

# Thermodynamic pressures for hard spheres and closed-virial equation-of-state

Marcus N. Bannerman,<sup>1</sup> Leo Lue,<sup>1,a)</sup> and Leslie V. Woodcock<sup>1,2,b)</sup>

<sup>1</sup>*School of Chemical Engineering and Analytical Science, The University of Manchester, P.O. Box 88, Sackville Street, Manchester M60 1QD, United Kingdom*

<sup>2</sup>*Colburn Laboratory, University of Delaware, Newark, Delaware 19716, USA*

(Received 14 January 2010; accepted 2 February 2010; published online 23 February 2010)

Hard-sphere molecular dynamics (MD) simulation results, with six-figure accuracy in the thermodynamic equilibrium pressure, are reported and used to test a closed-virial equation-of-state. This latest equation, with no adjustable parameters except known virial coefficients, is comparable in accuracy both to Padé approximants, and to numerical parameterizations of MD data. There is no evidence of nonconvergence at stable fluid densities. The virial pressure begins to deviate significantly from the thermodynamic fluid pressure at or near the freezing density, suggesting that the passage from stable fluid to metastable fluid is associated with a higher-order phase transition; an observation consistent with some previous experimental results. Revised parameters for the crystal equation-of-state [R. J. Speedy, *J. Phys.: Condens. Matter* **10**, 4387 (1998)] are also reported. © 2010 American Institute of Physics. [doi:10.1063/1.3328823]

## I. INTRODUCTION

Since van der Waals first modified the ideal gas equation to obtain his “second-virial” equation-of-state for the dilute gas of hard spheres, there have been many predictions of the hard-sphere equation-of-state. Theoretical equations, while yielding some physical insight into the behavior of hard-sphere systems, have all proven to be inaccurate when tested against computer experimental data. An essential starting point for an ultimate equation-of-state of the hard-sphere fluid is the known virial series. The expansion of pressure  $p$  in powers of density  $\rho$  for the fluid equation-of-state of hard spheres is

$$Z = 1 + b_2\rho + b_2\rho^3 + \dots + b_n\rho^{n-1} + \dots, \quad (1)$$

where  $Z = p/(\rho k_B T)$  is the compressibility factor,  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature,  $b_n$  is the  $n$ th virial coefficient, and  $\rho$  is the sphere number density ( $N/V$ ). Exact analytical expressions for the third and fourth virial coefficients were derived by Boltzmann,<sup>1</sup> and higher coefficients have now been computed numerically up to the tenth.<sup>2-14</sup> The numerical virial coefficients  $b_5$  to  $b_9$  were recalculated more accurately by Kolafa and co-workers<sup>12,13</sup> and also re-evaluated by Clisby and McCoy.<sup>2,14</sup> All their values, which we utilize here (Table I) are within the uncertainties quoted in Table V of Labik *et al.*<sup>13</sup>

Despite these efforts, the virial expansion truncated at the tenth virial coefficient is still not sufficient to accurately estimate the pressure when approaching the freezing transition. Many techniques have been used to attempt to estimate the contribution of the higher virial coefficients. Padé approximants, first used by Ree and Hoover,<sup>3</sup> are the most commonly used. These approximants utilize a rational func-

tion to exactly reproduce the known virial coefficients and provide a closed estimate for the remaining terms. The most recent attempt by Clisby and McCoy<sup>2,14</sup> to determine the pressure equation of the extended virial series utilizes all ten known coefficients. The predictions of these approximate methods cannot be tested without comparing to molecular dynamics (MD) simulation results for the thermodynamic pressures of very large systems. Recently, Kolafa *et al.*<sup>12</sup> performed a comparison using simulations of 13 500 spheres. They carefully studied the errors introduced by the use of periodic boundary conditions and simulation ensembles and duly corrected for finite size effects. The determination of some known virial coefficients to higher accuracy, and the calculation of the tenth virial by Clisby and McCoy<sup>2,14</sup> have prompted further developments on the equation-of-state.<sup>15-17</sup>

A new closed virial equation-of-state has been recently proposed for spheres and disks<sup>15,16</sup> based on the empirical observation that the higher known virial coefficients appear to be decreasing linearly. This implies that the difference  $B_n - B_{n+1}$  approaches a constant as  $n$  approaches infinity; in this case all higher virial coefficients are predictable from the known coefficients and the infinite series can be closed analytically.<sup>16</sup> Preliminary comparisons of this latest equation-of-state for hard spheres show it be extremely accurate, i.e., to within the uncertainty of prevailing thermodynamic pressure data from MD simulations. All previous theoretical and empirical hard-sphere fluid equations-of-state are reviewed recently by Mulero *et al.* in Ref. 18. In more than 100 years since van der Waals, more than a hundred different hard-sphere fluid equations have been proposed. Many analytic equations have poles at the physically unrealistic 100% packing fraction. Such theoretical equations,<sup>18</sup> as suggested by scaled-particle theory, Percus–Yevick theory, the hypernetted chain equations, and many empirical equa-

<sup>a)</sup>Electronic mail: leo.lue@manchester.ac.uk.

