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ON THE DIVERGENCY OF THE EQUATION OF STATE OF THE HARD-SPHERE FLUID AT HIGH DENSITIES

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The possible existence and situation of a singularity in the equation of state of the hard-sphere fluid at high densities is analysed from the existing simulation data, the known virial coefficients and Padé approximants. The convenience of introducing a prefixed pole in obtaining approximants for the equation of state of the hard-sphere fluid on the basis of the virial expansion is also discussed.

KEY WORDS: Hard spheres, equation of state, Padé approximants, singularities, phase transitions, Kauzmann paradox.

INTRODUCTION

In spite of its simplicity, the hard-sphere system is of great interest, since it presents several common features with real fluids. For example, as shown by simulation data, the hard-sphere system presents a gaseous state¹, a crystalline state², and several glassy states³. In addition, the hard-sphere fluid is the most common reference system in perturbation theories of fluids⁴, which requires the knowledge of an accurate analytical equation of state of the reference fluid, especially in the high density region.

For the hard-sphere fluid there has been a considerable amount of work devoted to the obtention of the virial expansion of the equation of state. However, the higher virial coefficients are difficult to calculate and, for this fluid, only the first seven are known. A question which arises is whether information about other phases, such as glass or solid, can be obtained from the known terms of the virial series of the fluid. This question is intimately related to some aspects such as instabilities and divergencies of the equation of state at close packing.

Several attempts have been made^{5–10} in order to determine instabilities and divergencies starting from the virial expansion. However, results seem to be contradictory. Some of them predicts instabilities whereas some others predicts divergencies for different values of close packing corresponding to either glass or solid. The aim of this work is to clarify these issues analyzing the problem from several viewpoints.

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THE EQUATION OF STATE OF THE HARD-SPHERE SYSTEM FROM SIMULATION DATA

Since the pioneering work of Metropolis *et al.*¹¹ much work has been devoted to the study of the equilibrium properties of the hard-sphere system. Thus, the equation of state of the fluid has been accurately determined¹ in the range $1.6 \leq V/V_0 \leq 25$, where $V_0 = N\sigma^3/\sqrt{2}$ is the closest packing volume for spheres of diameter σ , by means of 4000 particles simulations. The results are well reproduced by means of the well-known Carnahan-Starling (CS) equation of state¹²:

$$Z = \frac{PV}{NkT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (1)$$

where $y = Nv_m/V$ is the packing fraction for spheres of volume $v_m = \pi\sigma^3/6$.

The equation of state of the solid has been determined² in the range $1.005 \leq V/V_0 \leq 1.42$ by means of molecular dynamics simulation of 108 to 4000 face-centered hard spheres. The data are well reproduced by means of the expression¹³:

$$Z = \frac{3}{\alpha} + 2.566 + 0.55\alpha - 1.19\alpha^2 + 5.95\alpha^3 \quad (2)$$

where $\alpha = (V - V_0)/V_0$. The melting and freezing densities have also been determined¹³ and correspond to values of V/V_0 of 1.352 and 1.495, respectively.

Of special interest to us is the 512-particle molecular dynamics simulations of Woodcock³ for reduced densities $\rho^* = N\sigma^3/V > 0.943$, the normal freezing density. His data show that the system remains fluid at metastable equilibrium in the density range $0.943 < \rho^* < 1.085$. At this latter density the system unavoidably crystallises spontaneously, since the time for homogeneous nucleation is lower than the time necessary for the equilibration of the fluid. Of course crystallisation can also take place at any density in the metastable range. In this region, the equation of state of the fluid is also well reproduced by means of the CS equation (1).

In the same work, an amorphous or glassy (non-equilibrium) solid was obtained by means of rapid quenching (thus avoiding crystallisation) of the fluid at an initial reduced density of $\rho^* = 1.085$. The amorphous solid was shown to have a residual volume of $V_a^0 = 1.129V_0$, and its equation of state is well reproduced by means of the self-consistent free volume equation of state¹⁴:

$$Z = [1 - (V_0/V)^{1/3}]^{-1} \quad (3)$$

provided that the close packing volume V_0 is substituted by the above mentioned residual volume V_a^0 .

