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LETTER TO THE EDITOR

Virial expansions for hard-core fluids

D S Gaunt and G S Joyce
Physics Department, King's College, University of London, Strand, London WC2R 2LS, UK

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Abstract. We discuss some of the difficulties involved in drawing conclusions about the asymptotic behaviour of the virial coefficients for a hard-core fluid when only the first few coefficients are known. Particular consideration is given to the recent work of Baram and Luban for hard discs and spheres, and that of Baxter for hard hexagons on the triangular lattice.

In a recent Letter, Baram and Luban (1979) have used a new series analysis method (Levin approximants) to study the virial expansion

$$p/k_BT \equiv \Gamma(\rho) = \sum_{n=1}^{\infty} B_n\rho^n \tag{1}$$

for hard discs and hard spheres. Their main conclusion was that the radius of convergence, ρ_r, of the virial series for both discs and spheres is determined by a singularity at the density of closest-packing $\rho = \rho_0$. There is no singularity at the smaller density $\rho = \rho_c$ where, according to molecular dynamic calculations (Alder and Wainwright 1960), these systems undergo a fluid–solid phase transition.

The work of Baram and Luban (1979) is amongst the most recent contributions to the debate about the behaviour of the virial series for hard discs and spheres and, more particularly, the sign of the higher virial coefficients, that has been conducted over a number of years (see Temperley (1957) and Ree and Hoover (1964) for two early examples). The present Letter is a further contribution and its purpose is twofold. First, we wish to show that the main results of Baram and Luban (1979) can essentially be demonstrated by using a simple ratio technique (Gaunt and Guttmann 1974). We feel this is possibly more appropriate than Levin approximants for studying a short series of positive terms. Second, and more importantly however, we would like to sound a note of caution. It seems to us that to attempt to draw conclusions about the asymptotic form of the virial coefficients of a hard-core fluid from the first few terms is *particularly* hazardous. As we point out, the first seven virial coefficients for hard discs and hard spheres can be extrapolated with results quite different to, and possibly more plausible than, those of Baram and Luban (1979). Other possibilities are suggested by studying various lattice analogues. For example, the behaviour of the leading virial coefficients for hard discs and spheres is quite similar to the corresponding behaviour for several lattice models of hard-core fluids, whose virial coefficients are known to change their behaviour quite suddenly at higher order. Recently, it has been shown *rigorously* (Baxter 1980) that for hard hexagons on the triangular lattice (Gaunt 1967) the function $\Gamma(\rho)$ has a singularity at ρ_c corresponding to a fluid–solid phase transition. Using these

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exact results by Baxter it has been established (Joyce, unpublished work) that the radius of convergence ρ_r of the virial series for this lattice model is *less than* ρ_c, and is determined by a pair of non-physical singularities in the complex ρ-plane. Thus, for hard hexagons on the triangular lattice the asymptotic behaviour of the virial coefficients yields no information concerning the transition at ρ_c.

The first seven virial coefficients for hard discs and spheres are given in table 1 of Baram and Luban (1979) and we will not reproduce them again here. In figure 1 we plot the ratios $r_n \equiv B_n/(B_{n-1}B_2)$ against $1/n$. The points labelled D_c, D_0, S_c, S_0 on the right-hand axis show where the extrapolated limits would be if the virial coefficients for discs (D) and spheres (S) were dominated by singularities at either ρ_c or ρ_0. If one believes that by $n \simeq 7$ the ratios have essentially attained their asymptotic behaviour, then limits close to D_0 and S_0 do not seem unreasonable. Furthermore, it is conceivable that as $n \to \infty$ the ratios approach D_0 and S_0 with *zero* slope, i.e. something like the extrapolations shown as broken curves in figure 1. Such behaviour would correspond to the virial series diverging like a simple pole (with critical exponent $\gamma = 1$) as $\rho \to \rho_0^{-1}$ for both hard discs and hard spheres. This was precisely the conclusion drawn by Baram and Luban (1979).