<sup>b)</sup>Electronic mail: woodcock@udel.edu.

TABLE I. Known virial coefficients of the hard-sphere fluid.

$n$	$b_n/b_2^{n-1}$	$B_n$	$B_n - B_{n-1}$
2	1.000 000 00	2.961 921	...
3	0.625 000 00	5.483 111	2.521 190
4	0.286 949 50	7.456 345	1.973 234
5	0.110 252 10	8.485 568	1.029 223
6	0.038 881 98	8.863 719	0.378 154
7	0.013 023 54	8.793 670	-0.070 049
8	0.004 183 20	8.366 104	-0.427 566
9	0.001 309 40	7.756 405	-0.609 699
10	0.000 403 50	7.079 543	-0.676 822

tions such as the ubiquitous Carnahan–Starling. A discussion and summary of these equations can be found elsewhere.<sup>18,19</sup> None, however, can be potentially exact because they can never represent all the known virial coefficients precisely. One only has to look at the complexity of the highest analytic coefficient ( $b_4$ ) to see that the ultimate virial equation-of-state must incorporate the known virial coefficients explicitly.

Other authors<sup>19,20</sup> suggest the first pole is in the vicinity of the close packed density,  $\rho_0$ . Wang and Khoshkbarchi<sup>19</sup> parameterized closures of the form  $(1 - \rho/\rho_0)^{-n}$ , for values of  $n=1, 2$ , and  $3$ , but all three of their parameterized Eqs. (14–16 of Ref. 19) all begin to fail at the eighth virial coefficient by errors of the order 10%. Mulero and co-workers<sup>18,20</sup> also proposed an equation with the pole should be at  $\rho_0$  maximum packing fraction  $y_0 = \pi\rho_0\sigma^3/6 = 0.7405$  which they approximate to  $3/4$  and modify the Carnahan–Starling equation accordingly. The equation proposed by Yelash *et al.*,<sup>20</sup> however, is no more accurate than the Carnahan–Starling itself at equilibrium densities (see below), as their fifth, sixth, and seventh virial coefficients are all too high by around 10%.

There is now a need for more precise MD data to test more rigorously these approximate equations-of-state including the one proposed here. Recently, a new event-driven MD package has been developed,<sup>21,22</sup> namely DYNAMO, which allows the simulation of previously unattainable system sizes with up to six-figure accuracy. Using results from DYNAMO we are now able to apply a more rigorous test of the latest equations-of-state than was hitherto possible.

## II. VIRIAL EQUATION-OF-STATE

Computed numerical values of the  $n$ th virial coefficients are often presented as a dimensionless ratio of  $b_n/b_2^{n-1}$ , where  $b_2$  is the second virial coefficient, first determined by van der Waals to be  $b_2 = 2\pi\sigma^3/3$ . These values for all the known virial coefficients from Clisby and McCoy<sup>2,14</sup> are given in Table I. Also shown in Table I are the coefficients in powers of density relative to close packing which are more amenable to an analytic closure if the virial series is convergent for all densities up to the first pole at maximum packing  $\rho_0$ .<sup>15</sup>

Where there are no physical insights to go on, one way to mathematically extrapolate beyond the truncated virial se-

ries is to use a Padé approximant. Clisby and McCoy<sup>2,14</sup> have fitted approximants to the first ten virial coefficients. These take the forms

$$Z_{\text{CM Padé}}(5,4) = \frac{1 + C_{1a}\rho + C_{2a}\rho^2 + C_{3a}\rho^3 + C_{4a}\rho^4 + C_{5a}\rho^5}{1 + C_{6a}\rho + C_{7a}\rho^2 + C_{8a}\rho^3 + C_{9a}\rho^4} \quad (2)$$

and

$$Z_{\text{CM Padé}}(4,5) = \frac{1 + C_{1a}\rho + C_{2a}\rho^2 + C_{3a}\rho^3 + C_{4a}\rho^4 + C_{5a}\rho^5}{1 + C_{6a}\rho + C_{7a}\rho^2 + C_{8a}\rho^3 + C_{9a}\rho^4}. \quad (3)$$

Numerical values of all the constants are given in the original paper by Clisby and McCoy.<sup>2,14</sup> Also given here in Table I are the values of the known virial coefficients, when the virial expansion is expressed in powers of the density relative to the maximum density of the closest packed crystalline state  $\rho_0 = 2^{1/2}\sigma^{-3}$ .

$$Z = 1 + B_2(\rho/\rho_0) + B_3(\rho/\rho_0)^2 + \cdots + B_n(\rho/\rho_0)^{n-1} + \cdots. \quad (4)$$