Another glassy state was obtained³ in a similar way as the preceding but starting from the fluid at the normal freezing density $\rho^* = 0.943$. The resulting residual volume was $V_a^B = 1.163V_0$, which corresponds to the so-called Bernal density^{15,16}

The fact that the hard-sphere fluid undergoes a phase transition, at sufficiently high densities, either to a crystalline solid or to an amorphous solid is a necessary condition. This is due to Kauzmann's paradox¹⁷, according to which, if the entropy of a high density fluid can be extrapolated indefinitely towards increasing densities, then it would finally become lower than that of the crystalline solid thus violating the third principle of thermodynamics.

Although it has been pointed out¹⁸ that some of the simulation data of Woodcock in the metastable fluid region do not correspond to a fully equilibrated system, his results seem to indicate that there is no singularity in the equation of state of the hard-sphere fluid, since the system undergoes a phase transition either to a crystalline or to a glassy state, before reaching any pole. Obviously, the pressure in this latter states presents divergencies at the close packing densities corresponding to the residual volumes previously mentioned. However, it should be noted that these states are different from the fluid state, and such poles must not be attributed to the fluid.

THE EQUATION OF STATE OF THE HARD-SPHERE FLUID FROM THE VIRIAL EXPANSION

The compressibility factor Z of a fluid can be expressed as a series expansion in powers of the density, the virial expansion, in the form:

$$Z = 1 + \sum_{i=2}^{\infty} B_i \rho^{i-1} \quad (4)$$

As we mentioned previously, for the hard-sphere fluid only the first seven coefficients of this expansion have been determined from first principles (the last three with some uncertainty). They are¹⁹:

$$\begin{aligned} B_2 \equiv b &= \frac{2}{3}\pi\sigma^3, & B_3/b^2 &= 5/8, & B_4/B^3 &= 0.28695, \\ B_5/b^4 &= 0.110252 + 0.000001, & B_6/b^5 &= 0.0389 \pm 0.0004, \text{ and} \\ B_7/b^6 &= 0.0137 \pm 0.0006 \end{aligned} \quad (5)$$

The most frequently suggested poles for the equation of state of the hard-sphere fluid are the regular close packing density, corresponding to a volume V_0 or a packing fraction $y_0 = 0.74048$, and the Bernal density, corresponding to a volume $V_a^B = 1.163V_0$, or packing fraction $y_B = 0.6366$. Hoste and Van Dael²⁰ have drawn for $y = y_0$ and $y = y_B$ the inverse of the compressibility factor Z , as determined by the virial expansion (4), with $y = \rho^*\pi/6$, as a function of n^{-1} , where n is the number of virial coefficients considered. By visual extrapolation they obtain evidence that for $n = \infty$ the value of Z^{-1} may be zero for $y = y_0$, but not for $y = y_B$.

However, theoretical equations of state such as the Thiele²¹ and Wertheim²² solutions of the Percus-Yevick equation or the scaled particle theory²³ predict poles

