TOPICAL REVIEW

Virial expansions

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Abstract
The use and the properties of the virial expansion are reviewed and speculations given
concerning possible future developments. Firstly an account is given of the methodologies used
for calculating the virial coefficients, both in isotropic and liquid crystalline phases. We then
consider the isotropic phase, looking at the radius of convergence of the series for one
component systems, mixtures and systems with attractive interactions. We next consider the
application of a virial analysis to disordered liquid crystalline phases (nematic and cubatic).
Finally, we speculate as to future interesting lines of research in this area, in particular the
possibility of applying the virial series to positionally ordered phases.

Contents

1. Introduction

A powerful, systematic method for calculating the properties
of bulk matter is via a virial expansion—i.e., a property is
expressed as a power series in the density. The virial expansion
for the pressure, p, is given for a one component system [1–7]
by

$$\beta p = \rho + \sum_{n=2} B_n(T)\rho^n. \tag{1}$$

Here ρ is the number density and $\beta = (k_B T)^{-1}$, where T is
the temperature and k_B is Boltzmann's constant. The virial
coefficients, $B_n(T)$, depend on the temperature and the form
of the inter-molecular potential. Other properties may also
be expressed as a virial series, but here we shall concentrate
mostly on the pressure, though we will review work done on
expansions for liquid crystalline elastic constants in a later
section.

Questions that immediately arise are how one might
calculate the virial coefficients, when might one expect the
series to converge and whether this expansion is of practical
use. We firstly consider these questions for the isotropic phase
and then review the situation for anisotropic phases.

2. Calculating the virial coefficients

We firstly consider a one component, classical fluid in which
the particles interact via a pairwise additive potential, $u(1, 2)$.
Here '1' is short-hand for the positional and orientational co-
ordinates of particle 1 and a similar interpretation holds for '2'.
The Mayer function, $f(1, 2)$, is then defined by

$$f(1, 2) = \exp[-\beta u(1, 2)] - 1 \tag{2}$$

and the nth virial coefficient, B_n, is given by the sum of all
cluster integrals corresponding to labelled irreducible f-bond
diagrams with n points [2–7]. Expressions for the first few
virials are easily written down, namely

$$B_2(T) = -\frac{1}{2V\Omega^2} \iint f(1, 2)\, d1\, d2 \tag{3}$$

and

$$B_3(T) = -\frac{1}{3V\Omega^3} \iint f(1, 2) f(1, 3) f(2, 3)\, d1\, d2\, d3 \tag{4}$$

where V is the volume and, for linear molecules, $\Omega = 4\pi$,
whilst for non-linear molecules $\Omega = 8\pi^2$. After this, however,
the number of integrals required to calculate B_n rises rapidly

with n—e.g. there are three distinct integrals needed for B_4, while for B_9 there are 194 066 [8].

For sufficiently simple potentials of interaction, the lower order virials may be calculated analytically. Thus the virials up to B_4 are known for hard spheres and indeed also for hard hyper-spheres in d dimensions [9–15]. These virials have also been studied in the limit of infinite dimension, where only B_2 and B_3 are non-vanishing [16, 17]. Virials up to B_7 have also been calculated analytically for hard parallel squares and cubes [18–22]. For hard convex bodies, there exist explicit expressions for the second virial coefficient [23–27]. For hard non-convex shapes the calculations are harder, though there are analytical results for B_2 for fused diatomics [28–31], a special model of linear triatomics [30] and chains of tangent hard spheres [32], where the orientationally dependent form was also calculated. One may also analytically calculate the virials up to B_4 for hard spheres with square-well attractive potentials of interaction [33] and up to B_5 for parallel hard squares and cubes with both Ising- and square-well attractive potentials [34].

Even for simple potentials of interaction, however, the high order virials need to be calculated numerically. An exception is the Gaussian model, for which the Mayer f-function is taken to be a Gaussian. This corresponds to a spherically symmetric repulsive pair potential which diverges logarithmically at small separations. This choice permits considerable analytical progress, both for the one component case [35], where nine virials have been calculated in one to four dimensions, and for simple models of many component fluids [36, 37], in which only unlike interactions are considered. Here 13 virials have been calculated in two to ten dimensions for a two component fluid and ten virials for a three component system, again in two to ten dimensions.

