May lowdensity expansions for imperfect gases contain information about condensed phases?

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May low-density expansions for imperfect gases contain information about condensed phases?

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The question posed is examined within the context of two simple models, the Ford problem and the van der Waals equation, both of which possess two phases: (i) a low-density phase for which *all* the virial coefficients in the density power-series expansion are known and (ii) a high-density "condensed" phase. Padé extrapolation techniques are applied to the virial series in an attempt to predict the condensed phase branch.

I. INTRODUCTION

Since Kamerlingh Onnes introduced the virial series around 1902 to represent the experimental pressure isotherms of an imperfect gas, the question[1] has been asked whether successive virial coefficients contain any information about the intermolecular forces between pairs, triplets, etc. of molecules. When the theory of the structure of atoms and molecules and the quantum mechanics of their interactions was developed in the 20's the problem was transformed from the determination of the intermolecular potential function to that of finding the Helmholtz free energy $F(V,T,N)$ and hence the equation of state by calculating the pressure P through $P = -(\partial F/\partial V)_{N,T}$.

Ursell and Mayer[2] succeeded around 1930 in obtaining general expressions for all the virial coefficients in terms of the intermolecular forces. Knowledge of these coefficients is equivalent to solving exactly the classical statistical problem successively for two, three, etc., particles in a box of volume V and interacting at zero density. Afterwards it was debated whether the virial expansion for, say, the pressure, contains *all* the information about the *complete* equation of state for all phases. In particular, it was asked if this expansion is valid beyond the condensation point or if it is capable, at least, of locating this transition point.

The general question has been addressed and investigated[3] before but only, to our knowledge, within the context of *spin* manybody systems (e.g., Ising models) and not *continuous* systems as we consider here.

The purpose of this paper is to study two models in which all the coefficients of the virial series expansion are known and inquire if it contains information relevant to the condensed phases such as the liquid, crystalline, etc., which empirically occur at higher densities. One of these models, due to Ford,[4] leads to an equation of state with two distinct divergences in the pressure (poles) that could be thought of as analogous, respectively, to the random close packing[5] and the regular close packing in a hard sphere fluid. The other model is the well-known van der Waals equation of state, whose loops indicate the existence of metastable states and

whose critical point is well defined. In both cases we seek loops from the analytical continuation of the low-density expansion.

The fact that Padé approximants[6] have proved to be of great usefulness in representing a function that is originally given by a truncated power series (even beyond the radius of convergence of the series) provides, in principle, a mathematical tool specially suited for the purpose of *extending the region of validity* of the virial series expansion and discovering whether it correctly predicts the singularity associated with the phase transition.

II. FORD MODEL

Ford[4] proposed an example of a grand partition function that is volume and activity dependent and amenable to exact solution through the Mayer equations[2] to finally obtain an explicit equation of state. This model has a striking resemblance with the hard sphere system fluid-to-solid transition, except that in the Ford model the singularity giving rise to the fluid–solid equilibrium "tieline" is *known* to be, in the infinite particle (thermodynamic) limit, a "natural boundary"[7] in the fugacity plane. A natural boundary is an infinitely dense line of singularities beyond which analytic continuation is impossible by the classic Weierstrass method of reexpanding about points successively further away from the origin.

The proposed grand partition function is

$$\Xi(V,z) = (1+z)^V \frac{1-z^v}{1-z} = \sum_{i=0}^{V} \sum_{j=0}^{V-1} \binom{V}{i} z^{i+j},$$

where V is the volume in units of some length cubed so that V is large but integer and z is the fugacity $e^{\mu/\kappa T}$ with μ the chemical potential. The *pressure* in the thermodynamic limit is given by the first Mayer equation[2]

$$\frac{P(z)}{kT} = \lim_{V \to \infty} V^{-1} \ln \Xi(V,z) \tag{1}$$

$$= \begin{cases} \ln(1+z), & z < 1 \\ \ln z(1+z), & z > 1. \end{cases}$$

The density $\rho(z)$ is then defined through the second Mayer equation[2]

