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Phase behaviour of a binary mixture of long thin rods

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Résumé. — Nous étudions un mélange binaire de molécules en forme de bâtonnets au moyen d’un modèle où les bâtonnets ont une distribution d’orientation limitée et se différencient seulement en longueur. En supposant un potentiel de cœur dur, on calcule exactement les coefficients du viriel jusqu’au quatrième ordre. L’énergie libre est minimisée par rapport à la distribution d’orientation et donne la phase (isotrope ou nématique) du système en fonction de la concentration. On calcule ensuite les conditions de coexistence et le comportement de phase pour des mélanges avec des rapports de longueur de 2,0, 5,0 et 10,0, utilisant les approximations du deuxième et quatrième ordres.

Abstract. — We study a binary mixture of long thin rodlike particles using an idealised model in which the rods have restricted orientations and the two types of rod differ only in length. Assuming a hard core potential the virial coefficients up to fourth order are calculated exactly. The free energy is minimized with respect to the orientational distribution functions to give the phase (isotropic or nematic) of the system as the concentration is varied. Conditions for coexistence are then calculated, from which we predict the phase behaviour for mixtures with length ratios of 2.0, 5.0 and 10.0, in both the second and fourth virial approximations.

1. Introduction.

It is well established that in a solution of rodlike particles a transition from an isotropic to a nematic phase occurs as the concentration is increased. In the isotropic phase both the position and orientation of the rods is random, in the nematic phase the rods show some alignment whilst retaining translational disorder. Within a certain concentration regime the two phases may coexist, it is one of the aims of theory to predict the upper and lower bounds in concentration of this coexisting phase.

Considerable numerical work has already been performed on the theory of this transition in a binary solution of long thin rodlike particles. Lekkerkerker [1] extended the trial distribution function method proposed by Onsager [2] for a monodisperse solution, and Abe and Flory [3] adapted Flory’s lattice model [4]. In addition some analytical work has been presented by Odijk and Lekkerkerker [5]. A review of the Onsager approach as applied to a variety of problems in the statistical mechanics of rodlike particles is given in reference [6].

The starting point is the Helmholtz free energy expressed as a function of the concentration and the (concentration dependent) orientational distribution of the rods. The important terms
are the orientational entropy and the interaction free energy of the ensemble. The former is maximized when the rods are randomly oriented, whilst the latter is minimized when all the rods are aligned along a common director. It is the varying influence of these two competing factors as the concentration increases that brings about the first order transition from an isotropic to a nematic phase.

Onsager expanded the interaction energy as a virial series, but with his exact treatment of the orientational entropy it was only plausible to calculate the second virial coefficient. He justified this approximation by arguing that all higher orders would be negligible at the concentrations at which the transition occurred. Zwanzig [7] developed a model for a monodisperse solution, in which the rods had restricted orientations. With the central approximation shifted to the orientational entropy it becomes possible to calculate all coefficients exactly, hence he was able to test the validity of Onsager's approach. Zwanzig concluded that the predictions of the second order approximation are to within 10-20% of the values that would be found when many higher order coefficients are included, and that the convergence of the series, in some respects, was not as good as one might have hoped.

In this paper we extend Zwanzig's model to a mixture of long thin rodlike particles with different lengths but the same diameter. We calculate the coefficients up to and including fourth order, and solve the equations arising from the minimization of the free energy. We then determine the conditions required for coexistence of the isotropic and nematic phases.

2. Theory.

In this and the next section we summarize and extend the thermodynamic theory of rodlike particles with restricted orientations, developed in reference [7], as appropriate for a binary mixture. We use a hard core potential to model the interaction between particles and the rods are treated as rigid, with a rectangular parallelepiped shape.