Returning to more general potentials of interaction where the mathematical techniques described above are inapplicable, an important advance by Ree and Hoover [38] was to replace the irreducible Mayer graphs with graphs in which every pair of points was linked either by an f-bond or an e-bond, where

$$e(1, 2) = 1 + f(1, 2). \qquad (5)$$

Thus, for hard bodies, an f-bond means the two particles must overlap, whilst an e-bond means the particles must not overlap. This firstly significantly reduces the number of distinct integrals to be calculated (81 564 for B_9 [8]). Secondly, for hard bodies, this formulation allows the virials to be calculated via a straightforward Monte Carlo method, as any given configuration of particles can contribute to at most one Ree–Hoover diagram. Using such methods the first ten virial coefficients have been calculated for hard discs, hard spheres and for hyper-spheres up to dimension $d = 9$ [8, 39–56]

For virials up to B_5, the Ree–Hoover Monte Carlo method is as follows. Having placed particle 1 at the origin and at a given orientation, particle 2 is repeatedly placed in random positions and at random orientations until eventually it overlaps particle 1. Random placements are then attempted for particle 3 until it is found to overlap particle 2. Doing this repeatedly finally generates an overlapping chain of n-particles, where n is the order of the virial one wishes to calculate. One then checks

for overlaps between all pairs of particles and, generally using a look-up table, decides whether this configuration corresponds to a Ree–Hoover graph. If it does, one accumulates the Ree–Hoover weighting for this graph. One then generates a new chain of overlapping particles and the whole procedure is repeated. For virials of higher order than B_5, not all the Ree–Hoover graphs can be generated starting from a linear overlapping chain, and other, branched chains must also be used. A full discussion of the technicalities is given in [8, 28, 41, 43, 45, 47, 55].

One may also estimate virial coefficients by fitting to highly accurate equation of state simulation data. An example of this is the study of the hard disc fluid, where estimates have been made of $B_{11}-B_{15}$ [57].

The Monte Carlo method may also be readily applied to aspherical hard bodies, and to date the first eight coefficients have been reported for spheroids [47, 58–62], prolate sphero-cylinders [47, 63–66] and truncated spheres [47, 67]. The first six virials have been calculated for the hard Gaussian overlap model [68–70] and the first five for hard oblate sphero-cylinders [71–74] and hard diatomics [75–83]. The first four virials have been calculated for hard models of triatomics [82–84] and tetrahedral penta-atomics [85] and the first three for sphero-cylinder dimers [86, 87].

One may also calculate the virials corresponding to mixtures of hard particles using this method—hard sphere and hard disc mixtures have been the object of much study with up to seven virials calculated [47, 88–99]. Similarly, virials up to B_5 have been calculated for hard spheres with square-well potentials [47].

For more general pair potentials, this Monte Carlo method is more troublesome to implement. It is no longer the case, in general, that a given configuration of particles corresponds to only one Ree–Hoover graph. Numerical integration of the irreducible Mayer graphs has yielded the first five virials for Lennard-Jones particles [100–104], the first four virials for a two-centre Lennard-Jones model with point quadrupoles [105] and the first three virials for certain water models [106, 107]. An important new development, however, is the use of importance sampling to calculate high order virials in these cases. The basic idea here is to aim to calculate the ratio of B_n for the desired system to B_n for a reference system, typically hard spheres for which the virials are known. To date the sixth virial has been calculated for Lennard-Jones particles [108] and up to the seventh virial for various water models [109, 110]. This method may also be used to calculate the virial coefficients for flexible molecules, where one needs to average over the conformations of all the particles in the cluster.

In general, however, the potential of interaction in a real fluid is not pairwise additive—one finds irreducible three body and higher order contributions. This situation has been relatively little studied and, to my knowledge, only carried out to third virial level (see, e.g., [111–113]). Of particular note is the work described in [113], where the triplet potential of interaction is calculated at each point by *ab initio* methods, rather than using an analytic form. This is an attractive possibility for the modelling of real systems. It is also worth

noting that the importance sampling methodology described above is well suited for this type of investigation [112].

Finally, we very briefly consider systems in which the nuclear motion is treated quantum mechanically rather than classically, as has been the case considered so far. The second virial may be calculated by Regge pole analysis [114], but another, recent approach is to use a path integral methodology, with the result that the calculation transforms into the calculation of the second virial coefficient for two, flexible ring polymers [115–117]. One obtains the exact quantum mechanical result in the limit of a large number of beads in the polymer ring. Such calculations allow one also to incorporate exchange effects (i.e. to obtain both fermionic and bosonic virial coefficients). A practical question here is what form to use for the inter-particle pair potential, for most commonly used pair potentials have been parameterized with the assumption of classical behaviour. The most fundamental solution would be to calculate the pair potential at each point from *ab initio* calculations. There is no reason why quantum virials of third or higher order may not be calculated using the path integral approach, maybe combined with the use of importance sampling.

3. Convergence and quality of predictions—isotropic phase

We begin by considering one component hard body fluids, for which the only phase transition is fluid–solid. Examples are hard spheres (or, more generally, hyper-spheres in d dimensions), but systems such as hard parallel cubes, hexagons and triangles have also been studied. Very little is known rigorously about the convergence properties of the virial series. A lower bound has been established for the radius of convergence of the series [118], but numerical studies indicate the true radius of convergence to be significantly greater than this. An illustration of this is given in figure 1, where we compare the performance of the virial series for hard spheres with a quasi-exact equation of state due to Woodcock [119]. Increasing the order of the virial series brings the equation of state curves ever closer to simulation results and at the freezing packing fraction of 0.49 the virial series, truncated at the B_{10} level, predicts a compressibility factor that is in error by just 2%.