The  $B_n$  and  $b_n$  are related by

$$B_n = b_n\rho_0^{n-1}. \quad (5)$$

In the third column of Table I, we give the differences between consecutive virial coefficients. It has been observed<sup>15</sup> that, in this expansion, the difference  $B_n - B_{n-1}$  becomes constant. This has enabled the derivation of a closed analytic equation-of-state based only upon the known virial coefficients.<sup>15,16</sup> This closure of Eq. (2) assumes that  $B_n - B_{n-1}$  for  $n > 9$  is approaching a constant, and utilizes the extrapolated higher virials  $B_{11}$  and  $B_{12}$  as recommended.<sup>12,13</sup> The virial equation-of-state has been designated WC1 (Ref. 22) and can be written as

$$Z_{\text{WC1}} = 1 + \sum_{n=2}^m B_n(\rho/\rho_0)^{n-1} + (\rho/\rho_0)^m \times \left[ \frac{B_m}{1 - \rho/\rho_0} - \frac{A_1}{(1 - \rho/\rho_0)^2} \right], \quad (6)$$

where  $m=10$  and the constant  $A_1$  was found to be 0.682 19. This closed-virial equation requires only the value of  $A_1$  and the first few known virial coefficients. Equation (6) for hard spheres was found to be as accurate as the most accurate available MD data for the dense fluid.<sup>15</sup> Its derivation can be seen elsewhere, in Ref. 16, where an analogous equation-of-state for two-dimensional disks is also obtained, and found to be of similar accuracy to the three-dimensional case.

Rather than rely on higher virial coefficients, however, which have themselves been fitted numerically to MD data, to obtain the limiting constant, we can determine a value of the constant  $A_1$  in Eq. (6) from explicitly computed known virial coefficients (i.e., up to  $B_{10}$ ). Table I shows the difference approaches a limiting constant ( $A_0$ ) exponentially with  $n$ ; the convergence appears to be almost complete at  $B_{10}$ . Using values only of  $B_7$  to  $B_{10}$ , a plot of the difference between consecutive virial coefficients (see Fig. 1) reveals that

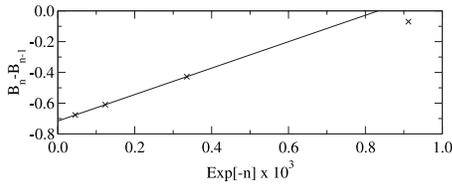


FIG. 1. The differences between the reduced virial coefficients for a hard-sphere fluid. The solid line is the linear fit to the eighth, ninth, and tenth virial coefficients; the intercept  $A_0$  is the limiting value of the constant  $A_2$  in WC2, Eq. (7).

the last three data points conform to an exponential decay, with a correlation coefficient of 0.999 99. If this expression were to accurately represent all higher coefficients, the hard-sphere fluid closed-virial equation, designated WC2,<sup>22</sup> is now

$$Z_{WC2} = 1 + \sum_{n=2}^m B_n (\rho/\rho_0)^{n-1} + (\rho/\rho_0)^m \times \left[ \frac{B_m}{(1-\rho/\rho_0)} - \frac{A_2(\rho)}{(1-\rho/\rho_0)^2} \right], \quad (7)$$

whereupon the constant  $A_1$  in WC1 Eq. (6) becomes  $A_2(\rho)$  in Eq. (7) and can be obtained from the three highest known virial coefficients

$$A_2(\rho) = \frac{e(B_{m+1} - B_m) - (\rho/\rho_0)(B_m - B_{m-1})}{\rho/\rho_0 - e}, \quad (8)$$

where  $B_{m+1}$  is the highest required known coefficient for a specific accuracy; i.e.,  $B_{10}$  at present.  $A_2(\rho)$  is a very weak function of density: It varies from the value of  $A_1$  in WC1 [see Eq. (6)] when  $\rho/\rho_0=0$ , to the limiting constant  $A_0$  when  $\rho/\rho_0=1$ . As  $m$  becomes very large,  $A_1 \rightarrow A_2 \rightarrow A_0$ . It is interesting to note that the constant  $A_0$  is close to the minimum volume per sphere at close packing: i.e.,  $V_0/(N\sigma^3) = 1/(\rho_0\sigma^3) = 2^{-1/2} = 0.7071$ . The value obtained here for  $A_0(0.7158)$  could be  $V_0/(N\sigma^3)$  to within the latitude of uncertainty arising from the computed higher coefficients  $B_8-B_{10}$  (see Fig. 1).

