RESEARCH NOTE

Virial coefficients of Onsager crosses

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Onsager crosses are particles formed by rigidly connecting three perpendicular, elongated rods of length $L$ and diameter $D$. We have investigated the behaviour of the virial coefficients of Onsager crosses as a function of the aspect ratio $L/D$ of the rods. The interest in these particles stems from the fact that they should exhibit a cubic liquid crystalline phase in the limit $(L/D) \to \infty$. It is shown that in order for the theory predicting this phase to be strictly valid, the rod aspect ratio should be extremely large ($(L/D) \approx 1000$).

1. Introduction

In 1949 Onsager showed that the isotropic–nematic phase transition in liquid crystals could be explained as an excluded volume effect [1]. The model used was a system of thin spherocylinders with length $L$ and diameter $D$. In the limit $(L/D) \to \infty$, this system undergoes a phase transition on compression from an isotropic fluid to a nematic phase, which can be explained by the fact that the loss of orientational entropy on ordering is compensated for a larger gain in translational entropy. The theory assumes that if the free energy is expanded in powers of the density all virial coefficients $B_n$ with $n \geq 3$ can be neglected. Onsager gave a qualitative argument to show that the third virial coefficient scales as $B_3 / B_2 = O(D/L) \log(L/D)$ and that higher virial coefficients also can be neglected. This leads to a theory which becomes exact in the limit $(L/D) \to \infty$. The validity of these assumptions was later confirmed by numerical evaluation of the virial coefficients as functions of the aspect ratio $L/D$.

Using arguments similar to that of Onsager in his explanation of the isotropic–nematic phase transition, Frenkel proposed the existence of a cubic phase in a system of Onsager crosses [3]. These particles are formed by three thin, perpendicular rods rigidly connected at their centres. Using simple generalization of the Onsager theory, Frenkel showed that these particles, upon increasing density, have a phase transition from the isotropic to the cubic phase. The latter is a homogeneous, orientationally ordered liquid crystalline phase for which there exists a frame of three perpendicular axes along which all the rods constituting the cross-like particles are preferably oriented. This leads to overall cubic symmetry, and hence the name cubic phase. Within the same approximation we have shown also that cross-like particles in which the rods have different aspect ratios can still exhibit a cubic phase [4].

In this paper we investigate the requirements for the aspect ratios of the rods, in order that the theory proposed by Frenkel and expanded by us remains valid. The theory predicting this transition is based on two assumptions, which we treat separately. The first assumption is that the third and higher virial coefficients can be neglected. The second assumption is that the leading contribution in the second virial coefficient can be approximated by the leading term in $L/D$, consisting of independent overlaps of the rods. This is plausible by arguing that in the limit $(L/D) \to \infty$ the probability of finding more than two overlapping rods will be negligible, similar to the case of higher virial coefficients.

2. The second virial coefficient

Since the rods are rigidly and perpendicularly connected to one another, they are not truly independent of each other. Intuitively one would expect that corrections for this effect are small because overlap for more than two rods will be unlikely. To check the validity of this assumption, we present the results of a numerical evaluation of the second virial coefficient of Onsager crosses formed by three identical spherocylinders.

In 1964 Ree and Hoover [5] reported a Monte Carlo technique to calculate the virial coefficients of hard core particles, based on trial configurations. In order to evaluate the second virial coefficient $B_2$, one particle with fixed orientation is put at the origin and for a second particle a position and an orientation are randomly generated in a large enough volume to allow all possible overlaps. Since the maximum distance between two
crosses which still touch is \( L + D \), a cubic volume with sides \( L + D \) is adequate. The value of \( B_2^{\text{cross}} \) will be given by

\[
B_2^{\text{cross}} = \frac{1}{2} \frac{\text{Number of overlaps}}{\text{Number of trials}} \times \text{Volume}. \tag{1}
\]

However, since our particles are extremely non-spherical this brute force technique of counting the number of occurrences of overlap is no longer useful because only a small fraction of the trials will result in an overlap. Instead we follow a modified version of the method used by Frenkel to calculate the virial coefficients of long spherocylinders \[2\] We generate only overlapping configurations, which enables us to evaluate the ratio of the second virial coefficients on Onsager crosses and spherocylinders with the same aspect ratio.

Onsager crosses consist of three rods and, therefore, \( 3 \times 3 = 9 \) distinct pairs of rods can be formed from two particles. Each of these pairs might or might not overlap. This leads to \( 2^9 - 1 = 511 \) combinations for which there is an overlap of the two particles. Some of these are identical and have just a different labelling. If we take this into account there remain 25 different overlap diagrams \( D_i \), as shown in figure 1. Each circle represents a rod of a cross, and rods belonging to the same particle have the same shade (white or grey). The lines indicate which pairs of rods are overlapping.

![Figure 1. The 25 different overlapping configurations of 2 cross-like particles. Points of the same shade (white or grey) correspond to different rods of the same particle. Only the connected points overlap.](image)

The number of overlaps in each diagram are listed in Table 1, together with the number of realizations.