For a mixture of \( N_1 \) rods of length \( \ell_1 \), \( N_2 \) rods of length \( \ell_2 \), all of diameter \( d \), in a volume \( V \), with number concentration, \( \rho = (N_1 + N_2) V = N/V \), the Helmholtz free energy of mixing may be written,

\[
\frac{F}{N k T} = \log \nu + \log \rho - 1 + S - \left( \frac{1}{N} \right) \sum_{i=2} \beta_i \rho^{i-1}
\]

(2.1)

\( \beta_i \) are the virial coefficients (see Sect. 3), and \( S \) the entropy is given by,

\[
S = \sum_{i=1}^\nu m(i) \log m(i)
\]

(2.2)

where \( \nu \) is the number of different species in the mixture, and \( m(i) \) is the mole fraction of species \( i \), subject to the condition,

\[
\sum_{i=1}^\nu m(i) = 1 .
\]

(2.3)

For our purposes a species is defined as a rod of given length with a given orientation. Hence for a mixture of rods with two different lengths allowed to lie in one of three directions we have \( \nu = 6 \). The species are assigned as \( i = 1, 2, 3 \) for rods of length \( \ell_1 \), \( i = 4, 5, 6 \) for rods of length \( \ell_2 \), \( i = 1, 4 \) for rods oriented in the \( x \) direction, \( i = 2, 5 \) the \( y \) direction and \( i = 3, 6 \) the \( z \) direction.
We introduce the orientation distribution variables $x$, $y$ and the relative mole fractions $a = N_1/N$, $b = N_2/N$, such that,

\[
\begin{align*}
\ m(1) &= ax \\
\ m(2) &= ax \\
\ m(3) &= a(1 - 2x) \\
\ m(4) &= by \\
\ m(5) &= by \\
\ m(6) &= b(1 - 2y) .
\end{align*}
\]

(2.4)

The condition (2.3) is then automatically satisfied. We have arbitrarily chosen the $z$ axis as our preferred direction of alignment in the nematic phase. Thus by knowing $x$ and $y$ one may determine the phase of the mixture.

Taking the above definitions into account we may write for the entropy of a binary mixture of rods,

\[
S = 2ax \log ax + a(1 - 2x) \log a(1 - 2x) + 2by \log by + b(1 - 2y) \log b(1 - 2y)
\]

(2.5)

3. The virial coefficients.

The virial expansion of the interaction free energy of a mixture of $u$ species of particles may be written [7]:

\[
\left( \frac{1}{N} \right) \sum_{\ell = 2} \beta_i \rho^i = \sum_{n(1)} \sum_{n(\ell)} B[n(1), . . , n(\nu)] \rho^{-1} \prod_{j=1}^{n(\ell)} \rho^{n(j)} (3.1)
\]

where

\[
B[n(1), . . , n(\nu)] = \frac{1}{V Hn(i)! \int} \Sigma P f
\]

(3.2)

the integral is over all space of the sum of products of two particle Mayer $f$ functions,

\[
f_{ij} = \exp \left\{ - \frac{U_{ij}}{kT} \right\} - 1
\]

(3.3)

and the summation is over all irreducible graphs in the cluster theory with $n(1)$ rods of length $\ell_1$ oriented along the $x$ axis, $n(2)$ rods of length $\ell_2$ oriented along the $y$ axis etc.

For a hard core interaction, with the interparticle potential, $U_{ij}$, infinite for intersecting rods and zero otherwise,

\[
f_{ij} = \begin{cases} 
-1 & \text{if rods intersect} \\
0 & \text{otherwise .}
\end{cases}
\]

(3.4)

In the limit of long thin rods $\ell_1, \ell_2 \gg d$, which we consider here, it was shown in reference [7] that the contribution from graphs with parallel rods connected, and from non planar graphs, (i.e. graphs with all rods long axis not in a plane) is negligible.