$$\rho = z \frac{\partial P(z)/kT}{\partial z}. \tag{2}$$

Eliminating z between Eqs. (1) and (2) we obtain the equation of state $P(\rho)$. [Huang[8] gives another example (he calls it a
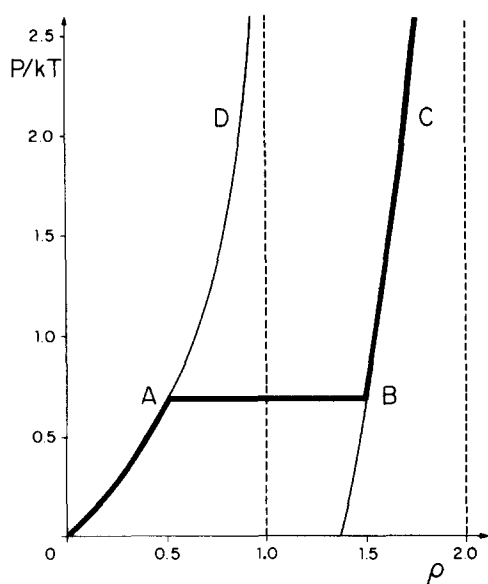
FIG. 1. Pressure vs density equation of state for the Ford example (Ref. 4) given by Eq. (3).

"trivial mathematical example") of a grand partition function $\Xi(z, V) = (1 + z)^V (1 + z^{\alpha V})$, $\alpha > 0$ that admits the same analysis and that reduces to the same equation of state as the Ford example[4] in the limit $V \to \infty$, when $\alpha = 1$.]

$$\frac{P}{kT} = \begin{cases} \ln \dfrac{1}{1 - \rho}, & (0 \leqslant \rho < \tfrac{1}{2}) \\ \ln 2, & (\tfrac{1}{2} \leqslant \rho \leqslant \tfrac{3}{2}) \\ \ln \dfrac{\rho - 1}{(2 - \rho)^2}, & (\tfrac{3}{2} < \rho < 2). \end{cases} \quad (3)$$

It clearly has two poles—one at $\rho = 1$, the other at $\rho = 2$ that can be seen (Fig. 1) to be analogous, respectively, to the ran-
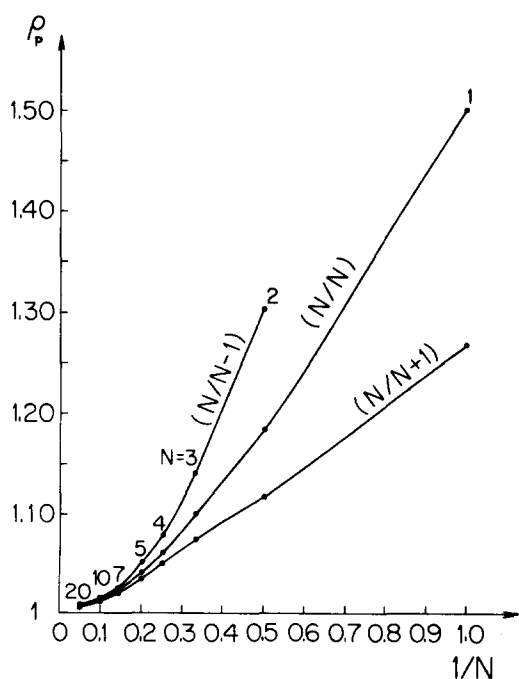

FIG. 2. Diagonal $[N/N](\rho)$ Padé approximants as compared with $[N/N - 1)](\rho)$ and $[N/N + 1](\rho)$ in their approach to the correct pole at $\rho = 1$ for different values of N.

TABLE I. Pole locations ρ_p for various diagonal Padé approximants $[N/N](\rho)$ representing the Ford model virial series (4) compared with the exact location.