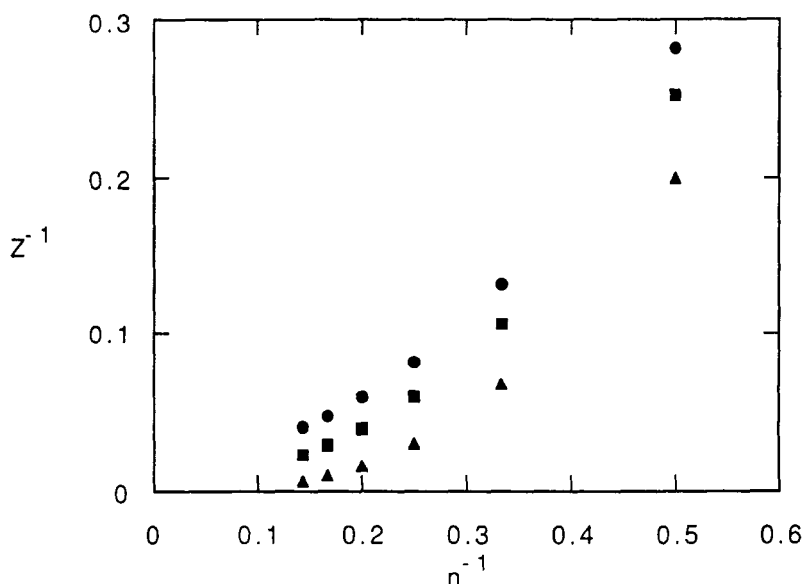


Figure 1 Inverse of the compressibility factor Z as a function of the inverse of the number n of terms considered in the virial equation of state (4) at densities corresponding to different possible poles. Circles: for random close packing density or Bernal density; squares: for regular close packing density; triangles: for the density $\rho = (6/n)\sigma^{-3}$, corresponding to packing fraction $y = 1$.

at $y = 1$, as does the Carnahan-Starling equation (1). Although this is an unrealistic pole, it being impossible to completely fill space with spheres, we have also considered this possibility.

In Figure 1 we have plotted Z^{-1} from (4) and (5) as a function of n^{-1} for the three packing fractions mentioned. It is clear that any extrapolation towards $n = \infty$ is uncertain. Moreover, if we accept that Z^{-1} approaches to zero as n increases towards infinite for $y = y_0$, this occurs more clearly for the unrealistic value $y = 1$, as Figure 1 shows. On the other hand, we must take into account that we cannot prejudge what would happen if more virial coefficients were known. In this sense, although estimated values of the virial coefficients B_8 to B_{10} have been obtained¹ from the expansion of an accurate equation of state, they must be considered with some caution, since different equations of state will lead to different estimations¹⁹.

The preceding discussion is based on the assumption that the compressibility factor must become infinite for a certain value of the packing fraction. However, if the equation of state presents an instability leading to a phase transition at high densities, as seems to be the case from the simulation data analyzed in the previous section, the compressibility coefficient, and consequently the slope of the pressure, must become negative. Consequently, the pressure and the compressibility factor must present a maximum and a plot such as that of Figure 1 should exhibit a minimum if a sufficiently large number n of virial coefficients were considered.

Thus, the direct analysis of the truncated virial expansion seems to be meaningless.

THE EQUATION OF STATE OF THE HARD-SPHERE FLUID FROM PADE APPROXIMANTS

Since the virial expansion (4) converges slowly, certain types of approximants have been proposed with the aim of accelerating the convergency of that series. One of the most widely used methods is that of Padé approximants²⁴. The $[L/M](y)$ Padé approximant for the compressibility factor Z is a quotient of polynomials of the form:

$$Z \equiv [L/M](y) = \frac{1 + p_1 y + p_2 y^2 + \cdots + p_L y^L}{1 + q_1 y + q_2 y^2 + \cdots + q_M y^M} \quad (6)$$

with the condition that $L + M \leq n - 1$, where n is the number of known virial coefficients. The undetermined coefficients p_i and q_i are obtained from the condition that the expansion of (6) in power series of y must reproduce the first $L + M + 1$ virial coefficients.