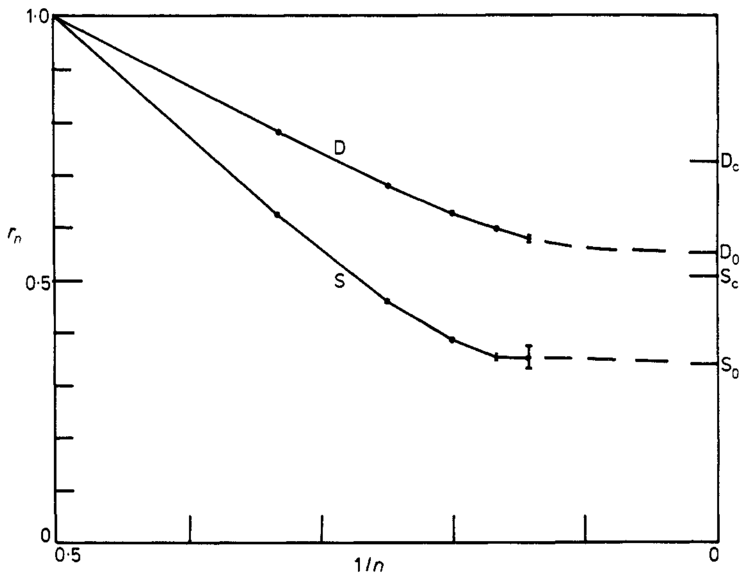

Figure 1. The ratios r_n plotted against $1/n$ for hard discs (D) and hard spheres (S).

However, it is clear that the curves in figure 1 are open to alternative interpretations. For example, even if they do approach D_0 and S_0, a more careful ratio analysis makes it appear unlikely that the limiting slope is zero, especially in the case of hard discs. Thus, calculating successive estimates, γ_n, of the exponent γ from $\gamma_n = 1 + n[(r_n/r_\infty) - 1]$, we find 1·938, 1·684, 1·490 and 1·329 for $n = 4$ to 7, and these are decreasing too rapidly for $\gamma = 1$ to be the likely limit. As a second possibility, one might try using N-shifts (Gaunt and Guttmann 1974) to remove the curvature that is apparent in the curve for hard discs by plotting against $1/(n+N)$ with $N = -1, -2, -3, \ldots$. Such an approach yields an intercept around 0·5 corresponding to a divergence at an unphysical density of about $1{\cdot}10\rho_0$ with an exponent $\gamma \simeq 1{\cdot}7$. For hard spheres, r_7 is rather uncertain but if the true value were to lie at the lower end of the error bar, then a similar conclusion might be drawn here. In this case, the divergence would be at $\rho \simeq 1{\cdot}18\rho_0$ with again $\gamma \simeq 1{\cdot}7$. These results, indicating a divergence at a physically unrealisable density and with an exponent $\gamma > 1$, are reminiscent of ones obtained by various approximate treatments such as the scaled-particle theory (Reiss *et al* 1959), and the Percus–Yevick (Thiele 1963) and Carnahan–Starling (1969) equations of state. If, on the other hand, the true value of r_7 for hard spheres is around the centre or towards the upper end of the error bar, then the curve may either have passed or is about to pass through a minimum. What would happen then is, of course, highly conjectural but it would, for example, be possible for the curve to approach S_c, corresponding to the transition density. If the curve for hard spheres does have a minimum around $n = 7$, then the corresponding curve for hard discs might exhibit one for slightly larger values of n. This kind of occurrence, in which the same sort of qualitative feature is exhibited by a system in both two and three dimensions but is 'seen' sooner for the three-dimensional system, is quite common. For example, the sixth virial coefficient for a fluid of hard parallel orientated cubes is known to be negative (Hoover and De Rocco 1962), whereas extrapolation (Gaunt, unpublished) suggests that the corresponding coefficients for orientated squares (Hoover and De Rocco 1962) do not become negative until $n = 9$ or 10.

Now let us examine the virial expansions for some lattice analogues of the above continuum models. The simplest possibility is a hard-core lattice gas in which the interaction potential between two atoms is infinite if the atoms occupy the same or nearest-neighbour sites of the lattice. This model has been studied numerically by Gaunt and Fisher (1965) and by Gaunt (1967) using low- and high-density series expansions. For the triangular lattice, Gaunt (1967) concluded that the fluid of hard hexagons undergoes a continuous (rather than first-order) transition to an ordered state at a point where the activity z and density ρ are given by

$$z_c = 11{\cdot}05 \pm 0{\cdot}15, \qquad \rho_c/\rho_0 = 0{\cdot}832 \pm 0{\cdot}008, \tag{2}$$

where the close-packing density $\rho_0 = \frac{1}{3}$. Very recently, Baxter (1980) has found the exact solution to this problem and this yields

$$\begin{aligned} z_c &= (11 + 5\sqrt{5})/2 = 11{\cdot}090\,16\ldots \\ \rho_c/\rho_0 &= 3(5 - \sqrt{5})/10 = 0{\cdot}829\,17\ldots. \end{aligned} \tag{3}$$

