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Hard-Sphere Fluid-to-Solid Transition and the Virial Expansion

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An exhaustive Padé approximant study of the Mayer virial series expansion is carried out for the classical hard-sphere system. As one increases the order of the different approximants a clear tendency is seen to reproduce both the random close packing divergence of the fluid branch as well as its instability (towards the crystalline phase) at the spinodal point.

KEY WORDS: Hard spheres; crystallization; random close packing; virial expansion; Padé approximants.

1. INTRODUCTION

One of the landmarks in twentieth century theoretical physics has been the derivation of the Mayer virial expansion(1) for the pressure of a classical fluid in powers of its density, with coefficients which are essentially integrals over the interaction between particles. Knowledge of these so-called virial coefficients is equivalent to solving exactly the classical statistical problem successively for two, three, etc., particles interacting at zero density. The question(2) of whether the resulting series contains information relevant to condensed phases, such as liquid, glass (amorphous solid), and crystal, which empirically occur at higher densities, is a very old one indeed.

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A recalculation of the multiple integrals involved in the sixth and seventh coefficients for hard spheres was recently carried out$^{(3)}$ and we now have, for the pressure P of N hard spheres of diameter σ enclosed in a volume V and at a temperature T, the expansion

$$\frac{PV}{NkT} \equiv Z(x) = 1 + \sum_{n=1}^{6} A_n x^n + \cdots \tag{1}$$

$$x \equiv \rho/\rho_0, \qquad \rho \equiv N/V, \qquad \rho_0 \equiv \sqrt{2}/\sigma^3 \tag{2}$$

$$\begin{aligned} A_1 &= 2.961921959, & A_2 &= 5.483113556 \\ A_3 &= 7.456363357, & A_4 &= 8.485568085 \\ A_5 &= 8.8678 \pm \epsilon_5, & A_6 &= 9.2504 \pm \epsilon_6 \\ \epsilon_5 &= 0.0912, & \epsilon_6 &= 0.4051 \end{aligned} \tag{3}$$

where A_n is traditionally called the $(n + 1)$th virial coefficient, and density x is referred to the presumably$^{(4)}$ maximum possible value ρ_0 corresponding to *regular* close packing of spheres in a face-centered-cubic configuration. Regarding convergence of the expansion (1) for hard spheres, rigorous lower bounds to the radius of convergence in x have been established at about 0.024$^{(5)}$ and subsequently at about 0.026,$^{(6)}$ i.e., still very small densities compared with physically relevant values.

The hard-sphere fluid is much more than an academic problem since (a) its partition function is nontrivial unlike the one-dimensional case; (b) it displays at least three distinct phases: (i) gas, (ii) amorphous solid,$^{(7)}$ and (iii) crystalline solid,$^{(8)}$ as computer experiments have determined; and (c) it provides a good starting point for perturbative treatments$^{(9)}$ of real classical fluids since it was discovered that the latter has a pair distribution function qualitatively similar to that of the hard-sphere gas. As long ago as 1704 Issac Newton stated, in his *Optiks*, that "All bodies seem to be composed of hard particles: For otherwise Fluids would not congeal."

That the physical richness related to condensed phases, even in a simple system like that of hard spheres, can be extracted from the virial expansion alone is an endeavor which has perhaps been inhibited by the Yang and Lee theorems$^{(10)}$ on possible phase transition mechanisms. Their specific application$^{(11)}$ to the two-dimensional lattice gas (a spin system) shows the presence of a "natural boundary" of singularities for the pressure in the activity plane, beyond which analytic continuation of a function represented by the activity virial series is impossible. It is, however, not known what kind of singularities are present in a continuum system like say, the hard-sphere fluid. And even if these singularities should turn out to constitute a natural boundary there are counterexamples(12) (involving Padé appproximants) whereby analytic continuation beyond the boundary *is* possible, albeit, of course, not by the standard (Weierstrass) technique of reexpanding about points successively farther away from the origin. Not only finding liquid, crystalline, etc. phases solely from the virial expansion but even the possibility of detecting the instability of the fluid phase(13) has been questioned.

We offer the present study as a step towards extracting more information from the virial series alone than was previously suspected, save for at least two previous attempts,(14) but leave for the future such prospects as obtaining the crystalline or glassy phases.