A still-unresolved question is whether the virial expansion in the isotropic, fluid phase has anything to say about the solid phase. One possibility is that the radius of convergence of the isotropic virial series is the freezing density and that it is impossible to analytically continue the line beyond this point [120]. Another possibility is that the radius of convergence of the isotropic fluid has nothing to do with the freezing transition and that freezing corresponds to a direct jump from a point on the isotropic equation of state to the corresponding crystalline equation of state. It should be noted that in two dimensions the situation is complicated by the possible existence of a hexatic phase in-between the fluid and solid phases [121], thus leading to even more possible radii of convergence of the isotropic virial series.

Given the lack of rigorous results, one must resort to numerical studies to attempt to resolve these questions. In what
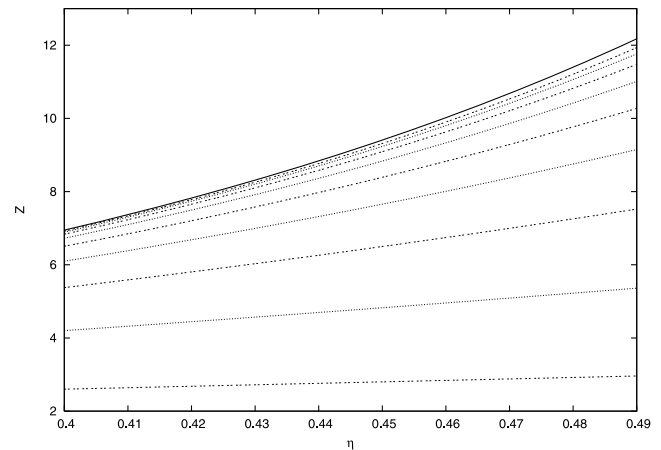

Figure 1. Plot of the compressibility factor, $Z = \beta p/\rho$, against packing fraction, η, for hard spheres. The solid line is a quasi-exact equation of state [119], while the other lines correspond to truncated virial expansions. The bottom curve corresponds to truncation at B_2, the next curve up corresponds to B_3 and so on until the top curve is reached, which corresponds to truncation at B_{10}.

follows it must be remembered that the analysis is based on knowledge of relatively few coefficients in the series, so the conclusions must necessarily be somewhat tentative.

For both hard spheres and hard discs (and, indeed, for hyper-spheres in four dimensions), all the virials calculated so far are positive. In five or more dimensions, negative virials appear. Ten virials have been explicitly calculated in these cases and, for hard discs, virials up to B_{15} have been estimated by fitting to simulation equation of state data. For one dimensional hard rods, there is no phase transition and all the virials are known and are positive [122]. In this case the radius of convergence is the density of closest packing, which is a packing fraction of one. For discs and spheres, previous Levin [123] and Padé [124] analyses based on the available coefficients (seven and eight respectively) predicted the radius of convergence of the series to be governed by a pole at a real, positive density, numerically close to the density of closest packing. It is also possible, however, to analyse the behaviour of a series using the ratio test [125]. The latest analysis on the convergence of the virial series for hyper-spheres, making use of the first ten virials, is given in reference [55]. This also presents an excellent review of research done to date on these systems. Using a variety of methods, these authors found that in two dimensions there is a positive pole near the density of closest packing. In three, four and five dimensions it proved very difficult to pin down the position or nature of the dominant pole. As often seems to be the case, more coefficients are needed to numerically establish the convergence properties of the virial series in this important, three dimensional case. For six dimensions and higher, the analysis indicated the dominant pole was at a real, negative density.

For parallel hard cubes B_6 and B_7 are negative. To my knowledge the higher virials have not been calculated and we do not have the same degree of analysis for the virial series in this case as we do for hard hyper-spheres.

If we now turn to one component systems of aspherical particles, the phase diagram is richer, with the possibility of

liquid crystalline phases and plastic solids, all of which could, in principle, have an influence on the properties of the isotropic virial series. To date, virials up to B_6 have been published for a range of hard Gaussian overlap models and virials up to B_7 have been published for a set of hard spheroids, spherocylinders and truncated hard spheres (these are spheres with upper and lower caps symmetrically removed, so the resulting shape is disc-like with a curved rim). We have recently calculated B_8 as well for these latter cases.

For both prolate and oblate spheroids (with aspect ratios in the range 1/3 to 3), the situation resembles hard spheres. All the virials are positive and a Padé analysis indicates a radius of convergence near the density of closest packing. Numerically, this corresponds to a real, positive pole. For more aspherical shapes, however, negative virials appear and the radius of convergence moves to lower packing fractions. A Padé analysis indicates that the radius of convergence corresponds to either a real, negative pole (prolate spheroids) or a pair of complex conjugate poles (oblate spheroids), both of which would be expected to lead to a series containing negative coefficients. Simply plotting the equation of state for various levels of truncation of the virial series shows that the various curves start to fan out at ever lower packing fractions as the particles become more aspherical.