Since no three particle planar graph with all rods perpendicular exists $\beta_3 = 0$. A further simplification is made when we extend Zwanzig’s symmetry relations (Eq. (37) in Ref. [7]) between coefficients,

\[
B[m, n, 0 ; p, q, 0] = B[m, 0, n ; p, 0, q] = B[0, m, n ; 0, p, q] = B[n, m, 0 ; q, 0, p] \]

(3.5)
It is gratifying that with the above assumptions we are able to rule out all but one of the possible graphs for each of the second and fourth order coefficients. Hence allowing for the different ways that a graph may be labelled in a binary mixture we have 3 2-body graphs and 6 4-body graphs, of the types labelled 1.1 and 4.1, respectively, in the work of Hoover and de Rocco [8] (see Fig. 1). Equation (3.1) can be rewritten as,

\[
\left( \frac{1}{N} \right) \sum_{i=2}^{\infty} \beta_i \rho_i^{t-1} = \sum_{m} \sum_{n} \sum_{p} \sum_{q} B[m, n, 0; p, q, 0] G_{mnpq}(a, b, x, y) \rho^{m+n+p+q-1} \quad (3.6)
\]

with,

\[
G_{mnpq}(a, b, x, y) = a^{m+n} b^{p+q} [x^{m+n} y^{p+q} + x^m (1 - 2x)^n y^p (1 - 2y)^q + x^p (1 - 2x)^m y^q (1 - 2y)^p]. \quad (3.7)
\]

We illustrate the calculation of the integrals \( B[m, n, 0; p, q, 0] \) in the appendix. The values for all integrals contributing to the second and fourth virial coefficients are given in table I, where we have introduced the ratio \( c = \ell_1/\ell_2 \).

Fig. 1. — The only interactions contributing to (a) the second virial coefficient, and (b) the fourth virial coefficient, in the limit \( \ell \gg d \). In (b) the long axes of the four particles are planar.

| Table I. — The coefficients contributing to the second and fourth virial approximations where \( c = \ell_1/\ell_2 \). |
|---------------|-----------------|
| \( m, n, p, q \) | \( B[m, n, 0; p, q, 0] \) |
| 1, 1, 0, 0 | -2 \( \ell_1^2d \) |
| 0, 0, 1, 1 | -2 \( \ell_1^2d/c^2 \) |
| 1, 0, 0, 1 | -2 \( \ell_1^2d/c \) |
| 2, 2, 0, 0 | 16(\( \ell_1^2d^3 \))/27 |
| 0, 0, 2, 2 | 16(\( \ell_1^2d^3 \))/27 c^6 |
| 2, 0, 0, 2 | 16(\( \ell_1^2d^3 \))/27 c^3 |
| 1, 1, 1, 1 | 16(c - 1/3)^2(\( \ell_1^2d^3 \))/3 c^6 |
| 1, 2, 1, 0 | 16(c - 1/3)(\( \ell_1^2d^3 \))/9 c^3 |
| 1, 0, 1, 2 | 16(c - 1/3)(\( \ell_1^2d^3 \))/9 c^6 |

We are now able to write the full expression for the free energy in the second and fourth order approximations in terms of the variables \( x \) and \( y \). We adopt the standard procedure of setting \( \ell_1^2 d = 1 \), so that the concentration is measured in units of \((\ell_1^2 d)^{-1}\). The minimization conditions are found by solving the non linear simultaneous equations,

\[
\frac{\partial }{\partial x} \left( \frac{F}{N k T} \right) = 0; \quad \frac{\partial }{\partial y} \left( \frac{F}{N k T} \right) = 0 . \quad (4.1)
\]

In the second order approximation equation (4.1) is equivalent to,

\[
\log \left[ \frac{x}{1 - 2x} \right] = -2 \rho \left\{ a(1 - 3x) + \frac{b}{c} (1 - 3y) \right\} \\
\log \left[ \frac{y}{1 - 2y} \right] = -2 \rho \left\{ \frac{b}{c} (1 - 3y) + a(1 - 3x) \right\} . \quad (4.2)
\]