2. PADÉ ANALYSIS OF VIRIAL SERIES

We represent (symbol $\doteq$) the virial series (1) by the ratio of an Lth- to an Mth-order polynomial, L and M nonnegative integers, such that

$$1+\sum_{n=1}^{6} A_n x^n \doteq \frac{1+p_1x+p_2x^2+\cdots+p_Lx^L}{1+q_1x+q_2x^2+\cdots+q_Mx^M} \equiv [L/M](x) \tag{4}$$

and define the L coefficients $(p_1, p_2, \ldots, p_L)$ and M coefficients $(q_1, q_2, \ldots, q_M)$ *such that* on Taylor expansion of $[L/M](x)$ about $x=0$ the first $(L+M)$ coefficients of the series are reproduced exactly. The extrapolant $[L/M](x)$ is called the L, M Padé approximant(15) and is a sort of analytic continuation beyond the neighborhood $x \ll 1$.

The system pressure, from (1), will thus be represented by

$$P/\rho_0 kT \doteq x[L/M](x) \tag{5}$$

In a recent study(16) several Padé approximants were found which correctly reproduced (to two digits), apparently for the first time, the empirical *random* (or *irregular*) close packing (RCP) density where the system pressure diverges. This density, also known as the Bernal density,(17) has been accurately determined (to four digits) in experiments with steel ball-bearings and turns out to be $\rho_{\mathrm{RCP}} = 0.8597\rho_0$, i.e., *less* than *regular* close packing density ρ_0. Computer generations of random close packings have thus far given a value about 3% smaller than this.(18) The study by Baram and Luban(14) places the pole at $\rho = \rho_0$, but this divergence is in reality associated with the *crystalline*, not the *fluid*, branch.

Table I. Poles and Maxima, If Any, for the Different Padé Approximant Representations of the Hard-Sphere Pressure, Eq. (5), Compared with Experiment

L	M	Behavior in $0 < x < 1$	max of $P/\rho_0 kT = x[L/M](x)$	Comments
0	1	Pole at $x = 0.3376$	∞	van der Waals
1	1	Pole at $x = 0.5402$	∞	
0	2	Max at $x = 0.5513$	1.5022	~BBGKY
2	1	Pole at 0.7354	∞	
1	2	Max at 0.6571	2.6750	
0	3	Max at 0.7265	3.3572	
3	1	Pole at 0.8787	∞	
2	2	Monotone increasing	—	
1	3	Pole at 0.4470	∞	
0	4	Pole at 0.5951	∞	
4	1	Pole at 0.9569	∞	
3	2	Monotone increasing	—	
2	3	Pole at 0.8731	∞	Third best RCP prediction
1	4	Pole at 0.6901	∞	
0	5	Max at 0.7100	6.0353	
5	1	Pole at 0.9586	∞	
4	2	Pole at 0.9587	∞	
3	3	Pole at 0.8618	∞	Best RCP prediction
2	4	Pole at 0.8624	∞	Second best RCP prediction
1	5	Max at 0.7292	6.8252	
0	6	Max at 0.7303	6.8676	
EXP		Max at $0.667 < x < 0.736$	> 8.14	
($N = \infty$)		Pole at 0.8597	∞	

Table I summarizes the complete Padé approximant table results for zero error $\epsilon_5 = 0 = \epsilon_6$ in (3). The $[L/0]$ approximants $L = 1, 2, \ldots, 6$, have not been listed since, all the A_n's being positive in (4), the $[L/0](x)$ are monotonic increasing for all x. Padé coefficients for some selected approximants are given in Table II. The simplest nontrivial Padé is the $[0/1](x)$ which gives the equation of state

$$\frac{P}{\rho_0 kT} \doteq x[0/1](x) = \frac{x}{1 + q_1 x} \underset{x \ll 1}{\simeq} x[1 - q_1 x + \cdots], \tag{6}$$

$$q_1 \equiv -A_1 = -\frac{2\pi}{3}\sqrt{2}$$

Table II. The p_i and q_i Coefficients of Some Selected Padé Approximants Based on the Hard-Sphere Virial Series (4)

	[3/3]	[2/4]	[2/3]
p_1	0.61789570	0.67873922	0.67146994
p_2	0.62793505	0.66878965	0.68086743
p_3	− 0.04142637	—	—
q_1	− 2.3440263	−2.2831827	−2.2904520
q_2	2.0876444	1.9482852	1.9818940
q_3	− 0.82866721	− 0.70808179	− 0.76777021
q_4	—	−0.04671385	—