The most recent analysis for spheroids is given in reference [62]. For spheroids with aspect ratios either less than 1/2.75 or greater than 2.75, the isotropic phase becomes nematic upon increasing the pressure. The available numerical analysis suggests that for significantly aspherical shapes, where the radius of convergence for the isotropic virial series is substantially less than close packing density, the radius of convergence is close to the isotropic–nematic co-existence density as observed by simulation. As the pole controlling the convergence would not appear to be at a real, positive density, it would be hard to claim any physical relation between the radius of convergence and the onset of the nematic phase transition. Nevertheless, this observation, if true, is important. As discussed later on, one may wish to calculate the virial series in both the isotropic and nematic phases and then use these two equations of state to locate the position of the transition (i.e. by equating pressures and chemical potentials). If this procedure is going to converge to the correct transition densities, one does require the isotropic virial series to be convergent in this density range.

The hard Gaussian overlap model [70] gives results which are very similar to those found for spheroids. Once the particles deviate significantly from a spherical shape one finds negative virial coefficients and that the radius of convergence decreases the more aspherical the particles become. The Padé analysis again suggests that the radius of convergence is determined by a pair of complex conjugate poles for significantly oblate shapes and a negative pole for prolate shapes. It was further noted that the 3/3 Padé approximant gave results in good agreement with Monte Carlo simulation.

Turning now to hard sphero-cylinders [62], the situation is less thoroughly studied but the general conclusions would appear to be similar. If the length of the cylinder is denoted by L and the diameter by D, then all the virials up to B_7 are positive for $L/D \leqslant 3.2$, but negative coefficients appear for more elongated shapes, leading to a radius of convergence less than the density of closest packing. For cut spheres [62], with diameter D and thickness L, the virials up to B_7 are positive for $L/D \geqslant 0.3$, but for more oblate shapes again negative virials set in and the radius of convergence, in terms of packing fraction, drops from the value at closest packing.

In general the conclusion is that the more aspherical the particle, the more negative virial coefficients tend to turn up and the smaller is the radius of convergence in terms of packing fraction. Numerically, however, there seems a good chance that the isotropic series converges up to the density at which there is a transition to a liquid crystalline phase.

When the particles are not hard, the virial coefficients depend on the temperature, so one may ask how the radius of convergence might depend on temperature. When attractive forces are also present, then one may find a liquid–gas transition as well as the solid–fluid transition mentioned above, so it is interesting to ask how the virial series fares at sub-critical, critical and super-critical temperatures. Formally, the virial series close to the critical point ought to contain information about the non-classical critical exponents, though all the indications to date are that one needs to carry out the expansion to extremely high order to see any signs of this.

Ree and Hoover [34] calculated the first five virials for parallel squares and cubes with both Ising-well and square-well attractive potentials and studied the behaviour of the series near the critical point. They found that, although the predicted critical pressure (P_c), volume (V_c) and temperature (T_c) all changed significantly as one altered the number of virials in the series, the product $P_c V_c$ remained remarkably constant, leading them to surmise that the virial series was convergent at the critical point.

The first five virials have also been calculated for hard spheres with a square-well attractive potential [47], but one would hesitate to draw any conclusions about convergence with so few terms. It is worth noting in passing that it is extremely hard to calculate virial coefficients in the vicinity of the critical temperature to good accuracy, as there is an extraordinary degree of cancellation between the Ree–Hoover graphs under these conditions.

The best characterized system so far is the Lennard-Jones fluid, for which the first seven virials have been calculated as a function of temperature [108, 126]. The reduced temperature is defined by $T^* = k_B T/\varepsilon$, where ε is the depth of the Lennard-Jones potential, and the reduced density is desired by $\rho^* = \sigma^3 \rho$, where σ is the distance at which the potential is zero. For a sub-critical temperature of 1.0, the virial series appears to be converging up to the spinodal density of 0.092, but past this density the high order terms make significant contributions to the pressure and it is not clear whether the series is converging or not. Here all the coefficients are negative except for B_3. At a near-critical temperature of 1.3, the situation is similar—there is apparent convergence up to the critical density. At a super-critical temperature of 2.0, the series appears to converge up to a density of 0.3, though after this the high order virials again contribute significantly and convergence is uncertain. At this temperature a B_7 series agrees well with simulation out to a density of 0.8, but more virials are needed to

check whether or not this is simply fortuitous. At present it seems the most one can say is that for sub-critical temperatures the virial series appears to converge up to the spinodal density, even when the temperature is close to critical.

We turn now to mixtures, where one has the possibility of fluid–fluid demixing. Again one may ask whether the virial series can predict such transitions and about the radius of convergence. The best characterized systems here are the Gaussian model studies by Baram, Maddox and Rowlinson [35–37]. Their two component system assumed no interaction between like particles, but the Mayer function describing unlike interactions took on a Gaussian form. They calculated 13 virials in a dimensionality, d, ranging from two to ten. They found a demixing transition and carefully analysed the series so as to extract the critical exponent of the susceptibility. For $d \geqslant 4$, their results were in accord with classical values of this exponent. For $d = 3$, the results suggested a non-classical value for this exponent, but the extrapolation was considerably less robust than in higher dimensions and the best estimate had a rather large error bar. For $d = 2$, the extrapolation procedure gave no conclusive result at all. The somewhat depressing conclusion was that many more virials (up to the order of 20 in three dimensions) would be needed to get convincing results for the system's critical behaviour.