The solution of these equations implicitly defines the functional relation between the coupled distribution variables \( x, y \) and the parameters \( \rho, a, b \). With \( x, y \) known it is possible to find the parameters of the coexisting isotropic and nematic phases, achieved by equating the chemical potentials, \( \mu^{(1)}, \mu^{(2)} \), and the osmotic pressure, \( \Pi \), of each phase,

\[
\mu^{(1)} = \frac{\partial }{\partial N_1} \left( \frac{F}{NkT} \right)_{N, x=y=\frac{1}{3}} = \mu^{(2)} = \frac{\partial }{\partial N_2} \left( \frac{F}{NkT} \right)_{N, x=y=\frac{1}{3}} \\
\Pi = \frac{\partial }{\partial V} \left( \frac{F}{NkT} \right)_{N, x=y=\frac{1}{3}} = \Pi = \frac{\partial }{\partial V} \left( \frac{F}{NkT} \right)_{N} . \quad (4.3)
\]

The subscript \( i \) refers to the parameters of the isotropic phase, and the subscript \( n \) refers to those of the nematic phase. Again, using the second order approximation as an example, the conditions for coexistence are the solutions to the equations,

\[
\log \rho_i + \log \left( \frac{a_i + \frac{b_i}{c}}{3} \right) = \log \rho_n + 2 \frac{x}{x} \rho_n \left( a_n (1 - 2x) + \frac{b_n}{c} \right) + 4 \rho_n \left\{ \frac{a_n}{c} \Psi_1 + \frac{b_n}{c} \Psi_\text{III} \right\} \\
\log \rho_i + \log \left( \frac{b_i + c}{3} \right) = \log \rho_n + 2 \frac{y}{y} \rho_n \left( a_n (1 - 2y) + \frac{b_n}{c} \right) + 4 \rho_n \left\{ \frac{b_n}{c} \Psi_\text{II} + a_n \Psi_\text{III} \right\} \\
\rho_i \left\{ 1 + \frac{2 \rho_i}{3} \left( \frac{a_i + \frac{b_i}{c}}{c} \right)^2 \right\} = \rho_n \left\{ 1 + 2 \rho_n \left[ \frac{a_n^2}{c} \Psi_1 + \left( \frac{b_n}{c} \right)^2 \Psi_\text{II} + 2 \frac{a_n}{c} b_n \Psi_\text{III} \right] \right\} . \quad (4.4)
\]

where \( b_i = 1 - a_i, b_n = 1 - a_n \) and \( \Psi_1, \Psi_\text{II}, \Psi_\text{III} \) are functionals of \( x(\rho_n, a_n) \) and \( y(\rho_n, a_n) \), the set of solutions to equation (4.2),

\[
\Psi_1 = x^2 + 2x(1 - 2x) \\
\Psi_\text{II} = y^2 + 2y(1 - 2y) \\
\Psi_\text{III} = x + y - 3xy . \quad (4.5)
\]
Hence we have four unknown variables $a_\alpha$, $\rho_\alpha$, $a_\beta$ and $\rho_\beta$ but only three equations, however the Gibbs phase rule states that the number of degrees of freedom for an athermal binary mixture in two phases is equal to 1, so we are free to fix one of the four. It is convenient from a computational viewpoint to fix $a_\alpha$.

5. Results.

We have calculated the parameters of the coexisting phase for mixtures with three different length ratios $c = 2.0$, $c = 5.0$ and $c = 10.0$. Firstly equations (4.1) were solved using Newton’s method, for $0.0 \leq a \leq 1.0$ and the required range of $\rho$. A typical set of results for $x$, $y$ (in the fourth order approximation) as a function of $\rho$, with $a = b = 0.5$, $c = 5.0$ are shown in figure 2. Clearly $x = y = 1/3$ is always a solution, this corresponds to the isotropic phase where the orientation of rods is random. At a critical concentration, dependant on $a$ and $c$, another set of solutions appear (1), these represent a more favourable nematic phase, which has a lower free energy than the isotropic phase. It can be seen that the orientational distribution function, $x$, of the longer rods shows a greater degree of alignment than that of the shorter rods.

\[ \frac{\partial^2 F}{\partial x^2} > 0 \quad ; \quad \frac{\partial^2 F}{\partial y^2} > 0 \quad ; \quad (\frac{\partial F}{\partial x}) (\frac{\partial F}{\partial y}) - (\frac{\partial^2 F}{\partial x \partial y}) > 0. \]

Fig. 2. — The set of solutions to equations (4.1) for $a = b = 0.5$, $c = 5.0$ in the fourth order approximation.