	ρ_p		ρ_p		ρ_p
1	1.5000	5	1.0415	9	1.013 48
2	1.1835	6	1.0302	10	1.013 37
3	1.0972	7	1.0230	15	1.009 22
4	1.0606	8	1.0181	20	1.007 19
				Exact	1.000 00

dom close packing density and to the regular close packing which occur[5] at 0.86 ρ_0 and ρ_0, respectively, in the hard-sphere system, with $\rho_0 \equiv \sqrt{2}/c^3$ being the hard sphere diameter. Expanding the first log term of (3) about $\rho = 0$ gives

$$\frac{P}{kT} = \sum_{m=1}^{\infty} \frac{1}{m} \rho^m \equiv \rho \pi(\rho),$$

(4)

$$\pi(\rho) \equiv \sum_{n=0}^{\infty} b_n \rho^n, \quad b_n = \frac{1}{n + 1}.$$

We now represent (symbol $\hat{=}$) the virial series for $\pi(\rho)$ by the ratio of an L th to an M th order polynomial

$$\sum_{n=0}^{\infty} b_n \rho^n \hat{=} \frac{1 + p_1 \rho + p_2 \rho^2 + \cdots + p_L \rho^L}{1 + q_1 \rho + q_2 \rho^2 + \cdots + q_M \rho^M} \equiv [L/M](\rho). \quad (5)$$

The L coefficients $(p_1, \ldots, p_L)$ and M coefficients $(q_1, \ldots, q_M)$ are defined such that on binomial expansion of $[L/M](\rho)$ about the first $(L + M + 1)$ coefficients of the original series are reproduced exactly. The extrapolant $[L/M](\rho)$ is called the $[L/M]$ Padé approximant[6] (see the Appendix). Since all virial coefficients are known for this problem it is possible to construct Padé approximants of any order. Figure 2 illustrates the convergence to the exact value of the pole at $\rho = 1$ as given by several selected Padé approximants. Some pole locations for various diagonal Padé approximants appear in Table I. No pressure maxima (spinodal points) were found in the Padé analysis, carried out up to order $L + M = 31$, indicating the failure of the virial series and/or the Padé approximant to supply information about the condensed phase for the Ford model. This is undoubtedly because of the purely mathematical nature of the model which is devoid of any physical content.

III. VAN DER WAALS MODEL

Recently, after almost 80 years of oblivion, new interest in the van der Waals equation of state has arisen due perhaps in part as noted by Uhlenbeck,[1] to the fact that the ideas expressed in the equation as early as 1862 are a step in the right direction in solving the basic problem of the vapor-liquid transition. However, the results are not correct quantitatively and all attempts to improve the equation to provide an exact description have thus far failed, even though the equation "explains" the condensation phenomena as well as the critical point. Although some authors[9] claim that the van der Waals equation is only an interpolation formula describing in a qualitative manner the transition from a liquid to a gas and as such must give correct results in both limiting

cases, it can also be conceived as a "mean-field" theory in statistical physics since it starts with an independent-particle canonical partition function for the N-particle system.[10]

The van der Waals equation of state for N molecules contained in a volume V at absolute temperature T is

$$P = \frac{kT}{v-b} - \frac{a}{v^2} \equiv P_{kin} - P_{coh} \quad (a,b > 0) \qquad (6)$$

which exhibits the pressure P of the fluid as the difference between a positive (kinetic) pressure due to the finite size of the molecules and a negative (cohesive) pressure that tends to keep the molecules together. Here $v = V/N = \rho^{-1}$, ρ being the particle density: b is the "excluded volume" per particle [it is interesting to note[10] that as long ago as 1738, Bernoulli considered the value of b as the volume of the molecules, which is somewhat remarkable since the atomic theory was still being objected to as late as 1890. Later, van der Waals showed (correctly) that b is four times the molecular volume, instead of the values of eight or 16 times the molecular volume proposed by Clausius and Maxwell, respectively] and P_{coh} is related to the "mean attractive field" as a function of the density obtained from the two-particle attractive pair interactions. An equivalent form of the equation is, of course,

$$\frac{P}{kT} = \frac{\rho}{1-b\rho} - \frac{a}{kT}\rho^2 \qquad (7)$$

which displays both the explicit dependence of P on ρ and a pole at $\rho = 1/b$. The conditions to be fulfilled at the critical point are

$$\left(\frac{\partial P}{\partial \rho}\right)_{Tc} = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{Tc} = 0. \qquad (8)$$

