	L/D				
A	10	20	30	40	50
0.0	0.3014	0.1779	0.1242	0.0955	0.0786
5.0	0.1823	0.1431	0.1064	0.0884	0.0761
6.0	0.1566	0.1182	0.0951	0.0797	0.0689
7.0	0.1352	0.1043	0.0848	0.0714	0.0621
8.0	0.1185	0.0930	0.0762	0.0646	0.0564
9.0	0.1058	0.0840	0.0695	0.0591	0.0517

against the corresponding average (related to the second virial coefficient)

$$L^{-2}D^{-1}B = \iint f(\hat{\mathbf{m}} \cdot \hat{\mathbf{n}}_0) f(\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_0)(1 - (\hat{\mathbf{m}} \cdot \hat{\mathbf{n}})^2)^{1/2}\, \mathrm{d}\hat{\mathbf{m}}\, \mathrm{d}\hat{\mathbf{n}}. \quad (22)$$

With increasing order (and A) the weighted averages decrease since configurations of nearly parallel rods get largest weight.

6. Conclusions

The merit of the Onsager approximation can be judged by comparing the contributions of the second and third virial terms to the free energy or pressure. The contributions will be comparable if

$$(L^2D\rho_c)L^{-4}D^{-2}C \gtrsim L^{-2}D^{-1}B \tag{23}$$

where B and C represent some average values of the second and third virial coefficients. Inspection of Fig. 3 shows that the inequality holds for $L < 20D$. The left side of (23) decreases relative to the right side as D/L; in order that the third virial term to be no more than 10% of the second term near the phase transition, L must be about $100D$.

Some attempts were made to see how the TVC affects the location of the phase transition. The study was restricted to the case $L = 40D$; and in making these studies Fig. 3 was summarized by an interpolation form such as

$$L^{-4}D^{-2}C = 0.15L^{-2}D^{-1}B \tag{24}$$

or some more complicated form.

Since the average TVC decreases as the gas becomes more highly ordered, it is to be expected that the equilibrium phase determined by minimization of Eq. (1) with the TVC term included will be relatively more ordered; this effect was observed ($A = 12$ near the phase transition vs. $A = 8$ without the TVC). It was also found that the density jump at the phase transition increases (about 25%), and that the density of the ordered phase at the transition is little affected; but these latter results seem to be fairly sensitive to the precise form of the interpolation formula.

These considerations seem to indicate that the Onsager approximation is only qualitatively correct for $L/D = 40$, and that quantitative accuracy cannot be claimed for $L/D < 100$. It should be emphasized, however, that these results raise no doubts about the reality of the phase transition Onsager predicts; indeed, the effect of the third virial term is to promote its occurrence.

Other theories which have been proposed for the hard rod gas

arrive at forms for the equation of state which differ from the Onsager form in that they possess singularities at close packing density. In order to judge the significance of these high-density corrections, the equation of state will be expanded in a density series so that we may characterize each by an effective TVC. The equation of state for the Lasher theory[3] is

$$P/kT = (1-\rho v_0)^{-2}(\rho + 2\rho^2 v_0 + \rho^2 B) \tag{25}$$

where $v_0 = \frac{1}{4}\pi D^2 L$ is the volume of a cylinder and B is defined in Eq. (22). This expression may be expanded to give

$$P/kT = \rho + (4v_0 + B)\rho^2 + (5v_0^2 + 2v_0 B)\rho^3 + \ldots. \tag{26}$$

Similarly the Alben theory[4] gives

$$\begin{aligned} P/kT &= -\ln(1-\rho v_0) + [\rho(1-\rho v_0)^{-1} + v_0^{-1}\ln(1-\rho v_0)][7v_0 + 2B] \\ &= \rho + (4v_0 + B)\rho^2 + (5v_0^2 + \tfrac{4}{3}v_0 B)\rho^3 + \ldots. \end{aligned} \tag{27}$$

The Onsager theory gives the corresponding expression

$$P/kT = \rho + (4v_0 + B)\rho^2 + \tfrac{2}{3}C\rho^3 + \ldots. \tag{28}$$

The dependence of C on B is shown in Fig. 3; it might be crudely summarized by

$$C = 6v_0 B. \tag{29}$$

This representation of the equation of state suggests that the Lasher and Alben theories somewhat underestimate the high density corrections to the Onsager equation of state.

Appendix. Approximation of the Kernel H.

Here is presented an approximate evaluation of the function H defined in Eq. (21) appropriate to distribution functions of the form (18) with large A.