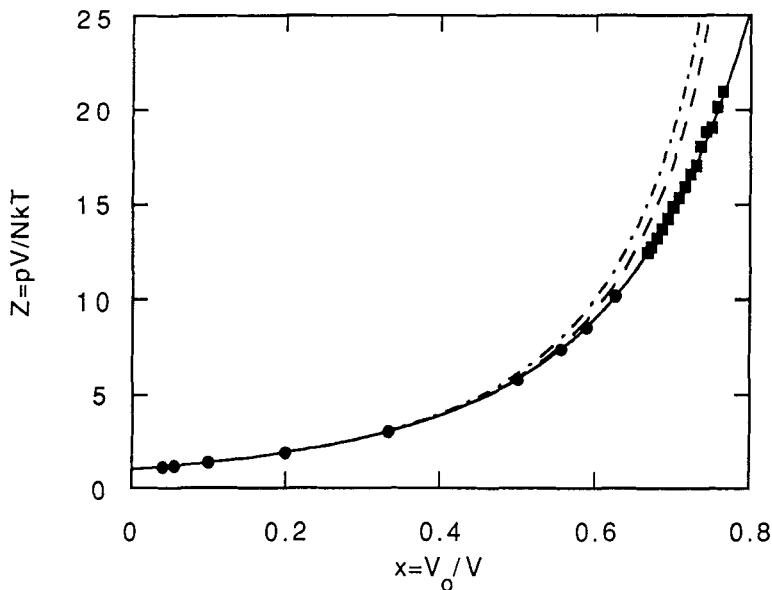


Figure 2 Compressibility factor Z for the hard-sphere fluid as a function of the density in units of the close packing density $x = \rho/\rho_0 = V_0/V$. Circles: simulation data for the stable fluid, from Ref. 1. Squares: simulation data for metastable fluid from Ref. 3. Dash-dotted line: $[3/1]$ Padé approximant. Dashed line: $[2/4]$, $[2/3]$ and $[3/3]$ approximants (nearly indistinguishable at the scale of the figure). Continuous line: $[2/4]$ and $[3/3]$ approximants with the values of B_6 and B_7 given in Table 1 (all of these approximants are indistinguishable at the scale of the figure).

Extensive studies on the behaviour of the Padé approximants for the equation of state of the hard-sphere fluid have been made by Aguilera *et al.*^{6,7}. From the analysis of the approximants [2/4], [2/3], [3/1] and [3/3] divergencies for values of y close to y_B were obtained⁶. They consider y_B to be the correct packing fraction for the divergency of the pressure of the hard-sphere fluid and suggest this result as a criterion for the goodness of an equation of state for this fluid. However, as we can see in Figure 2, none of these approximants reproduce the simulation data^{1,3} at high densities with enough accuracy. Consequently, from the preceding results we cannot ensure that the equation of state diverges at packing fraction y_B .

On the other hand, the analysis of the approximants [0/2], [1/2], [0/3], [0/5], [1/5] and [0/6] revealed⁷ maximums in the pressure for increasingly higher densities reaching for the [0/6] approximant a value of $\rho^* = 1.033$, corresponding to $V/V_0 = 1.369$, in reasonable agreement with the value $V/V_0 = 1.352$ obtained¹³ for the freezing volume as mentioned previously. However, as Figure 3 shows, all these approximants are far from accurately reproducing the simulation data for the equation of state at high densities. Nevertheless, these results seem to be promising since the accuracy increases as the value of $L + M$, or equivalently the number $n = L + M + 1$ of virial coefficients, considered for obtaining the approximant increases. However, in order to obtain enough accuracy, and thus conclusive results, it probably would be necessary to know much more virial coefficients.

We can make a more reliable analysis from the work of Erpenbeck and Wood¹ who fitted the values of B_6 and B_7 , within their uncertainty, on the basis of the best

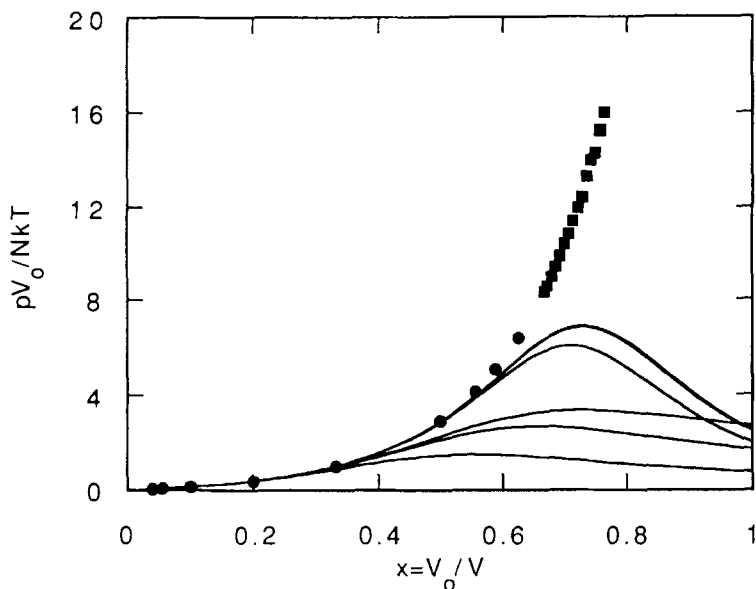


Figure 3 Pressure of the hard-sphere fluid in units of NkT/V_0 as a function of $x = V_0/V$. Lines from top to down: approximants [0/6] and [1/5] (nearly indistinguishable at the scale of the figure), [0/5], [0/2], [0/3] and [1/2]. Points: simulation data as in Figure 2.