	[0/6]	[1/5]	[0/5]	[0/2]
p_1	—	0.06021415	—	—
q_1	− 2.9619220	−2.9017078	−2.9619220	−2.9619220
q_2	3.2898681	3.1115785	3.2898681	3.2898681
q_3	− 0.96014158	− 0.76204498	− 0.96014158	—
q_4	− 1.5952579	− 1.6530720	− 1.5952579	—
q_5	1.7248968	1.6288397	1.7248968	—
q_6	− 0.10386319	—	—	—

and by definition reproduces the first coefficient A_1 of the series (4), i.e., the *second* virial coefficient, exactly. Equation (6) is *precisely* the van der Waals equation of state for a system of hard spheres

$$\frac{P}{kT} = \frac{\rho}{1 - b\rho} = \frac{N}{V - bN} \qquad b \equiv \frac{2\pi}{3}\sigma^3 \tag{7}$$

with b, the "excluded volume per particle," being half the exclusion volume of a single sphere. This approximant produces a (first-order) pole at $x = (2\sqrt{2}\,\pi/3)^{-1} \simeq 0.3376$, still quite below the empirical $x_{\text{RCP}} = 0.8597$. However, the "richest" approximants $[3/3](x)$ and $[2/4](x)$, respectively, give the pole at $x = 0.8618$ and 0.8624.

To investigate whether the Mayer virial series can also predict the spinodal point we seek solutions of

$$\left(\frac{dP}{d\rho}\right)_{\rho = \rho_s} = 0 \tag{8}$$

for a spinodal point density ρ_s, such that

$$0 < x_s \equiv \rho_s/\rho_0 < 1 \tag{9}$$

Equations (9) and (6) are identical to

$$\left\{[L/M](x)^{-1}x\frac{d}{dx}[L/M](x)\right\}_{x=x_s}=-1 \tag{10}$$

which was found to be satisfied, together with (9), by *several* approximants as listed in Table I with the designation "max at x_s". Figure 1 shows the associated pressure-vs.-density curves.

The simplest approximant which satisfies (10) is the $[0/2](x)$ which gives

$$\frac{P}{\rho_0 kT}\doteq x[0/2](x)=\frac{x}{1+q_1x+q_2x^2}$$

$$\underset{x\ll 1}{\simeq} x\left[1-q_1x+(q_1^2-q_2)x^2+(2q_1q_2-q_1^3)x^3+O(x^4)\right] \tag{11}$$

The coefficients $A_1\equiv -q_1$, $A_2=(q_1^2-q_2)$ of (4) are reproduced exactly, by definition. In other words, the second and third virial coefficients are correctly reproduced by (11) just as in the Born–Green–Yvon (BGY) integral equation theory,(1,19) which is based on the Kirkwood superposi-

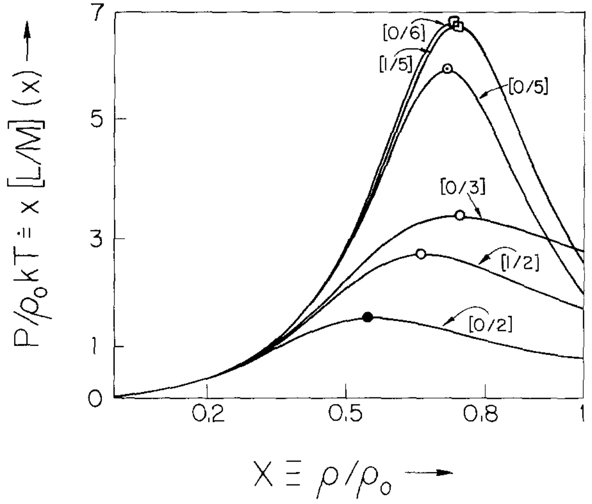

Fig. 1. Pressure (in units of $\rho_0 kT$) vs. density (in units of ρ_0) for the hard-sphere fluid as given by all the possible Padé approximants $[L/M](x)$ showing a maximum in pressure, i.e., a spinodal point.

tion approximation[20] for the triplet distribution function. This theory gives[21] for A_3 the value

$$A_3(\mathrm{BGY}) = 5.852998 \tag{12}$$

in contrast to the value given by (11)

$$A_3 = (2q_1q_2 - q_1^3) = 6.4962218 \tag{13}$$

which is closer to the exact A_3 of (3). It is well known that BGY theory for hard spheres predicts[22] a spinodal point even though it only reproduces up to the third virial coefficient exactly. Other integral equation theories such as the Percus–Yevick[23] (PY) and hypernetted chain approximation[24] equations also reproduce[19] the third virial coefficient exactly. These three theories have been generalized[25] (into what is called[26] BGY2, PY2, and HNC2) so as to reproduce correctly up to and including the fourth virial coefficient but the resulting schemes are very difficult and expensive to solve. To our knowledge it is not known whether any of them would continue to predict spinodal points. The latter is indeed seen in Table I to be the case with our next approximants, the $[1/2](x)$ and $[0/3](x)$, both of which reproduce exactly up to and including A_3 of (4), i.e., the fourth virial coefficient.