(1) Other solutions were found, but these did not satisfy the conditions necessary for minimization,
These results were then used in equations (4.3) which were, again, solved using Newton's method. The results are given in tables II, III and IV, and plotted in figures 3, 4 and 5, with sample tie lines drawn to illustrate the fractionation of the shorter rods into the isotropic phase. The concentration in the isotropic phase is always less than in the nematic.

Table II. — The parameters of the coexisting phases for $c = 2.0$ in the $n$-th approximation.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$a_n$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
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<td>0.000</td>
<td>7.679</td>
<td>5.042</td>
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<td>4.221</td>
<td>0.067</td>
<td>7.450</td>
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<td>0.400</td>
<td>0.172</td>
<td>5.409</td>
<td>3.322</td>
<td>0.185</td>
<td>5.818</td>
<td>3.638</td>
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</tr>
<tr>
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<td>4.025</td>
<td>2.461</td>
<td>0.381</td>
<td>4.353</td>
<td>2.713</td>
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<td>0.800</td>
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<td>2.887</td>
<td>1.755</td>
<td>0.663</td>
<td>3.164</td>
<td>1.965</td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>1.000</td>
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<td>1.000</td>
<td>2.144</td>
<td>1.421</td>
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</tr>
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</table>

Table III. — The parameters of the coexisting phases for $c = 5.0$ in the $n$-th approximation.

<table>
<thead>
<tr>
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<th>$a_n$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
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<td>0.000</td>
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<td>47.993</td>
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<td>0.000</td>
<td>53.572</td>
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<td>0.200</td>
<td>0.941 x 10^-3</td>
<td>44.168</td>
<td>26.241</td>
<td>0.134 x 10^-2</td>
<td>46.280</td>
<td>28.146</td>
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<tr>
<td>0.400</td>
<td>0.118 x 10^-1</td>
<td>27.479</td>
<td>10.192</td>
<td>0.138 x 10^-1</td>
<td>28.213</td>
<td>18.814</td>
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<td>1.260</td>
<td>1.000</td>
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<td>1.421</td>
<td></td>
</tr>
</tbody>
</table>

Table IV. — The parameters of the coexisting phases for $c = 10.0$ in the $n$-th approximation.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$a_n$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
<th>$a_i$</th>
<th>$\rho_n$</th>
<th>$\rho_i$</th>
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<tr>
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<td>0.876 x 10^-4</td>
<td>111.289</td>
<td>74.384</td>
<td>0.115 x 10^-3</td>
<td>113.489</td>
<td>76.599</td>
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<td>1.924</td>
<td>0.672</td>
<td>3.193</td>
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</tr>
<tr>
<td>1.000</td>
<td>1.000</td>
<td>1.921</td>
<td>1.260</td>
<td>1.000</td>
<td>2.144</td>
<td>1.421</td>
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6. Discussion.

In this paper we have studied the theory of the phase transition in a binary mixture of long thin rods. Particular attention has been given to the development of the fourth order approximation. We have shown that the shorter rods go preferentially into the isotropic phase, for higher values of c and low values of a they do so almost to the exclusion of the longer rods. We also predict the interesting phase behaviour of isotropic-biphasic-nematic-biphasic-nematic as the concentration is increased in a mixture with \( c = 10.0 \) and the fraction of long rods is roughly between 0.52 and 0.6.
Our results agree qualitatively but differ quantitatively from those of reference [1], the greatest disparity is that the re-entrant behaviour described above was predicted for $c = 5.0$. A small region of the diagram within which the concentration in the isotropic phase is greater than in the nematic phase was also predicted. That such differences should occur is not surprising given the assumptions of the models, indeed with the simplifications that we have made it is astonishing that we should produce results which in many ways are so similar.