These forms of the equation-of-state predict that the higher-order virial coefficients will eventually go negative giving an unphysical negative pressure at very high density and a negative pole at maximum packing  $\rho_0$ . Interestingly, there are no terms oscillating in sign which are significant in higher dimensions. Following the extrapolation of Eq. (6) or Eq. (7), the virial coefficients beyond  $B_{10}$  are all negative. The higher virial coefficients predicted by WC1 or WC2 are very close to the predictions of the Padé (5,4) approximant of Clisby and McCoy.<sup>2,14</sup>

The new equations-of-state, either WC2 or the simpler version WC1 with the single closure constant  $A$ , can be compared with previous empirical analytical closures, such as the Carnahan–Starling<sup>23</sup> and the numerically parameterized equations-of-state determined by Kolafa *et al.*<sup>12</sup> from their MD simulation data. Carnahan and Starling’s equation-of-state is based on a simple recursion formula for the variation in the virial coefficients when the expansion is expressed in powers of the packing fraction  $y$ . It is usually written

$$Z_{CS} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad (9)$$

where  $y = \pi\rho\sigma^3/6$  and is the packing fraction of the spheres. It is known only to be an approximation for the analytic fourth virial and all higher coefficients. While serving as a useful first approximation, Eq. (9) could never be a true representation of the virial equation-of-state of the equilibrium hard-sphere fluid.

By fitting to both the known virials and their accurate MD data, Kolafa, Laboratoryk, and Malijevsky<sup>12</sup> (KLM) parameterized the equation-of-state data according to

$$Z_{KLMlow} = 1 + 4x + 6x^2 + C_{1l}x^3 + C_{2l}x^4 + C_{3l}x^5 + C_{4l}x^6 + C_{5l}x^7 + C_{6l}x^8 + C_{7l}x^{12} \quad (10)$$

$$Z_{KLMhigh} = 1 + 4x + 6x^2 + C_{1h}x^3 + C_{2h}x^4 + C_{3h}x^5 + C_{4h}x^6 + C_{5h}x^7 + C_{6h}x^8 + C_{7h}x^{14} + C_{8h}x^{22}, \quad (11)$$

where  $x = y/(1 - y)$ ; numerical values for the constants can be found in the paper by Kolafa *et al.*<sup>12</sup> We note that the number of unknown constants in the KLM equations, Eqs. (10) and (11), respectively, are as many as the number of numerically determined virial coefficients used in the WC virial equation-of-state, Eq. (6) or Eq. (7).

Below we report extensive MD simulations so that the closed-virial equations-of-state WC1 and WC2, Eqs. (6) and (7) respectively, can be tested more rigorously, i.e., by comparing the accuracy with that of the numerical equations of Kolafa *et al.*<sup>12</sup> Eqs. (10) and (11) and the Padé approximants of Clisby and McCoy, Eqs. (2) and (3), in the whole stable fluid region. We also compare with the Carnahan–Starling equation-of-state, Eq. (9).

### III. MD SIMULATION

To test the various equations-of-state and to explore the whereabouts of the first phase transition in the hard-sphere fluid, i.e., where the virial equation and the thermodynamic equation-of-state diverge, we have performed new MD simulations. Pressure of hard-sphere systems have been determined to a high degree of precision. The simulation package DYNAMO was used to execute the simulations. Further details of the program and the basic algorithm can be found in Ref. 22.

The simulation data are summarized in Table II. Data with a superscript  $F1$  are from simulations with 1 098 500 spheres started in a fcc lattice, equilibrated for  $2.197 \times 10^8$  collisions, and run for  $8.788 \times 10^8$  collisions; data with a superscript  $F2$  are for 108 000 spheres started in a fcc lattice, equilibrated for  $2.249\,728 \times 10^8$  collisions and run for  $8.998\,912 \times 10^8$  collisions. The data with a superscript  $S1$  and  $S2$  correspond to systems with 1 124 864 and 125 000 spheres, respectively, started in a simple cubic lattice, equilibrated for  $10^8$  collisions, and run for  $10^9$  collisions. Two simulation runs were performed for each system, and estimates of the uncertainty of the data are provided by the standard deviation of the reported values between each simulation run. The pressure was calculated using the collision rate formula<sup>24</sup>

TABLE II. Simulation values for the hard-sphere equation-of-state: Superscripts indicate the initial condition (F=face-centered cubic or S=simple cubic) and system (1 or 2, see text). Values in parenthesis are the standard deviations of the last two digits: state points between  $\rho\sigma^3=0.95$  and 0.995 are on the metastable fluid branch. The state point at  $\rho\sigma^3=1$  is on the metastable solid branch.