The value of each diagram can be obtained by analysing the overlapping configurations and determining the diagram to which it belongs, leading to a modification of equation (1):

\[
D_i = \frac{\text{Number of occurrences } D_i}{\text{Number of realizations}} \times \frac{\text{Volume}}{\text{Number of trials}}. \tag{2}
\]

where we have corrected for the number of different realizations of diagram \( D_i \). The second virial coefficient \( B_2^{\text{cross}} \) of the crosses is given by half of the sum of all diagrams multiplied by the number of realizations.

We now generate trial configurations, for which a chosen pair of rods, say the pair labelled 1–1, is always overlapping. For each diagram \( D_i \) with \( k_i \) overlaps, only \( k_i / 9 \) times the total number of realizations is now allowed. This enables us to express the value of the diagram \( D_i \) under this constraint:

\[
D_i = \left( \frac{k_i}{9} \right) \times \frac{\text{Number of occurrences } D_i}{\text{Number of realizations} \times \text{Number of trials} \times \text{Volume}_{1-1 \text{ overlap}}}. \tag{3}
\]

The restricted volume leading to an overlap for the 1–1 pair is the average volume over all orientations leading to a spherocylinder overlap, and hence is twice the second virial coefficient \( B_2^{\text{sphero}} \), given by

\[
B_2^{\text{sphero}} = \frac{4}{3} \pi L^2 D + \pi L D^2 + 2 \pi D^3. \tag{4}
\]

For the second virial coefficient of the crosses this leads, therefore, to

Table 1. Number of overlaps and realizations of the diagrams \( D_i \).

<table>
<thead>
<tr>
<th>Diagram</th>
<th>Overlaps</th>
<th>Realizations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>2, 3</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>4, 5</td>
<td>3</td>
<td>36</td>
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<tr>
<td>6, 7</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>8, 9, 10</td>
<td>4</td>
<td>36</td>
</tr>
<tr>
<td>11, 12</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>13, 14, 15</td>
<td>5</td>
<td>36</td>
</tr>
<tr>
<td>16, 17</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>18, 19</td>
<td>6</td>
<td>36</td>
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<tr>
<td>20, 21</td>
<td>6</td>
<td>9</td>
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<td>22, 23</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td>24</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>25</td>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>
The probability of finding an overlap for two spherocylinders, however, depends on their relative orientation. For a given orientation, we can either generate the orientations randomly and give the configuration a weight proportional to the excluded volume, or generate the orientations proportional to the excluded volume. This excluded volume $\varepsilon$ of two spherocylinders is given by

$$\varepsilon(\gamma) = 2L^2D \left| \sin(\gamma) \right| + 2\pi L D^2 + \frac{4}{3} \pi D^3,$$

where $\gamma$ is the angle between the main axes of the rods.

In summary, we put one cross-like particle with fixed orientation at the origin and generate a random orientation for the second particle. We place the second particle randomly in the excluded volume of the 1–1 pair to ensure overlap and give the configuration a weight proportional to the excluded volume, which will depend on the relative orientation of the 1–1 pair only.

The results for the second virial coefficient are given in figure 2, where their value is terms of $B^2_{\text{sphero}}$ is plotted. In the same figure the contributions of the two diagrams $D_1$ and $D_{25}$ are included. The first diagram corresponds to a single pair overlap and has the leading contribution for large aspect ratios. The second diagram corresponds to the overlap of all pairs of rods and will be the leading term for small aspect ratios. For completeness we have listed the numerical values for the diagrams in table 2 as a function of the aspect ratio $L/D$ in powers of 10. The

<table>
<thead>
<tr>
<th>$L/D$</th>
<th>$B^2_{\text{cross}}/B^2_{\text{sphero}}$</th>
<th>$D_1/B^2_{\text{sphero}}$</th>
<th>$D_{25}/B^2_{\text{sphero}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>1.009 93(1)</td>
<td>0.003 46(1)</td>
<td>0.991 33(3)</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>1.099 28(2)</td>
<td>0.035 97(2)</td>
<td>0.916 79(1)</td>
</tr>
<tr>
<td>$10^0$</td>
<td>1.951 2(1)</td>
<td>0.508 4(1)</td>
<td>0.449 19(1)</td>
</tr>
<tr>
<td>$10^1$</td>
<td>4.971 3(1)</td>
<td>3.093 9(1)</td>
<td>0.025 06(1)</td>
</tr>
<tr>
<td>$10^2$</td>
<td>8.005 3(1)</td>
<td>7.229 2(1)</td>
<td>3.44(1) $\times 10^{-4}$</td>
</tr>
<tr>
<td>$10^3$</td>
<td>8.855 12(3)</td>
<td>8.726 5(1)</td>
<td>3.5(1) $\times 10^{-6}$</td>
</tr>
<tr>
<td>$10^4$</td>
<td>8.981 88(1)</td>
<td>8.965 22(2)</td>
<td>4(1) $\times 10^{-8}$</td>
</tr>
<tr>
<td>$10^5$</td>
<td>8.997 83(3)</td>
<td>8.995 82(1)</td>
<td>?</td>
</tr>
<tr>
<td>$10^6$</td>
<td>8.999 73(1)</td>
<td>8.999 49(2)</td>
<td>?</td>
</tr>
</tbody>
</table>