If we compare the parameters of the coexisting phase in the second and fourth approximations we see, to a large extent, a uniform increase of about 10% in the transition
Fig. 5. — The phase transition for $c = 10.0$, showing the region of coexistence, in the $n$-th approximation. The re-entrant phase is clearly illustrated. The tie lines show that the high degree of fractionation of the short rods into the isotropic phase increases as the length ratio, $c$, increases.

Concentrations. The most notable effect occurs for $c = 10.0$ where the width (in $a$) of the re-entrant phase has been reduced. The parameters of the nematic phase in this region show very little change from the second to the fourth approximation (this is also true for a small region centred on $a = 0.5$ when $c = 5.0$).

We have no evidence that a region of triphasic equilibrium exists in our model even when the higher order approximation which accounts for interparticle interactions of more than two
bodies is included. This is contrary to the predictions of Flory [3], and the experimental evidence of Inoue et al. [9]. A more precise model allowing continuous orientations, and including higher order virial coefficients may predict such behaviour, but this will be difficult to set up within the present Onsager based theories. It may even be necessary to allow for the finite width of the rods. The latter is easily accommodated in the theory of this paper but would involve lengthy calculations, since many more graphs would be needed for each virial coefficient.

Acknowledgments.

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Appendix.

Calculation of the virial coefficients.

An example of the method used to calculate $B[m, n, 0; p, q, 0]$ is presented using the graph $m = 1, n = 2, p = 1, q = 0$, where the rods of types $m$ and $p$ are both connected to the two rods of type $n$. The integral,

$$
\frac{1}{V n(i)} \int dR_1 \int dR_2 \int dR_3 \int dR_4 \int f_{12} f_{23} f_{34} f_{41}
$$

(A1)

is easily evaluated with the knowledge of equation (3.4). We may immediately integrate out one volume, so that we are left with the integral over all possible configurations of the rods in which they remain connected as specified above, with the additional constraint that the position of one rod is fixed. The one 3-dimensional integral becomes the product of three 1-dimensional integrals, with appropriate limits.

We take the long axis of each rod to be parallel to the $z = 0$ plane. In the $x$ and $y$ directions we neglect the effect of the thickness $d$, which is equivalent to retaining only leading order terms in $\ell_1^2 d$. In the $z$ direction the rods « look » like four parallel lines of length $d$. We also introduce the parameter $c = \ell_1/\ell_2$, and take $c \approx 1.0$. With this in mind we have,

$$
B[m = 1, n = 2, 0; p = 1, q = 0, 0] = \frac{1}{2} [I_x I_y I_z]
$$

(A2)

with

$$
I_x = \int_0^{\ell_1/c} dx_1 \int_0^{\ell_1/c} dx_2 \int_{x_1}^{x_2} dx_3 + \int_0^{\ell_1/c} dx_1 \int_0^{\ell_1/c} dx_2 \int_{x_1+\ell_1}^{x_2+\ell_1} dx_3 = \frac{\ell_1^3(c - 1/3)}{c^3}
$$

$$
I_y = 2 \left[ \int_0^{\ell_1} dy_1 \int_0^{\ell_1} dy_2 \int_{y_1-\ell_1}^{y_2-\ell_1} dy_3 \right] = \frac{2 \ell_1^3}{3}
$$

$$
I_z = 2 \left[ \int_0^{\ell_1} dz_1 \int_0^{\ell_1+c+d} dz_2 \int_{z_1-d}^{z_1+c+d} dz_3 + \int_0^{\ell_1} dz_1 \int_0^{\ell_1+c+d} dz_2 \int_{-d}^{z_1+c+d} dz_3 \right] = \frac{16 d^3}{3}
$$

(A3)

hence,

$$
B[m = 1, n = 2, 0; p = 1, q = 0, 0] = \frac{16(c - 1/3)}{9 c^3} \ell_1^6 d^3
$$

(A4)
References