We have used the exact solution to derive the following virial expansion through order ρ^{24}:

$$\begin{aligned} \Gamma(\rho) = \rho &+ 3\tfrac{1}{2}\rho^2 + 10\tfrac{1}{3}\rho^3 + 28\tfrac{3}{4}\rho^4 + 78\tfrac{1}{5}\rho^5 + 206\tfrac{1}{6}\rho^6 + 504\tfrac{1}{7}\rho^7 + 1019\tfrac{3}{8}\rho^8 + 923\tfrac{4}{9}\rho^9 \\ &- 6254\tfrac{3}{10}\rho^{10} - 55\,709\tfrac{10}{11}\rho^{11} - 313\,295\tfrac{11}{12}\rho^{12} - 1497\,875\tfrac{12}{13}\rho^{13} \\ &- 6543\,419\tfrac{1}{2}\rho^{14} - 26\,835\,701\tfrac{14}{15}\rho^{15} - 104\,484\,570\tfrac{5}{16}\rho^{16} \\ &- 387\,395\,897\tfrac{16}{17}\rho^{17} - 1363\,590\,949\tfrac{5}{18}\rho^{18} - 4509\,026\,459\tfrac{18}{19}\rho^{19} \\ &- 13\,675\,297\,630\tfrac{3}{4}\rho^{20} - 35\,864\,768\,558\tfrac{11}{21}\rho^{21} - 66\,222\,040\,160\tfrac{15}{22}\rho^{22} \\ &+ 37\,406\,582\,958\tfrac{1}{23}\rho^{23} + 1279\,147\,832\,226\tfrac{1}{24}\rho^{24} + \ldots. \end{aligned} \tag{4}$$

Gaunt (1967) derived this expansion through ρ^8, to which order the coefficients are all positive, and conjectured that some higher-order terms must be negative. We see from (4) that B_{10} is, in fact, the first of 13 negative coefficients. These are followed by a sequence of positive coefficients, then negative coefficients, and so on. This behaviour is caused by a pair of singularities in the complex ρ-plane at

$$\rho = 0{\cdot}234\,86\ldots \pm i0{\cdot}056\,04\ldots. \tag{5}$$

These unphysical singularities are the closest ones to the origin $\rho = 0$ and therefore determine the radius of convergence of the virial expansion as

$$\rho_r/\rho_0 = 0{\cdot}724\,36\ldots. \tag{6}$$

The physical singularity at ρ_c lies just (14·5%) outside the circle of convergence. A detailed exact analysis of the singularity structure of the virial series and its analytic continuations in the ρ-plane has been carried out by one of us (Joyce, to be published).

The ratios r_n for hard hexagons are plotted against $1/n$ in figure 2 (curve T) for $n \leqslant 9$. For $n \leqslant 5$ the curve is similar to the one for hard discs, i.e. it is slightly concave-up and so may be extrapolated linearly against $1/n$ by using N-shifts. This gives an intercept which corresponds to an apparent singularity at an unphysical density of $\rho \simeq 1{\cdot}15\rho_0$ with an exponent γ between 1·0 and 1·2. The main way in which it differs from the curve for hard discs is that by $n = 5$ the ratios r_n are already well below T_0 making it seem rather unlikely that the curve approaches, with zero slope, a point corresponding to a singularity at the close-packing density. Nevertheless, the similarities between the curves for hard discs and hard hexagons for $n \leqslant 5$ are worth noting, as is the abrupt and unheralded change in behaviour for hard hexagons when $n > 5$. The curvature changes from being concave-up to concave-down, and the ratios fall rapidly towards zero, changing sign at $n = 10$. Similar behaviour (see also figure 2, curve F) is found in three dimensions for the face-centred cubic lattice (Gaunt 1967) for which the curvature of the plot changes for $n > 4$ and the first negative virial coefficient is B_7. For