The next level of approximants, order $L + M = 4$, however, is qualitatively distinct: no maximum appears *below* the first divergence, and Fig. 2

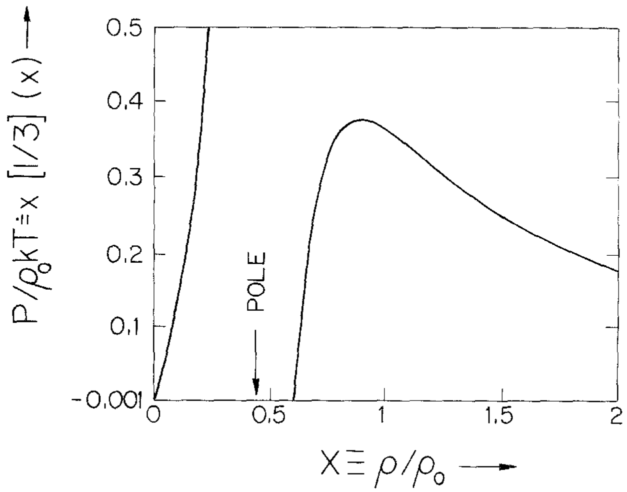

Fig. 2. Same as Fig. 1, for the $[1/3](x)$ Padé approximant which develops a pole *below* the maximum, and is hence discarded.

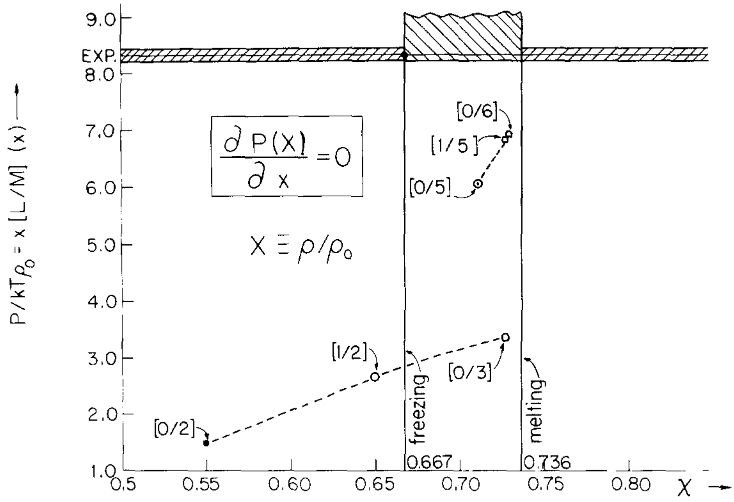

Fig. 3. Same as Fig. 1, showing how the pressure–density location of the predicted spinodal point tends to the computer experiment results.$^{(31)}$

illustrates a typical case. The spinodal point reappears in order $L + M = 5$ and increases in its value of pressure and of density up to $P/\rho_0 kT = 6.8676$ and $x \equiv \rho/\rho_0 = 0.7303$ for the $[0/6](x)$ approximant. Figure 3 illustrates these values for all the spinodal-point-bearing approximants. Computer experiments$^{(27)}$ give $x = 0.667$ for the freezing density and $x = 0.736$ for melting, both at $P/\rho_0 kT = 8.27 \pm 0.13$, for the infinite particle limit (where strictly speaking *no* spinodal points would be present). For a large but finite number of particles the size of $P/\rho_0 kT$ at freezing would be somewhat smaller$^{(27)}$ than the above-quoted value.

We finally note that the "best" Padé representation giving the spinodal point, the $[0/6](x)$, can be written as a generalized van der Waals equation$^{(8)}$

$$P/kT \doteq \rho_0 x[0/6](x) = \frac{\rho}{1 - b(x)\rho} \tag{14}$$

with the density-dependent "excluded volume" per particle

$$b(x) \equiv \frac{2\pi}{3}\sigma^3 \left[1 + \sum_{i=2}^{6} \frac{q_i}{q_1} x^i\right] \tag{15}$$

This is found to decrease monotonically from $(2\pi/3)\sigma^3$ at $x = 0$ to ~ 0.2 times this at $x = 1$.