These conditions are satisfied if

$$\rho_c = \frac{1}{3b}; \quad P_c = \frac{1}{27}\frac{a}{b^2}; \quad kT_c = \frac{8}{27}\frac{a}{b}.$$

After putting

$$\pi \equiv \frac{P}{P_c}; \quad y \equiv \frac{\rho}{\rho_c}; \quad t \equiv \frac{T}{T_c},$$

Eq. (7) becomes

$$\pi(y) = \frac{8yt}{3-y} - 3y^2,$$

the so-called reduced equation of van der Waals. It is precisely this equation, with a pole at $y = 3$, which is to be expanded about $y = 0$ as a virial series and then represented by a Padé approximant. The expansion yields

$$\pi(y) = \frac{8yt}{3}\left[1 + Ay + \sum_{n=2}^{\infty}\frac{1}{3^n}y^n\right] \doteq \frac{8yt}{3}[L/M](y),$$

$$A \equiv \tfrac{3}{8}(1 - 27/8t). \qquad (10)$$

Padé coefficients for some selected approximants for the value of $t = 0.5$ are given in Table II. In Figs. 3 and 4 are graphed the reduced pressure $\pi(x)$ vs x, where $x \equiv 1/y$, for the two reduced temperatures $t = 0.9$ and 0.5. The reduced pressure $\pi(y)$ represented by several Padé approximants $[L/M]$ is compared with the exact curve as given by (9). We note that while for the higher temperature a $[3/0]$ approximant, which is just a third order polynomial, is sufficient to give spinodal points, one must go to $[L/M]$ approximants $M \neq 0$ to correctly reproduce the pole at $y = 3$ ($x \equiv 1/y = \tfrac{1}{3}$). A relatively low order approximant $[2/1]$ is sufficient to reproduce the exact loop behavior *and* pole.

To investigate whether this type of representation would also predict spinodal points y_s we seek the solution of

$$\left(\frac{\partial \pi(y)}{\partial y}\right)_{y_s} = 0$$

or, from Eq. (9),

$$y_s^3 - 6y_s^2 + 9y_s - 4t = 0. \qquad (11)$$

This is to be compared with $\pi'(y)$ calculated from Eq. (10), or

$$0 = \pi'(y) = \frac{8t}{3}\left[1 + 2Ay + \sum_{n=2}^{\infty}\frac{n+1}{3^n}y^n + \right]$$

$$\doteq \frac{8t}{3}[N/0](y).$$

In Fig. 5 are shown the exact values, y_+ and y_- that satisfy Eq. (11) for $t \leqslant 1$ as compared with values predicted by the Padé approximants $[N/0]$. y_+ and y_- are the maximum and minimum roots, respectively, of Eqs. (11) and (12). One finds that the Padé approximants nicely predict spinodal points for different temperatures and the agreement between the roots of Eq. (11) and those obtained by approximants increases monotonically with N.

IV. DISCUSSION

From this analysis it is seen that Padé approximants afford a very simple scheme to construct successively better equations of state for imperfect gases with condensed phases, such as liquid, crystalline, etc., at higher densities. It is evident that they reproduce the low density virial coefficients in both cases studied and in the case of the van der Waals model show a clear tendency to approximate the metastable branch

TABLE II. The p_i and q_i of some selected approximants based on the van der Waals virial series for $t = 0.5$. Notice that approximants $[N/1](y) = [N+M/1](y)$, $M = 1,2...$ are equal.