$\rho\sigma^3$	$Z_{MD}$	$\rho\sigma^3$	$Z_{MD}$
0.100 <sup>F1</sup>	1.239 724 3(69)	0.850 <sup>S2</sup>	9.118 56(14)
0.150 <sup>F1</sup>	1.385 949 9(44)	0.875 <sup>S2</sup>	9.898 90(38)
0.200 <sup>F1</sup>	1.553 610 9(77)	0.900 <sup>F1</sup>	10.762 95(36)
0.250 <sup>F1</sup>	1.746 288(31)	0.900 <sup>S2</sup>	10.762 50(29)
0.300 <sup>F1</sup>	1.968 242(26)	0.910 <sup>S1</sup>	11.134 01(21)
0.350 <sup>F1</sup>	2.224 609(29)	0.920 <sup>S1</sup>	11.521 73(17)
0.400 <sup>F1</sup>	2.521 648(39)	0.925 <sup>S2</sup>	11.721 837(60)
0.450 <sup>F1</sup>	2.866 821(48)	0.930 <sup>S1</sup>	11.925 85(24)
0.500 <sup>F1</sup>	3.269 361(52)	0.940 <sup>S1</sup>	12.348 79(59)
0.550 <sup>F1</sup>	3.740 700(47)	0.950 <sup>S2</sup>	12.790 55(27)
0.600 <sup>F1</sup>	4.294 94(10)	0.950 <sup>S1</sup>	12.791 33(40)
0.650 <sup>F1</sup>	4.949 678(25)	0.960 <sup>S1</sup>	13.253 95(94)
0.675 <sup>S2</sup>	5.321 49(16)	0.970 <sup>S1</sup>	13.739 66(88)
0.700 <sup>F1</sup>	5.726 86(15)	0.975 <sup>S2</sup>	13.991 2(16)
0.700 <sup>S2</sup>	5.727 007(39)	0.980 <sup>S1</sup>	14.248 32(74)
0.725 <sup>S2</sup>	6.170 06(17)	0.990 <sup>S1</sup>	14.784 3(12)
0.750 <sup>F1</sup>	6.655 21(25)	0.995 <sup>S1</sup>	15.062 66(92)
0.750 <sup>S2</sup>	6.655 057(70)	1.000 <sup>F2</sup>	10.249 03(56)
0.775 <sup>S2</sup>	7.186 56(33)	1.100 <sup>F2</sup>	13.267 11(23)
0.800 <sup>F1</sup>	7.769 97(27)	1.200 <sup>F2</sup>	19.468 35(24)
0.800 <sup>S2</sup>	7.769 75(24)	1.300 <sup>F2</sup>	36.751 66(44)
0.825 <sup>S2</sup>	8.411 88(18)	1.400 <sup>F2</sup>	298.057 6(80)
0.850 <sup>F1</sup>	9.118 67(26)	1.410 <sup>F2</sup>	1006.450 3(96)

$$Z_{MD} = 1 + \frac{\gamma(N)\sqrt{m\sigma^2\pi\beta}N_{coll}}{3N\Delta t}, \quad (12)$$

where  $N_{coll}$  is the number of collisions between spheres, and  $\Delta t$  is the duration of the simulation. The quantity  $\gamma(N)$  is a correction factor to convert the pressure calculated in the constant- $NVEM$  ensemble (where  $\mathbf{M}$  is the total momentum vector of the system), to the value for the  $NVT$  ensemble and is given by

$$\gamma(N) = \frac{\Gamma[(3(N-1)+1)/2]}{\Gamma[3(N-1)/2](3N/2)^{1/2}}, \quad (13)$$

where  $\Gamma$  is the gamma function. There are two further sources of error which will cause the MD results to differ from the theoretical equations-of-state. There is the ensemble error caused by the microcanonical ensemble suppressing fluctuations possible in the grand canonical ensemble. Second, there is the error arising from the periodic boundary conditions necessary for simulation of a bulk fluid element. Following the analysis Kolafa *et al.*,<sup>12</sup> these errors are found to be overshadowed by the uncertainty in the simulation results and are essentially negligible for the largest system examined here.

## IV. RESULTS AND COMPARISONS

The complete MD data are summarized in Table II, including estimates for the uncertainty, and pressures plotted in Fig. 2. All systems in the metastable fluid branch between

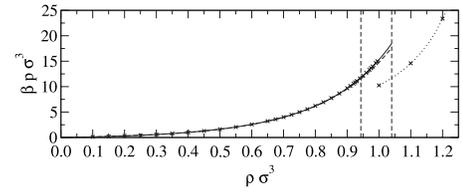


FIG. 2. Equation-of-state for the hard-sphere system in the fluid, solid, and two-phase coexistence regions. The dashed vertical lines are at the approximate freezing and melting points. The solid lines are the predictions of the Carnahan–Starling equation-of-state [see Eq. (9)], the dashed line is the truncated ten-term virial series, and the dotted line is Speedy’s equation-of-state for the fcc crystal [see Eq. (14)]; the present MD thermodynamic pressures are represented by crosses.

the fluid-solid transition densities, i.e.,  $0.943 < \rho\sigma^3 < 1.04$ , were stable and showed no indications of freezing over the duration of the simulation. This is remarkable given the system size studied and the proximity of the state-point  $\rho\sigma^3 = 0.995$  to the solidus density.

Figure 2 shows that the predictions of the truncated virial series and the Carnahan–Starling equations are poor at higher densities when directly compared against the MD data up to five-figure accuracy. The deviations become even more apparent for the truncated virial equation (known terms only) in the metastable branch. To allow accurate comparisons of the equations-of-state for the fluid and metastable branch the results are re-plotted in Fig. 3. The parameter plotted is the relative deviation of the compressibility from the MD results given by  $\Delta Z = (Z_{MD} - Z)/Z_{MD}$ . The truncated virial series begins to noticeably deviate from the MD results at a density of  $\rho\sigma^3 = 0.5$  where it consistently underestimates the compressibility factor. The Carnahan–Starling equation-of-state is only accurate to within 0.3% and underestimates the compressibility factor for all densities examined. The deviation of the Carnahan–Starling equation-of-state<sup>23</sup> also displays a minimum around the freezing density of the fluid.