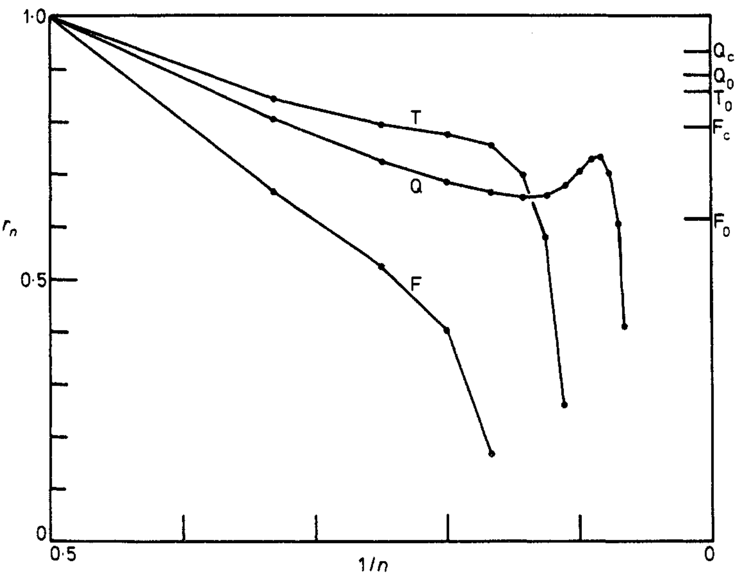

Figure 2. The ratios r_n plotted against $1/n$ for lattice-gases with first-neighbour exclusions on the triangular (T) lattice (i.e. hard hexagons) and the face-centred cubic (F) lattice, and with exclusions extending over both first- and second-neighbour sites of a square (Q) lattice.

the square, simple cubic and body-centred cubic lattices, the virial coefficients change sign even sooner (Gaunt and Fisher 1965, Gaunt 1967). In view of the similarities between the lattice and continuum problems there can be no certainty that sooner or later similar behaviour will not occur for hard discs and/or spheres. In other words, with so few terms available, it is dangerous to assume that the virial coefficients for discs and/or spheres do not become negative. As mentioned earlier, they are known to do so for another continuum model, namely, hard parallel orientated cubes, while for orientated squares the possibility is virtually certain on the basis of numerical extrapolation. However, it is only fair to point out that the curves which are the analogues of those in figure 1 are concave-down right from the very beginning ($n \geqslant 2$) for orientated squares and cubes.

The possibility of negative virial coefficients for hard discs and spheres was suggested by considering the analogous lattice models. As already discussed, other possibilities are apparent from a consideration of figure 1. One of those possibilities was that the curve for hard spheres either has passed or is about to pass through a minimum. Such behaviour is not unknown for a lattice model of a hard-core fluid, namely, a hard-square lattice gas in which the infinite repulsive forces extend over both first- and second-neighbour sites of a square lattice. This model may exhibit a third-order transition (Bellemans and Nigam 1967, Ree and Chesnut 1967) at a density $\rho_c/\rho_0 = 0{\cdot}953 \pm 0{\cdot}002$, where the close-packing density $\rho_0 = \frac{1}{4}$. The virial coefficients have been calculated by Van Craen *et al* (1968) through $n = 16$ and the ratios r_n are plotted against $1/n$ in figure 2 (curve Q). Once again, the curve for $n \leqslant 7$ is slightly concave-up and extrapolation using N-shifts suggests a divergence at an unphysical density of $\rho \simeq 1{\cdot}38\rho_0$ with an exponent $\gamma \simeq 1$. In fact, subsequent coefficients reveal that the ratios pass through a minimum at $n = 7$. The behaviour of the next few ratios ($8 \leqslant n \leqslant 11$) suggests the possibility of a limit close to either Q_c or Q_0, corresponding to the densities ρ_c and ρ_0, respectively. However, at $n = 12$ the ratios exhibit a maximum, after which they decrease rapidly changing sign at $n = 16$ corresponding to B_{16} being negative. Such behaviour demonstrates very strikingly the dangers inherent in any attempt to extrapolate the leading terms of a virial expansion.

So far we have not examined any of the lattice models which are expected to exhibit, in common with hard discs and spheres, a first-order phase transition. Of these, the triangular lattice gas with exclusions extending up to second neighbours (Orban and Bellemans 1968) behaves like the models of orientated squares and cubes, i.e. the ratio plot is concave-down right from the very beginning, first becoming negative at $n = 7$. If the exclusion range extends to third or fourth neighbours (Orban and Bellemans 1968), then the ratio plots are initially concave-up but change to concave-down at $n = 7$ and $n = 6$, respectively, the last known coefficient in each case. This behaviour is reminiscent of that seen in figure 2 for hard hexagons (first-neighbour exclusions only) and suggests that the virial coefficients for these higher-neighbour exclusion models may soon become negative. The square lattice model with exclusions extending up to third neighbours also exhibits a first-order transition. Here the ratio plot is concave-up for all known n, although the virial coefficients are only available through B_5 (Bellemans and Nigam 1967). For any of these lattice models displaying a first-order phase transition it would clearly be very dangerous to speculate, on the basis of such short series, about the asymptotic behaviour of the virial coefficients.

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