3. CONCLUSIONS

We therefore see that Padé approximants offer a very simple scheme for constructing successively better equations of state for fluids from first principles. They correctly reproduce low-density virial coefficients as do more complicated approaches such as integral equation theories, as well as go considerably beyond these, and provide a clear tendency to approximate the terminal density of the fluid branch both as regards random close packing divergence as well as the instability to the ordered phase. It is a hope that the present or similar methods will also eventually constitute a means of extracting the actual condensed phases of the amorphous and crystalline solid—and even the liquid, if attractions are included—directly from the Mayer virial series.

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REFERENCES

1. J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (2nd ed.) (Wiley, New York, 1977).
2. G. E. Uhlenbeck, in *The T. Y. Wu Festschrift*, S. Fujita, ed. (Gordon & Breach, New York, 1978).
3. K. W. Kratky, *Physica (Utrecht)* **A87**:584 (1977).
4. C. A. Rogers, *Proc. Lond. Math. Soc.* **8**:609 (1958); *Packing and Covering* (Cambridge U.P., Cambridge, 1964).
5. J. L. Lebowitz and O. Penrose, *J. Math. Phys.* **5**:841 (1964).
6. F. H. Ree, *Phys. Rev.* **155**:84 (1967).
7. L. V. Woodcock, *J. Chem. Soc. Faraday Trans. II* **72**:1667 (1976); in *Structure and Mobility in Mobility in Molecular and Atomic Glass*, J. M. O'Reilly and M. Goldstein, eds., Annals N.Y. Acad. Sci. Vol. 371 (N.Y. Acad. Sci., New York, 1981), p. 274.
8. J. G. Kirkwood, E. K. Maun, B. J. Alder, *J. Chem. Phys.* **18**:1040 (1950); B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **31**:459 (1959); *Phys. Rev. Lett.* **18**:968 (1959); *Phys. Rev. A* **1**:18 (1970); W. W. Wood and J. D. Jacobson, *J. Chem. Phys.* **27**:1207 (1957).
9. J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**:587 (1976).
10. C. N. Yang and T. D. Lee, *Phys. Rev.* **87**:404 (1952).
11. C. N. Yang and T. D. Lee, *Phys. Rev.* **87**:410 (1952).
12. J. Gammel, *J. Math. Anal. Appl.* **43**:694 (1973); *Rocky Mtn. J. Math.* **4**:203 (1974).
13. S. Katsura, *Adv. Phys.* **12**:391 (1963).
14. M. Alexanian and D. E. Wortman, *Phys. Rev.* **143**:96 (1966); A. Baram and M. Luban, *J. Phys.* **C12**:L659 (1979).
15. G. A. Baker, Jr. and P. Graves-Morris, *Padé Approximants*, in *Encycl. of Math. and its Applications*, G.-C. Rota, ed. (Addison-Wesley, Reading, Massachusetts, 1981), Vols. 13 and 14.
16. V. C. Aguilera-Navarro, M. Fortes, M. de Llano, and A. Plastino, *J. Chem. Phys.* **76**:749 (1982).

17. J. D. Bernal, *Nature* **188**:910 (1960).
18. V. M. Visscher and J. E. Gubernatis, in *Dynamical Properties of Solids*, G. K. Horton and A. A. Maradudin, eds. (North-Holland, Amsterdam, 1980).
19. R. O. Watts and I. J. McGee, *Liquid State Chemical Physics* (Wiley, New York, 1976).
20. J. G. Kirkwood, *J. Chem. Phys.* **3**:300 (1935).
21. G. S. Rushbrooke and H. I. Scoins, *Phil. Mag.* **42**:582 (1951).
22. K. U. Co, J. J. Kozak, and K. D. Luks, *J. Chem. Phys.* **66**:581 (1977).
23. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
24. T. Morita, *Prog. Theor. Phys.* **20**:920 (1958).
25. G. Stell, *Physica (Utrecht)* **29**:517 (1963); S. A. Rice and J. Lekner, *J. Chem. Phys.* **42**:3559 (1965).
26. Y. T. Lee, F. H. Ree, and T. Ree, *J. Chem. Phys.* **48**:3506 (1968); **55**:234 (1971).
27. W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**:3609 (1968).