From Fig. 3, first, we see that the equation-of-state of Kolafa *et al.*,<sup>12</sup> gives perfectly accurate predictions with our simulation data within the estimated uncertainties, as it must for self-consistency. The KLM equation-of-state is a semi-empirical expression fitted to their MD data. It further serves as a comparison of the present MD simulation results against

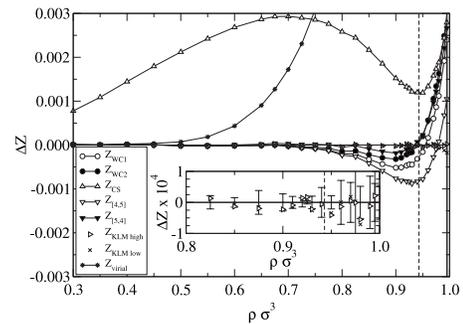


FIG. 3. The difference between the simulation results for the compressibility factor  $Z$  and the predictions of the various equations-of-state for the hard-sphere fluid. The dashed vertical line indicates the approximate freezing density for the hard-sphere fluid.  $Z_{virial}$  is the truncated ten-term virial equation. The inset is a closeup of the high density region for  $\Delta Z_{KLM}$ , showing the accuracy and agreement of our MD results.

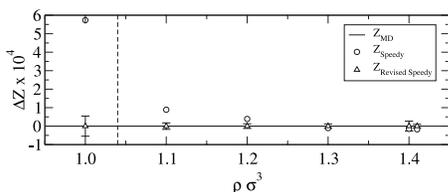


FIG. 4. The difference between the simulation results for the compressibility and the predictions of the equations-of-state for the hard-sphere solid. The vertical dashed line denotes the approximate melting point for the hard-sphere crystal. The circles are from Eq. (14) with the original coefficients of Speedy (Refs. 25 and 26); the triangles are from Eq. (14) with the three constants having been readjusted to best fit the present MD data.

the accurate simulations of Kolafa *et al.*<sup>12</sup> from which the  $Z_{KLM}$  equations were parameterized, and highlights the small system size dependency at these state points. Both Padé approximants perform accurately, but the  $Z(5,4)$  predictions are everywhere better than  $Z(4,5)$ . In view of the accuracy of  $Z_{WC1}$  or  $Z_{WC2}$ , however, it appears we need no longer resort to numerical parameterization.

The WC2 equation-of-state is a marginal improvement on its predecessor WC1.<sup>15</sup> Interestingly, the more accurate of the Padé approximants,  $Z(5,4)$  and the WC closure equations-of-state can be seen to have the same limiting form at higher densities. This agreement is indicative that the complete virial series is indeed convergent everywhere up to the pole of negative divergence at  $\rho_0$  in the WC equations.

The results for the solid branch (see Fig. 4) were compared against the equation-of-state of Speedy<sup>25,26</sup> for hard-sphere fcc solids, given by

$$Z_{\text{fcc}} = \frac{3}{1 - \rho/\rho_0} - A \frac{\rho/\rho_0 - B}{\rho/\rho_0 - C}, \quad (14)$$

where  $A=0.5921$ ,  $B=0.7072$ , and  $C=0.601$  are empirical values of the constants originally obtained by fitting to MD data. Speedy's equation-of-state performs remarkably well at high densities near to  $\rho_0$  due to the inclusion of the exact limiting free volume equation of state form  $3/(1 - \rho/\rho_0)$ .

At lower densities, the equation is accurate but shows signs of difficulties when approaching the solid metastable branch. A straightforward regression of the parameters in Eq. (14) from the original coefficients to the current data given in Table II yields revised values of  $A=0.620\,735$ ,  $B=0.708\,194$ , and  $C=0.591\,663$ . The resulting equation-of-state using these revised values yields predictions that are indistinguishable from the MD simulation data for the densities studied, even into the metastable region.

There are various suggestions in the literature<sup>25,27–29</sup> that the virial equation-of-state should extrapolate beyond the first-order freezing transition to describe the metastable fluid, and eventually have its first pole at random close packing (RCP). This was originally suggested by Le Fevre<sup>27</sup> and has resulted in a number of such equations-of-state being proposed.<sup>25,27–29</sup> Continuous virial equations with the first pole at RCP are based upon the premise that the low density gas and the high density metastable amorphous branch extrapolation belong to one and the same phase, with the pressure as a function of density being continuous in all its derivatives over this whole range.