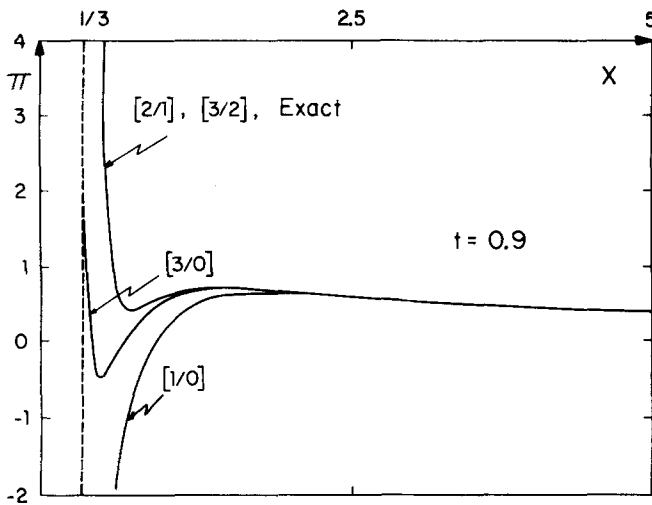| L, M	[2/1]	[3/0]	[3/1]	[3/2]
p_1	$-2.250\,000$	$-1.916\,66$	$-2.250\,000$	$-1.416\,860$
p_2	$0.750\,000$	$0.111\,111$	$0.750\,000$	$-1.124\,565\,0$
p_3	$\cdots$	$0.037\,37$	$\cdots$	$0.624\,855$
q_1	$-0.333\,333$	$\cdots$	$-0.333\,33$	$0.499\,807$
q_2	$\cdots$	$\cdots$	$\cdots$	$-0.277\,713$

FIG. 3. Pressure π (in units of $\rho_0 kT$) vs density (in units of ρ_0) for several Padé approximants $[L/M](y)$, $y = 1/x$, as compared with the exact value given by the van der Waals equation (9) for $t = T/T_c = 0.9$.

FIG. 5. Spinodal values y_+ and y_- as solutions of the exact Eq. (11) and of $[N/0](y)$ [Eq. (12)] obtained for different values of N. The lower values approach the exact value faster (small values of N) than the upper ones.

(loop) in which the phase transition takes place. Accordingly, Padé approximants may constitute a useful means of extracting information about the condensed phase from the low-density expansion of the imperfect gas.

APPENDIX: PADÉ APPROXIMANTS: AN ILLUSTRATION

Given a power series expansion

$$f(x) = \sum_{i=0}^{\infty} a_i x^i$$

to a given function $f(x)$, one can define the $[n/m]$ Padé approximant to the $[n + m]$ partial sum of the series as

$$[n/m](x) \equiv \frac{a_0 + p_1 x + p_2 x^2 + \cdots + p_n x^n}{1 + q_1 x + q_2 x^2 + \cdots + q_m x^m},$$

such that

$$[n/m](x) - \sum_{i=0}^{n+m} a_i x^i \equiv O(x^{n+m+1}).$$
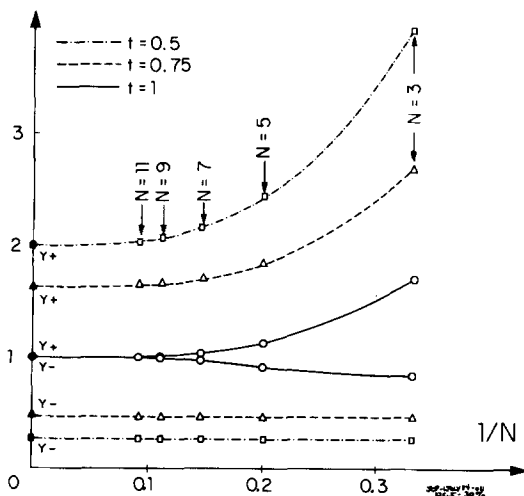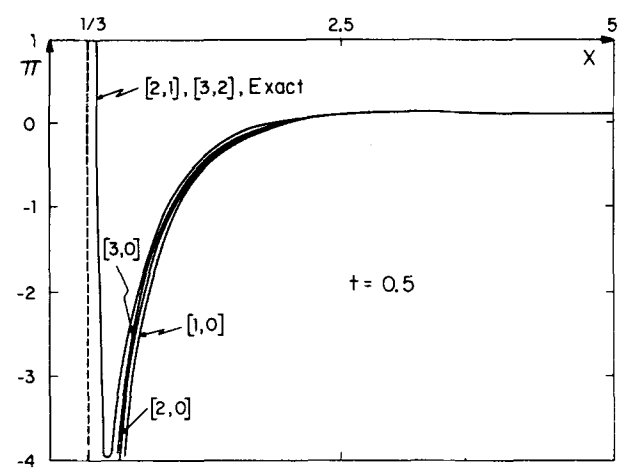
Namely, binomial expansion of the denominator of $[n/$

$m](x)$, and multiplication of the ensuing series by the numerator, differs by definition, from the $(n + m)$th partial sum by terms of order *higher* than $n + m$. This yields $n + m$ linear equations for determining the Padé coefficients $p_1, p_2, \ldots, p_n$; $q_1, q_2, \ldots, q_m$ in terms of the given $a_0, a_1, \ldots, a_{n+m}$.