Table 1 Fitted values of the two higher virial coefficients for the [3/3] and [4/2] Padé approximants, from Ref. 1.

Approximant	B_6/b^5	B_7/b^6
[3/3]	0.039009	0.013060
	0.039000	0.013056
[4/2]	0.038996	0.013067
	0.038989	0.013063

fitting of the [4/2] and [3/3] Padé approximants to their simulation data. For each of these two approximants they give two sets of values for B_6 and B_7 , listed in Table 1, which agree to four decimal figures with those of (5) within uncertainty. The optimal choice is the [4/2] approximant with $B_6/b^5 = 0.0390$ and $B_7/b^6 = 0.01307$. When we use the fitted values of Table 1 for B_6 and B_7 in conjunction with the corresponding [3/3] or [4/2] Padé approximants, we obtain that none of them predict poles in the range $0 \leq y \leq 1$. Instead, they predict maxima for the pressure at packing fractions around $y = 0.88$ (or $x = V_0/V = 1.19$). Moreover, although the fittings were made to simulation data corresponding to the stable fluid ($\rho^* \leq 0.943$ or $x < 0.667$), these approximants are very accurate for the whole range of densities, including the metastable fluid ($0.943 < \rho^* < 1.085$ or $0.667 < x < 0.767$), as Figure 2 shows.

DISCUSSION

From the direct analysis of the virial series made in the second section of this work, it seems difficult to reach conclusions about the possible existence and situation of a pole in the equation of state of the hard-sphere fluid. On the other hand, the simulation data indicate an unavoidable phase transition before any pole is reached. Finally, the more accurate Padé approximants present maxima for the pressure better than poles. This means that the fluid becomes unstable at high densities and must undergo a phase transition, presumably to a solid, in agreement with the simulation data. However, it is to be noted that the packing fraction $y \approx 0.88$ at which the maxima appear corresponds to a density $\rho^* = 1.68$, much higher than the density $\rho^* = 1.085$ at which crystallisation unavoidably occurs, according to the simulation data. Probably the location of the instability point would approach the simulation value if more virial coefficients were known and the corresponding approximants were obtained from them.

It remains unexplained why the CS equation is so accurate for all densities in spite of the fact that it predicts a singularity at the unrealistic packing fraction $y = 1$. That is, according to the CS equation, hard spheres seems to ignore packing effects other than the proper volume of the spheres until crystallisation occurs. It has been shown²⁵ that the $y = 1$ pole in this equation arises from the assumption that the motions of a particle in different directions are uncorrelated. Of course, this must not be confused

with the uncorrelation in the movement of different particles, which is only true at low densities.

The CS equation is obtained¹² from the expansion of the compressibility factor Z in terms of the packing fraction y . The corresponding virial coefficients are approached to their nearest integers and a recurrence formula is obtained for the approximate virial coefficients. After substitution of the recurrence formula in the virial expansion, the summations involved in the virial series can be performed from the properties of the geometrical series and their derivatives, resulting finally in the CS equation (1).

It is to be noted that, as a consequence of the method employed in its obtention, the virial coefficients B_4 and B_5 are not reproduced exactly by the CS equation. Thus, the excellent accuracy of this equation seems to be somewhat fortuitous. Although, in obtaining equations of state for the hard-sphere fluid from approximants, it may be convenient to prefix a pole at $y = 1$, as in the Carnahan-Starling equation (1). This is the case for generalized approximants recently proposed by the authors²⁶. Some of them, in addition to reproducing exactly all known virial coefficients, provide excellent accuracy with simulation data for the whole density range.

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