All the evidence we have, however, suggests that the virial equation reflects neither the meta-stable branch nor any RCP density.<sup>15,30</sup> Moreover, it appears from our comparisons that the virial series “sees” neither the first-order freezing transition nor the metastable fluid branch. The first phase transition in the hard-sphere fluid is the bifurcation of the thermodynamic fluid or its metastable extrapolation from the virial equation-of-state. The present results suggest this higher-order phase transition could be at the fluid-crystal freezing transition.

## V. CONCLUSIONS

MD simulations were performed to generate accurate compressibility data for the testing of various equations-of-state. The accurate results of Kolafa *et al.*<sup>12</sup> are in perfect agreement with, and hence validate the accuracy of MD results reported here, and vice versa, through comparison against their parameterized empirical equations of state. The Padé approximants of Clisby and McCoy<sup>2,14</sup> are also excellent representations of the MD pressures to six-figure accuracy; the (5,4) variant is slightly more accurate than the (4,5) form. Our new equation-of-state closures WC1 and WC2, however, which use an analytic form to close the series, both perform just as well, remarkably so given the simple nature of the closure. WC1 is simpler but WC2 is slightly more accurate and uses only known virial coefficients to effect the closure. If the limiting  $B_n - B_{n+1}$  parameter,  $=A_0$  as  $n \rightarrow \infty$ , turns out to be a constant, perhaps equal to  $V_0/(N\sigma^3)$ , WC1 and WC2 become the same, and essentially exact if the functional form is confirmed as higher values of the hard-sphere virial coefficients become available. This new virial equation-of-state is found to be as accurate as the best high precision machine data up to the uncertainties in both the MD data and the current uncertainties in  $B_9$  and  $B_{10}$  from which  $A_1$  or  $A_2$  are derived. If a theory could be found to validate the closure form, and also determine the constant analytically, then we have here a truly correct equation-of-state for the hard-sphere fluid, with no empirical parameters, other than known virial coefficients.

We have also attempted to determine higher coefficients from the new MD data presented here, but this exercise proved to be unsuccessful. Numerically fitted values for  $B_{11}$  and higher, however, are unreliable. Using the equation

$$Z_{\text{MD}} - Z_{10} = B_{11}(\rho/\rho_0)^{10} + B_{12}(\rho/\rho_0)^{11} + \dots + \text{higher-order terms} \quad (15)$$

we find that determination of  $B_{11}$  from both the present data, and also using the KLM lower density data, gives too wide a margin of uncertainty, of the order 10%–15% in  $B_{11}$ , increasing to 50% for  $B_{12}$  in the case of spheres. For disks the accuracy is even worse.

We find no evidence here for a first phase transition at density well below freezing, for example at a density of the free volume percolation transition as has been suggested previously.<sup>5–8</sup> We cannot, however, rule out this possibility. There could be an extremely weak higher-order phase transition at a lower density that is imperceptible even given the present high precision MD pressures.

The evidence for metastability of the MD fluid systems beyond  $\rho_0$ , rather than instability, comes from reproducibility of  $Z$  data from 0.95 to 0.99, where there is agreement within five-figure accuracy between present MD and KLM from very long runs for very large systems. Accordingly, this can be used as evidence to show there is a phase transition accompanying the first-order fluid-to-crystal transition, but in stable fluid to metastable fluid branch. This description as a “thermodynamic” phase transition also requires the metastable pressure to be a state function of density, and continuous in all its derivatives.

Kolafa<sup>31</sup> has expressed a similar viewpoint; he suggests that the region of discrepancy, between virial equation and thermodynamic pressure, both prefreezing and the metastable branch, is due to incipient crystal nuclei within the equilibrium fluid configurations, and hence nonanalytic. For the thermodynamic pressure equation-of-state Kolafa proposes a closure for the thermodynamic pressure equation of the form

$$Z_{K-Th} = 1 + \sum_{n=2}^m B_n \left( \frac{\rho}{\rho_0} \right)^{n-1} + \beta \Psi[\alpha(\rho - \rho_f)], \quad (16)$$

where  $\alpha$  and  $\beta$  are fitted parameters, and  $\Psi$  is a nonanalytic function at the thermodynamic freezing transition density  $\rho_f$ ; the form of the function  $\Psi$  is derived based on ideas from homogeneous nucleation theory.

The point at which the infinite virial series departs from the stable or thermodynamic fluid equation-of-state must be characterized by a higher-order thermodynamic phase transition. Consequently, we are drawn to the conclusion that at, or near, the fluid freezing transition, the thermodynamic hard-sphere fluid on passing continuously to the metastable fluid also undergoes a higher-order phase transition. This follows because the complete virial equation-of-state, which represents the equilibrium fluid, is itself everywhere convergent and continuous in all its derivatives.

This observation of a discontinuity from stable to metastable fluid has been reported and discussed previously by van Megen.<sup>32</sup> Our finding that the virial equation and the thermodynamic metastable branch begin to deviate at the freezing transition is consistent with a conclusion of van Megen *et al.*<sup>33</sup> from studies of structural fluctuations in hard-sphere colloidal dispersions by light scattering around the freezing transition density. Williams *et al.*<sup>34</sup> have also reported extensive MD computations of spectra obtained from the long-time tails of the velocity autocorrelation, which also show a change in dynamical behavior on passage from stable fluid to metastable fluid.