The same authors also treated a ternary mixture, again with no like–like interactions, and with the Mayer function for unlike pairs all having an identical Gaussian form. This system was found to exhibit tri-critical points. Ten virials were calculated in dimensionalities two to ten and the evidence was strongly that for $d \geqslant 4$ the tri-critical points were 'normal' or asymmetrical. For $d = 3$ the situation was less clear, but the evidence was still in favour of this asymmetrical scenario. For $d = 2$, however, there appeared to be a single 'anomalous' tri-critical point. As in the two component case, the results in lower dimensions were not as convincing as those in higher dimensions, and again, presumably, many more virials would be needed to completely settle the issue.

The best studied 'realistic' binary system is that of a mixture of additive hard spheres. A long standing issue has been whether a hard sphere mixture could exhibit a fluid–fluid phase transition. Certain integral equation approaches predicted that such a transition would occur when the ratio of the diameter of a small sphere to that of a large sphere, λ, was around 0.1. Technically, this is an extremely challenging system for simulation, and strictly speaking the existence or otherwise of this transition has not been established. The general consensus, however, is that this transition does occur but only in a meta-stable region—thermodynamically, the system solidifies prior to this transition.

For mixtures, the nth virial coefficient is composition dependent, i.e.

$$B_n = \sum_{r=0}^{n} \binom{n}{r} B_n (r, n - r) x^r (1 - x)^{n-r} \qquad (6)$$

where x is the mole fraction of component 1, $\binom{n}{r}$ is the combinatorial factor and $B_n(r, n-r)$ is a partial virial

coefficient. These coefficients have been calculated for a range of diameter ratios up to $n = 6$ and up to $n = 7$ when $\lambda = 0.1$ [47, 99]. All the partial virial coefficients calculated thus far are positive. The conclusions are that a demixing transition is predicted for $\lambda = 0.1$, but at an overall packing fraction that is higher than the freezing density. The predicted consolute point, however, converges very sluggishly on increasing the number of virial coefficients, so these conclusions cannot be taken to be overly definitive. This number of coefficients calculated is also far too small to make any estimates about critical exponents.

One may also consider the case of non-additive spheres, where the pair contact distance, σ_{12}, is given by

$$\sigma_{12} = \left(\frac{\sigma_{11} + \sigma_{22}}{2} \right) (1 - \Delta) \qquad (7)$$

where σ_{11} and σ_{22} are the diameters of spheres 1 and 2 respectively. For $\Delta = 0.1$ and $\lambda = 0.1$, negative partial virials make an appearance for $n = 6$ [99], and, as is normally the case in such situations, an effect of this is to worsen the convergence properties of the virial series. Thus the equation of state of these non-additive spheres appears to converge less rapidly than the corresponding system of additive spheres.

High-level virials would not appear to have been calculated for other binary mixtures, so there is little as yet to report on the effect of attractive forces on the properties of the virial expansion for such mixtures.

4. Convergence and quality of predictions— anisotropic phases

The virial series may also be applied to inhomogeneous phases. For a one component system, it takes the form [127]

$$-\beta \Omega = \beta A_0 + \beta \int \rho(1) \left[V_{\text{ext}}(1) - \mu \right] \mathrm{d}1$$
$$+ \int \rho(1) \left\{ \ln \left[\Lambda^3 \rho(1) \right] - 1 \right\} \mathrm{d}1 + \sum_{n=2} \frac{V_n(T)}{n-1}. \qquad (8)$$

Here Ω is the grand potential, A_0 contains the non-translational contributions to the ideal gas Helmholtz energy (i.e. arising from rotations, vibrations and electronic excitations), μ is the chemical potential, V_{ext} is the external potential, Λ is the de Broglie thermal wavelength and $\rho(1)$ is the one particle density, dependent in general both on position and orientation. '1' is shorthand for the position and orientation of particle 1. The coefficient V_n is given by

$$V_n = \int B_n (1, 2, \ldots, n) \rho(1)\rho(2) \ldots \rho(n) \, \mathrm{d}1 \, \mathrm{d}2 \ldots \mathrm{d}n \quad (9)$$

where $B_n (1, 2, \ldots, n)$ is the nth virial coefficient for n particles with fixed positions and orientations. V_n is given by the same Mayer or Ree–Hoover graphs as described earlier, except that the densities corresponding to the field points now depend on both position and orientation. One may obtain $\rho(1)$ as that function which minimizes equation (9) and, given this, one may calculate all thermodynamic properties.