For small values of $L/D$, the particles are almost spheres, and hence all 9 pairs of rods are likely to overlap. The main contribution for the virial coefficient will therefore come from diagram $D_{25}$. In this region the difference between the shape of a cross and a single spherocylinder is marginal, because both are almost spherical, and the virial coefficient of the first will be only slightly larger. For increasing values of $L/D$, however, the cross-like particles become very open clusters of rods for which it is very unlikely that more than one pair of rods will overlap. The main contribution therefore will come from diagram $D_1$, with only one overlapping pair of rods. However, since there is 9 possible pairs of rods the virial coefficient of the crosses will be approximately 9 times higher than that for single spherocylinders. For these aspect ratios the rods which form the cross can be treated independent of each other and the assumption becomes valid. To satisfy this requirement within 1% we require an aspect ratio of about $2.0 \times 10^3$.

3. **Higher virial coefficients**

In order to calculate higher virial coefficients we evaluate the necessary diagrams [5] using Frenkel’s method of growing random chains of overlapping particles [2]. The first particle is put at the origin with a fixed orientation. Using the brute force method of generating a random position and orientation until there is a new particle to overlap with the last particle in the chain which would again have poor efficiency for large aspect ratios. Instead we select randomly one of the three rods of the last particle of the chain which will overlap with the new particle. Whereas for the calculation of the second virial coefficient we could choose the 1–1 pair to overlap, for higher virial coefficients this is no longer allowed, because only a restricted set of diagrams

Figure 2. Second virial coefficient of Onsager crosses (○) as a function of $L/D$ in terms of the second virial coefficient of spherocylinders. The contributions of the diagrams $D_1$ (□) and $D_{25}$ (◆) are shown as well.

Table 2. Reduced values for second virial coefficients of crosses, as a function of length over diameter ratio. The estimated error in the last digit is indicated in parentheses.
would be sampled. We also need to correct for the fact that there is at least one pair of rods which will overlap. In order to do so we assign a weight to each consecutive pair of overlapping particles. This weight should be proportional to the contribution of these two-particle configurations to the second virial coefficient which, as can be seen from equation (5), is inversely proportional to number of overlapping pairs of rods.

The results of our calculations for the third, fourth and fifth virial coefficients are shown in figure 3 and table 3. These data are obtained by averaging over 100 blocks in which we have grown $10^6$ independent chains of 5 particles. Note that there is a range of aspect ratios with negative values for the fifth virial coefficient, while for rod-like particles this remains positive [2, 6]. In particular there is a region ($(L / D) \approx 15-35$) where both the fourth and fifth virial coefficients, are negative. To our knowledge this is the first time such behaviour has been observed.

In order to observe the asymptotic behaviour of the virial coefficients, we plot the scaled virial coefficients $B_n^{\text{scaled}}$ in figure 4,

$$B_n^{\text{scaled}} = \frac{L}{D} \frac{B_n}{B_2^{\text{scaled}}}.$$  

Unlike the behaviour of the scaled third virial coefficient of elongated particles, which for large aspect ratios scales as $(L / D) \log (L / D)$, for cross-like particles all three scaled virial coefficients are proportional to $L / D$.

Therefore in the limit $(L / D) \to \infty$ higher virial coefficients can be neglected. For more modest aspect ratios, however, these particles can no longer be described by simple Onsager theory.

### 4. Discussion

In the same fashion as hard elongated spherocylinders are considered to be a prototypical model for a nematic liquid crystal, Onsager crosses provide a model for the cubic phase. Although we can neglect higher virial coefficients in the limit described, the assumption that the second virial coefficient can be approximated by a sum of independent contributions of the rods constituting the cross is valid only for extremely large aspect ratios (for accuracy within $1\%$, $(L / D) \geq 1000$).

This does not necessarily mean that a cubic phase for cross-like particles cannot be found for smaller aspect ratios, but rather that the predicted densities at which the transition should occur according to the theory will not be accurate. We expect that the qualitative description of the theory [4] should still be correct for a large range of rod aspect ratios, as in the case of the isotropic–nematic phase transition for long rods, which for spherocylinders is found for aspect ratios $(L / D) \geq 4$ [7].

For small aspect ratios the possibility of crystallization should be considered as well, although it is likely that these systems will not form normal crystals. As
indicated by preliminary computer simulations, systems of particles with aspect ratios $l/D = 25$ show glass-like behaviour due to entanglement of the particles [8].

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References