The kernel may be written

$$H = (4\pi)^{-1} f_0^3 \int \exp(AJ)\, d\hat{\mathbf{n}}_0, \tag{A1}$$

where

$$J = (\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{l}})^2 + (\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{m}})^2 + (\hat{\mathbf{n}}_0 \cdot \hat{\mathbf{n}})^2 - 3. \tag{A2}$$

It is readily seen that J is a negative definite function of $\hat{\mathbf{n}}_0$, so that there is a vector $\hat{\mathbf{p}}$ which maximizes J. If we use $\hat{\mathbf{p}}$ to define the pole of a polar coordinate representation, J may be written

$$J = J_0 + J_1' \sin^2\theta + J_2' \sin^2\theta \cos^2\varphi + J_3' \sin^2\theta \cos\varphi \sin\varphi \quad \text{(A3)}$$

or equivalently

$$J = J_0 + J_1 \sin^2\theta + J_2 \sin^2\theta \cos 2(\varphi - \varphi_0), \quad \text{(A4)}$$

where

$$J_0 = \cos^2 P + \cos^2 Q + \cos^2 R - 3$$

$$J_1 = \tfrac{3}{2}(1 - \cos^2 P - \cos^2 Q - \cos^2 R)$$

$$J_2 = \tfrac{1}{2}[J_0^2 - 4(\sin^2 P \sin^2 Q \sin^2 B + \sin^2 P \sin^2 R \sin^2 C + \sin^2 Q \sin^2 R \sin^2 A)]^{1/2},$$

and where the angles P, Q, R, A, B, C are defined in Fig. 4.

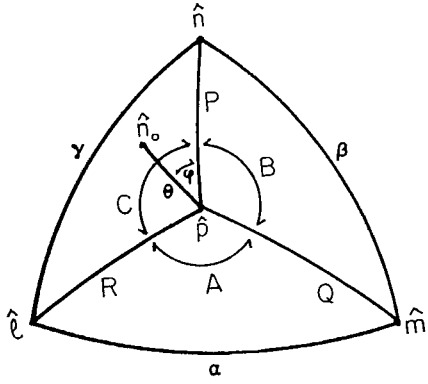

Figure 4. Definitions of angles. The vectors $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, $\hat{\mathbf{n}}$ are the orientations of the axes of the rods, and $\hat{\mathbf{n}}_0 = \hat{\mathbf{p}}$ minimizes the absolute value of J. The angles between $\hat{\mathbf{p}}$ and $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$, $\hat{\mathbf{n}}$ are R, Q, P. Note that α, β, and γ are the *cosines* of the arcs indicated. Description of arbitrary n_0 introduces the two angles θ and φ.

The approximation that was made for H consists in neglecting the J_2 term. This may be justified by observing that for A large enough the only contribution to the integral (A1) comes from the configurations where $|J_0|$ is small, which is the region where $\sin P$, $\sin Q$, and $\sin R$ are small. For these nearly parallel configurations $|J_2|$ is small, and the integral is dominated by the J_1 term. Furthermore, if the integrand of Eq. (A1) is expanded in a series in J_2, the integral of the first order term vanishes: the lowest order corrections are of magnitude J_2^2/J_1^2.

With the J_2 term omitted, the integral (A1) becomes

$$H = \tfrac{1}{2} f_0^3 \int \exp(A J_0 + A J_1 \sin^2\theta) \sin\theta \, d\theta \quad \text{(A6)}$$

which can be reduced to Dawson's integral.[10] An asymptotic expansion for this integral was used as the form for H in the numerical integrations. Tests were written into the programs to check that the neglect of J_2 is justified.

There remains to relate P, Q, and R to the quantities α, β, and γ, which are determined by $\hat{\mathbf{l}}$, $\mathbf{m}$, and $\hat{\mathbf{n}}$. The condition that $\hat{\mathbf{p}}$ maximizes J gives rise to a set of simultaneous equations

$$\begin{aligned} K\cos P + \beta\cos Q + \gamma\cos R &= 0, \\ \beta\cos P + K\cos Q + \alpha\cos R &= 0, \\ \gamma\cos P + \alpha\cos Q + K\cos R &= 0, \end{aligned} \tag{A7}$$

where $K = 1 - \cos^2 P - \cos^2 Q - \cos^2 R$. Consistency of these equations requires

$$K^3 - (\alpha^2 + \beta^2 + \gamma^2)K + 2\alpha\beta\gamma = 0; \tag{A8}$$

the most negative real root of this equation is the one desired. In terms of this root,

$$\cos^2 R = (1 - K)(K^2 - \beta^2)/(3K^2 - \alpha^2 - \beta^2 - \gamma^2), \tag{A9}$$

and similarly for P and Q.

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