To date, most high-level virial work has concentrated on positionally disordered liquid crystalline phases (mainly

nematic but also cubic) in the absence of an external field. In this case

$$\rho(1) = \rho f(\Omega) \qquad (10)$$

where $f(\Omega)$ is the one particle orientational distribution function and Ω denotes the particle orientation. In this case we can carry out the integration over positions in equation (9), but we still require an expression for the orientationally dependent virial coefficients. Onsager instigated this methodology for treating nematic phases and he obtained a theory for hard sphero-cylinders by truncating the virial series at the B_2 level [128]. He obtained an explicit expression for the orientationally dependent B_2 coefficient and then estimated the location of the isotropic–nematic phase transition by making use of a variational principle. This level of truncation turns out to give exact results for very long rods, where the transition occurs at such low densities that the higher order virials are negligible. For finite rods and any type of disc, however, the higher virials may not be neglected, though, as one may imagine, the calculation of these terms is considerably harder than the corresponding calculation in the isotropic phase.

The most fundamental approach is to expand these orientationally dependent virial coefficients in terms of a rotationally invariant angular basis set. For axially symmetric molecules this entails products of spherical harmonics, whilst for non-axially-symmetric cases Wigner functions are needed. Almost all work to date has concentrated on the simpler axially symmetric case [129–132], except for a third virial calculation on bent-core molecules [88]. The coefficients in these expansions must be calculated numerically, using generalizations of the techniques used for calculated isotopic virials. In the Monte Carlo procedure, for any configuration of particles contributing to a Ree–Hoover graph, one must accumulate a large set of functions involving the orientations of all the particles. Details are given in [129–132].

An issue here is how complete the angular basis set must be. A stringent test is that it should be large enough to give a good prediction of the virial coefficients in the limit where all the particles are aligned. The more aspherical the particles, the more terms are needed to achieve this. For high order virials, this becomes a real problem, as the higher order the virial the more coefficients are required. Often these coefficients can be relatively small and thus have a rather high associated statistical error resulting from the Monte Carlo integration. For significantly aspherical particles, one is thus in the position of requiring a large number of small coefficients, all calculated to good accuracy, if one is to be confident of having a sufficiently high quality basis set to give confidence in one's predictions.

In the existing work on hard spheroids, this methodology has led to reliable coefficients for B_3 for $1/10 \leqslant a/b \leqslant 10$, for B_4 for $1/5 \leqslant a/b \leqslant 5$ and for B_5 for $1/3 \leqslant a/b \leqslant 3$. Here a and b are the lengths of the spheroid along and perpendicular to the symmetry axis respectively. Sets of angular coefficients have been calculated up to B_8 level in all these cases, and, given the fact that nematics are not perfectly orientationally ordered, one may be able to get away with fewer coefficients than required by the strict alignment test.

Using these data, the easiest thing to calculate is the instability density—i.e. the density at which the isotropic

phase becomes mechanically unstable with respect to nematic ordering. This calculation simply requires knowledge of the lowest order, rank 2, coefficients, so the basis set completeness question does not arise. In all cases studied, the instability density converges rapidly with the level of virial series used [129–132] and approaches the value predicted by extrapolation of simulation results in the isotropic phase ($a/b = 3, 1/3, 5, 1/5$).

The coefficients may also be used, however, to predict both the equation of state of the nematic phase and the location of the isotropic–nematic transition. In general, it would seem that in all cases increasing the number of virials improves the predicted nematic equation of state. This is plausible as it is known that a system of perfectly aligned spheroids is isomorphic to a system of hard spheres, so the perfectly aligned coefficients are identical to those of hard spheres. Given the good convergence properties of the latter, one may hope for similarly good behaviour in the nematic. What is more disappointing, however, is that the location of the predicted isotropic–nematic transition does not show such monotonic convergence. Indeed, for certain truncations, one cannot locate a transition at all. In these cases, although one may find a stable nematic phase at high density, as the density is lowered there comes a point below which no nematic solution exists. It is quite possible that this point comes at too high a density to allow isotropic–nematic co-existence. More details are given in [132].

The cases of sphero-cylinders and truncated spheres are similar [133, 134]. The more aspherical the particles are, the harder it is to obtain an angular basis set that yields the correct aligned limit. The general conclusions about instability densities and the properties of the nematic phase are similar to those given for spheroids.

Simulation studies indicate that truncated hard spheres with $L/D = 0.2$, where L is the thickness and D the sphere diameter, undergo an isotropic–cubatic transition upon increasing the pressure. In a cubatic phase the particles are positionally disordered but exhibit an orientational ordering with cubic symmetry. Virial expansions may also be used to investigate the properties of this phase. If one simply truncates the series at B_2, the nematic phase is always favoured over the cubatic. At higher levels of theory, however, the cubatic phase is increasingly stabilized, and at the B_5 level becomes the predicted stable phase [131, 134]. The cubatic phase for truncated spheres thus relies for its stability on many-body packing effects and cannot be understood simply in terms of pair excluded volumes.