The various results of van Megen and co-workers,<sup>32–34</sup> taken together with the present analysis, suggest that this new phase transition is weak second order and may physically be explained by the onset of first crystalline nucleations, i.e., new fluctuations with a different symmetry, “kicking in” at the start of the two-phase region.

## ACKNOWLEDGMENTS

We wish to thank the National University of Singapore for a Visiting Professorship 2007–2008 (to L.V.W.), and to acknowledge support from the EPSRC (U.K.) for the award of a Research Studentship (to M.N.B.). We are also grateful to Professor Bill Hoover for various helpful discussions and comments.

- <sup>1</sup>J. H. Nairn and J. E. Kilpatrick, *Am. J. Phys.* **40**, 503 (1972).
- <sup>2</sup>N. Clisby and B. M. McCoy, *J. Stat. Phys.* **122**, 15 (2006).
- <sup>3</sup>F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964).
- <sup>4</sup>F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **46**, 4181 (1967).
- <sup>5</sup>K. W. Kratky, *Physica A* **85**, 607 (1976).
- <sup>6</sup>K. W. Kratky, *Physica A* **87**, 584 (1977).
- <sup>7</sup>K. W. Kratky, *J. Stat. Phys.* **27**, 533 (1982).
- <sup>8</sup>K. W. Kratky, *J. Stat. Phys.* **29**, 129 (1982).
- <sup>9</sup>E. J. J. van Rensburg and G. M. Torrie, *J. Phys. A* **26**, 943 (1993).
- <sup>10</sup>E. J. J. van Rensburg, *J. Phys. A* **26**, 4805 (1993).
- <sup>11</sup>A. Y. Vlasov, X. M. You, and A. J. Masters, *Mol. Phys.* **100**, 3313 (2002).
- <sup>12</sup>J. Kolafa, S. Labík, and A. Malijevský, *Phys. Chem. Chem. Phys.* **6**, 2335 (2004).
- <sup>13</sup>S. Labík, J. Kolafa, and A. Malijevský, *Phys. Rev. E* **71**, 021105 (2005).
- <sup>14</sup>N. Clisby and B. N. McCoy, *J. Stat. Phys.* **114**, 1361 (2004).
- <sup>15</sup>L. V. Woodcock, arXiv:0801.4846v3.
- <sup>16</sup>L. V. Woodcock, arXiv:0804.0679v2.
- <sup>17</sup>J.-W. Hu and Y.-X. Yu, *Chin. Phys. Lett.* **26**, 086404 (2009).
- <sup>18</sup>A. Mulero, M. I. P. C. A. Galán, and F. Cuadros, *Theory and Simulation of Hard-Sphere Fluids and Related Systems*, Lecture Notes in Physics Vol. 753 (Springer-Verlag, Berlin, 2008).
- <sup>19</sup>W. Wang, M. K. Khoshkbarchi, and J. H. Vera, *Fluid Phase Equilib.* **115**, 25 (1996).
- <sup>20</sup>L. V. Velash, T. Kraska, and U. K. Deiters, *J. Chem. Phys.* **110**, 3079 (1999).
- <sup>21</sup>M. N. Bannerman, R. Sargant, and L. Lue, “An O(N) general event-driven simulator: DYNAMO,” *J. Comp. Chem.* (submitted).
- <sup>22</sup>M. N. Bannerman, Ph.D. thesis, The University of Manchester, 2009.
- <sup>23</sup>N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
- <sup>24</sup>J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**, 321 (1984).
- <sup>25</sup>R. J. Speedy, *J. Phys.: Condens. Matter* **9**, 8591 (1997).
- <sup>26</sup>R. J. Speedy, *J. Phys.: Condens. Matter* **10**, 4387 (1998).
- <sup>27</sup>E. J. L. Fevre, *Nature (London), Phys. Sci.* **20**, 235 (1972).
- <sup>28</sup>L. V. Woodcock, *Ann. N. Y. Acad. Sci.* **371**, 274 (1981).
- <sup>29</sup>G.-W. Wu and R. J. Sadus, *AIChE J.* **51**, 309 (2005).
- <sup>30</sup>L. V. Woodcock, arXiv:0801.1559v1.
- <sup>31</sup>J. Kolafa, *Phys. Chem. Chem. Phys.* **8**, 464 (2006).
- <sup>32</sup>W. van Megen, *Phys. Rev. E* **73**, 020503 (2006).
- <sup>33</sup>W. van Megen, T. C. Mortensen, and G. Bryant, *Phys. Rev. E* **72**, 031402 (2005).
- <sup>34</sup>S. R. Williams, G. Bryant, I. K. Snook, and W. van Megen, *Phys. Rev. Lett.* **96**, 087801 (2006).