Consider the function

$$f(x) = \sqrt{\frac{1+x}{1+2x}} \Big|_{|x| < 1/2} = 1 - \frac{1}{2}x + \frac{7}{8}x^2 - \frac{25}{16}x^3 + \cdots$$

whose Taylor series expansion converges for $|x| < \frac{1}{2}$ but *diverges* beyond this radius. The exact function is plotted in Fig. 6 and compared to the first two partial sums, both of which clearly represent $f(x)$ erroneously in a qualitative way for all but the smallest values of x. The simplest Padé approximant, the $[1/1](x)$, however, is seen to have *all* the qualitative features of our function for *all* x, even though its construction required no more information than is contained in the quadratic partial sum. The $[1/2](x)$ Padé is not quite as good—it clearly vanishes as $1/x$ for large x whereas
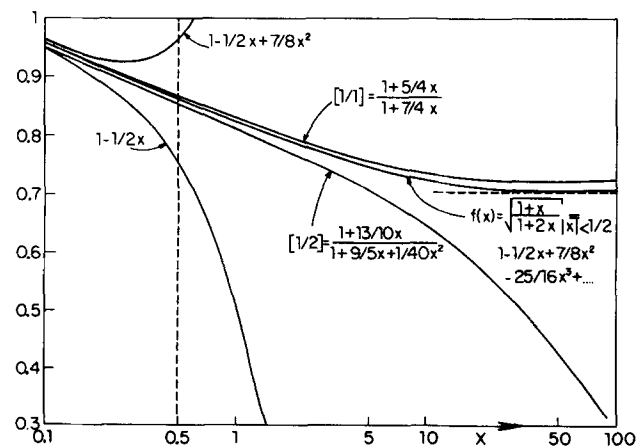

FIG. 4. The same as Fig. 3 but for $t = T/T_c = 0.5$.

FIG. 6. The function $f(x) = \sqrt{1 + x/1 + 2x}$, the first two partial summations, $1 - \frac{1}{2}x$ and $1 - \frac{1}{2}x + \frac{7}{8}x^2$, of its power series expansion about $x = 0$ (which diverges beyond $x = \frac{1}{2}$) compared with the $[1/1]$ and $[1/2]$ Padé approximants.

our function tends to the constant $1/\sqrt{2}$. The next Padé, the [2/2], is not shown since it *would coincide* with the curve $f(x)$ (to the scale used here). An analysis of the relative error of several Padé approximants, for x from 1 to 10^3, shows that going from [1/1] to [3/3] reduces the relative error by *three* orders of magnitude and likewise in going from [3/3] to [5/5]. The $[n/n + 1](x)$ get closer to $f(x)$ but from *below*, although not as rapidly as the "diagonal" approximants are doing (from *above*).

The example we have chosen is, in fact, a so-called Stieltjes function and thus it can be rigorously proved[6] not only that

$$[n/n + 1](x) \leqslant f(x) \leqslant [n/n](x), \quad (n = 0,1,2,...),$$

but also that

$$[n/n](x) \leqslant [n + 1/n + 1](x).$$

as well as

$$[n/n + 1](x) \leqslant [n + 1/n + 2](x).$$

Hence (i) increasing the order of a given $[n/m]$ or $[n/m + 1]$ Padé does not increase the relative error, and (ii) for sufficiently large n the upper and lower bounds to $f(x)$ coincide.

Unfortunately, the series we deal with in physics and engineering are, in general, not of the Stieltjes kind nor do we have rigorous convergence criteria for the different Padé approximants thereof.

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