Given the practical problems involved in calculating orientationally dependent virials, it is not surprising that the treatment of positionally ordered phases from a virial expansion is harder still. It is worth mentioning, however, that it is not difficult at all to use the virial series to calculate the density at which the isotropic phase becomes unstable with respect to positional ordering. For a strong first order transition, such as fluid–crystal, the calculated density may bear little relation to the density of the phase transition, but for weaker first order transitions, such as isotropic–smectic A, this calculation may prove useful and also give

information as to the structure of the ordered phase close to the phase transition. At high level, this approach has been applied to spherocylinders, where a direct isotropic–smectic A transition is observed by simulation, but the calculations were unsuccessful in the sense that the isotropic–nematic instability density occurred before any smectic-like instability [133]. We also note that this type of analysis was used to investigate the isotropic—biaxial nematic transition in systems of hard bent-core molecules, going up to B_3 level [87, 88]. In a biaxial nematic, the particles are positionally disordered but all three molecular axes exhibit orientational ordering. This was, to our knowledge, the first prediction that molecules of this shape would form this phase—a prediction that was later verified experimentally (though we note that attractive forces doubtless play important roles in these experimental systems).

　　An alternative approach to calculating the isotropic–nematic transition from a virial expansion is to return to Onsager's original idea of making use of a trial function. Onsager assumed the orientational distribution function to have the form

$$f(\Omega) = \frac{\alpha}{4\pi \sinh\alpha} \cosh(\alpha\cos\theta) \tag{11}$$

where θ is the angle between the symmetry axis of the particle and the nematic director (i.e. the direction in which the particles point on average). α is a variational parameter and is varied so as to minimize equation (8). A different one parameter trial function was used in reference [135]. In principle, one could improve the description by introducing trial functions with more than one parameter, though the amount of numerical calculation required would then increase greatly.

　　Numerically, the problem is now significantly simplified. One calculates each virial coefficient in the standard Ree–Hoover manner for a sufficient number of α values that one may smoothly interpolate between the calculated values [135, 136]. For a given particle shape we thus have in equation (9), $V_n \equiv V_n(\alpha)$. The best value of α is then obtained by minimizing equation (8) with respect to α. The disadvantage of this approach is naturally that of having assumed a form for the orientational distribution function. The great advantage, however, is that as α varies from zero to infinity one goes smoothly between the isotropic and fully aligned limits. The results therefore are exact in these two cases and one does not experience the numerical difficulties described above of dealing with incomplete angular basis sets.

　　Results have been obtained using this method up to B_8 level. The qualitative conclusions are as before, but now the description of the nematic and cubatic equations of state is much improved. An example for the isotropic and nematic phases for 3:1 prolate hard spheroids is shown in figure 2. At co-existence, simulation [59] predicted the packing fractions of the co-existing isotropic and nematic phases to be 0.507 and 0.517 respectively. The B_8 truncation gives these values as 0.538 and 0.550.

　　One may ask, just as for the isotopic phase, for the radius of convergence of the virial series in liquid crystalline phases. The analysis is complicated by the fact that the V_n coefficients that give the virial series for the pressure are integrals over
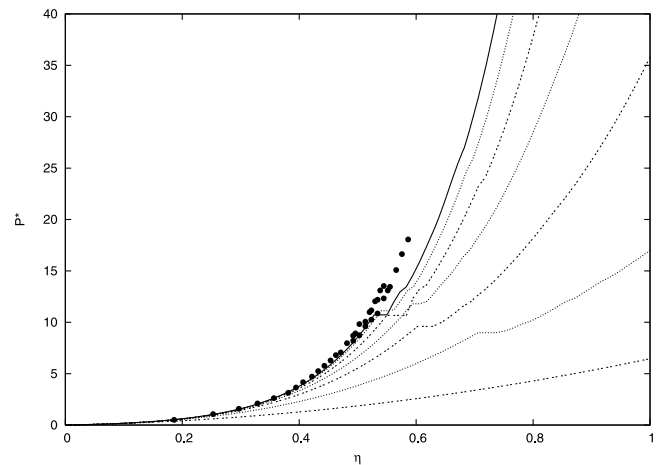

Figure 2. Plot of the reduced pressure, $P^* = \beta p v_0$, where v_0 is the spheroid volume, against packing fraction, η, for hard prolate spheroids with aspect ratio 3:1. The points correspond to simulation results [59] and the curves correspond to truncated virial expansions, making use of the trial function, equation (11), to calculate nematic phase properties. The bottom curve corresponds to truncation at B_2, the next curve up corresponds to B_3 and so on until the top curve is reached, which corresponds to truncation at B_8.

the orientational distribution functions, and this function itself is a function of density. To date very little is known about this. Nematic-forming hard spheroids undergo a nematic–crystal transition at high enough density, with no intervening liquid crystalline phase. One's guess in this case is that the nematic virial series closely resembles the virial series for isotropic hard spheres. This is because at high density the spheroids will be highly aligned and the virial coefficients for perfectly aligned spheroids are identical to the hard sphere virials. The situation is more complicated for spherocylinders, as here simulation indicates the occurrence of a nematic–smectic A transition. Available data thus far give no indication that the nematic virial series 'knows' about the location of this transition, but to date these conclusions are tentative. A similar situation occurs for truncated hard spheres, where a nematic–columnar transition can occur for sufficiently thin discs. As is always the case, one really does not have enough virial coefficients to make reliable judgements about these convergence issues.

　　Another set of important material properties of liquid crystals is their elastic constants. In the nematic phase, these elastic constants measure the Helmholtz energy penalty upon introducing orientational distortions into the material. For the case of hard spheroids and infinitely thin hard discs [137], virial calculations have been carried out to eighth order, making use of the Onsager trial function approach, and the results appear to converge well to those obtained by simulation. These coefficients are expected to show anomalous behaviour in the vicinity of a nematic–smectic A transition, and it will be interesting to investigate the convergence properties of this series for the case of sphero-cylinders, for example, which exhibit this transition.

　　Finally, we note that a theoretically simple model of liquid-crystal formation may be obtained by studying systems

where particles are only allowed to possess certain discrete orientations. An example is that of hard rods, which may only point along the three Cartesian axes. The isotropic phase corresponds to equal numbers of rods pointing along each axis, whilst a nematic phase would have a preponderance of rods pointing along just one axis. Smectic, columnar and crystalline phases may also be found in this model. The first seven virials have been calculated for infinitely thin rods [138] and the isotropic–nematic transition predicted accordingly, but to my knowledge the virial approach has not been used to high order for other cases. We similarly note the prediction on the nematic–smectic A instability density in the case of perfectly aligned cylinders [139], carried out to fourth order, with every indication of good convergence. It is certainly possible to pursue these models with considerably greater ease than the freely rotating cases described previously, and maybe this could generate new insights into the convergence properties of the virial series for anisotropic phases.

5. Discussion and speculations

From a practical point of view, it would seem that for one component hard core systems one may use the virial expansion to calculate to a good level of accuracy the properties of the isotropic and positionally disordered liquid crystalline phases right up to the transition to the crystal (or the next positionally ordered phase). Current numerical studies suggest that for hyper-spheres in dimension greater than five and for significantly aspherical particles the radius of convergence is much less than the density of closest packing and that the pole determining this quantity is either negative or complex. My conclusion from this is that it is merely coincidence that the radius of convergence for discs and possibly spheres is near that of closest packing. It is hard to see what singles these shapes out from the rest. Again, sticking my neck out, it would seem to me that the available evidence is that the isotropic virial series knows nothing about any impending first order transition, be this to a crystalline, nematic or cubatic phase. This is perhaps more clear-cut in studies of the isotropic–nematic transition, where good quality predictions are obtained by calculating coexistence between states on the isotropic and nematic virial curves. My suspicion is that, given enough virial coefficients, calculated for all the different phases, one can construct a very accurate phase diagram, but that the radius of convergence of each of the virial series in each phase has no physical significance. The hope is simply that the virial series in a given phase converges at high enough density that the system may leap-frog onto the virial series corresponding to the phase that comes next. These comments are clearly highly speculative and it will be interesting to see whether future research proves them right or wrong.

As for binary mixtures of hard core systems, only spheres have been studied to any great degree, and while the general equation of state appears to converge somewhat like that of one component spheres, predictions as to demixing transitions converge much more sluggishly. Much less work has been done on systems with attractive forces, but studies to date on the Lennard-Jones potential indicate that for sub-critical

temperatures the virial series appears to converge up to the spinodal density, even when the temperature is close to critical.

Too few virials are known to make strict statements either about the radius of convergence of the series or about the values of critical exponents. It would be interesting to have more data on systems with attractive forces to gain better insight into the effect of the liquid–vapour transition on the virial series, as very little is known about this. Importance sampling methods will no doubt prove most useful in this regard. It would similarly be interesting to have more data about mixtures and to what extent the virial series can predict fluid–fluid demixing transitions.

To really crack the convergence issues, however, considerably more virials need to be calculated. The number of Ree–Hoover graphs, however, increase extremely rapidly with the order of virial and it is hard to imagine that one can reach B_{20} or above (estimated variously as the level at which hard sphere virials might be negative or the level needed to estimate critical exponents for a binary mixture of Gaussian model fluids) using these methods. One may be able to resort to obtaining these coefficients from extremely accurate simulation studies, but if one is seeking a direct means of calculation computationally less intensive approaches will simply have to be found.

Another area of new research is the use of the virial expansion to predict the properties of positionally ordered phases. While it is likely to prove incredibly difficult to calculate high order positionally dependent virial coefficients, it should be possible to make use of trial functions. While it may sound a bit mad, it would be fascinating to see if one can describe the hard sphere solid in terms of a virial expansion and thereby calculate the full hard sphere phase diagram using such methods. Similarly, one might be able to use similar methods to predict the properties of ordered liquid crystalline phases. In principle, one could also use trial functions to provide a virial theory of interfaces and inhomogeneous fluids, but for good accuracy one presumably needs a rather sophisticated trial function, which may not be readily available.

Acknowledgments

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