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Padé Approximants Applied to the Equation of State and Heat Capacity of Quantum Ideal Gases

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Padé approximants have been applied to the equation of state and heat capacity of the quantum ideal gases. For the Bose gas the agreement is almost perfect. For the Fermi gas, the maximum relative error is 0.03% for the former and 0.4% for the latter.

KEY WORDS: Bose and Fermi quantum ideal gases; equation of state; heat capacity; Padé approximants.

1. INTRODUCTION

The treatment of quantum ideal systems by using equilibrium statistical mechanics presents well-known difficulties: approximate simple expressions exist for the extreme cases but not for the intermediate range. This holds true for the quantum ideal gases of Bose and Fermi as well as for solids at low temperatures (Debye model). Rational expressions for the whole possible range would be very useful for everyone interested in such systems from all branches of physics.

In most cases, the problem can be approached by using integer potential series. In the low-density range, these series are very similar to the virial expansions of classical statistical mechanics. However, in this case the virial coefficients are due to the quantum behavior, whereas in the classical fomulation they originate from molecular interactions.

One way of improving the results would be to increase the number of terms of the series. However, this would involve obvious difficulties. Another way would be to substitute Padé approximants [1] for the integer

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potential series. The Padé approximant $[L/M](x)$, in terms of the variable x, is a quotient of polynomials of the form

$$[L/M](x) = \frac{1 + p_1 x + p_2 x^2 + \cdots + p_L x^L}{1 + q_1 x + q_2 x^2 + \cdots + q_M x^M} \tag{1}$$

with the condition that $L + M \leqslant k - 1$, where k is the number of coefficients of the expansion that are known. The unknown coefficients p_i and q_i are obtained from the condition that the expansion of Eq. (1) in power series of the variable x must reproduce the first $L + M + 1$ coefficients of the development. Here we develop the treatment for Bose and Fermi ideal gases.

2. BOSE IDEAL GAS

The equation of state (EOS) for a Bose ideal gas given by a standard textbook on equilibrium statistical mechanics [2] is

$$\frac{P}{kT} = \frac{1}{\lambda^3} g_{5/2}(z) \tag{2}$$

where $\lambda = (h^2/2\pi mkT)^{1/2}$ is the thermal wavelength,

$$g_{5/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}$$

and z is the fugacity. This quantity varies between 0 and 1. If $z = 1$ (region of Bose–Einstein condensation), this function coincides with the Riemann zeta function of the same argument: $g_{5/2}(1) = \zeta(5/2) = 1.341\ldots$. In this case, the problem is completely solved. Outside of this region, the fugacity is implicity determined by the relation

$$\frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} g_{3/2}(z) \tag{3}$$

where

$$g_{3/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$$

Thus, z must be obtained by numerical methods.

The same question arises for the reduced specific heat capacity (C_V, in units of Nk), which is determined by the relation

$$\frac{C_V}{Nk} = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \tag{4}$$

where

$$g_{1\,2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{1\,2}}$$

Obviously $g_{1\,2}(z)$ diverges for $z = 1$. The difficulty is the same as for the EOS. To our knowledge, data for the three g functions are very scarce. Robinson [3] furnished polynomial expressions for these functions corresponding to values of α ($\alpha = -\ln z$) between 0 and 1. Later, London [4] calculated their values for $\alpha = 2$. Finally, tables for $g_{1\,2}$, $g_{3\,2}$, and $g_{5\,2}$, for $0 \leqslant \alpha \leqslant 5$ are given by Kincaid and Cohen [5].

Although these functions converge very slowly, when they do so, we have calculated their values to five exact digits by means of a computer program. In this way we have tabulated the values of $Z = PV/NkT$ and C_V/Nk.

Moreover, the earlier relations can be expressed in the form of a virial expansion, namely,

$$Z = \sum_{l=1}^{\infty} a_l \left(\frac{\lambda^3}{v}\right)^{l\ \ 1} \tag{5}$$

$$\frac{C_v}{Nk} = \frac{3}{2} \sum_{l=1}^{\infty} \frac{5-3l}{2} a_l \left(\frac{\lambda^3}{v}\right)^{l\ \ 1} \tag{6}$$

The first four coefficients of this virial expansion were found by Pathria [6]. To improve the approximation, we have calculated the fifth coefficient:

$$a_5 = \frac{1}{2^{5\,2}} + \frac{7}{2^6} + \frac{2}{3^3} - \frac{4}{5^{5\,2}} - \frac{1}{12^{1\,2}} = -3.5405 \times 10^{\ \ 6} \tag{7}$$

Ziff and Kincaid [7] calculated the virial coefficients for the d-dimensional ideal Bose gas ($d = 1, 2 \ldots 6$). For $d = 3$ the virial coefficients are given through the tenth order. Our numerical value for a_5 coincides exactly.

Alternatively making $x = \lambda^3/v$ we can write

$$Z = 1 + \sum_{l=2}^{\infty} a_l x^{l\ \ 1} = 1 + a_2 x \left(1 + \sum_{l=3}^{\infty} \frac{a_l}{a_2} x^{l\ \ 2}\right) \tag{8}$$

$$\frac{C_v}{Nk} = \frac{3}{2}\left(1 + \sum_{l=2}^{\infty} \frac{5-3l}{2} a_l x^{l\ \ 1}\right)$$

$$= \frac{3}{2}\left\{1 - \frac{1}{2} a_2 x \left[1 - \sum_{l=3}^{\infty} (5-3l) \frac{a_l}{a_2} x^{l\ \ 1}\right]\right\} \tag{9}$$

Table I. Variation of the Compressibility Factor Z for a Bose Ideal Gas as a Function of λ^3/v

	λ^3/v											
	0	0.1037	0.2159	0.3383	0.4734	0.6248	0.7982	1.0031	1.2586	1.6144	2.2714	2.6124
Z_{ex}	1	0.9816	0.9617	0.9398	0.9156	0.882	0.8567	0.8192	0.7721	0.7055	0.5800	0.5135
$Z[L, M]$	"	"	"	"	"	"	"	"	"	"	"	"
$Z[0, 4]$	"	"	"	"	"	"	0.8568	0.8195	0.7727	0.7076	0.5899	0.5315
Z_{Rob}	—	—	—	—	0.9210	0.8909	0.8584	0.8203	0.7728	0.7060	0.5803	0.5135

Z_{ex}, direct calculation with all exact digits; $Z[L, M]$, all Padé approximants excepting $[0, 4]$; $Z[0, 4]$, Padé $[0, 4]$; Z_{Rob}, Robinson's estimation; —, mean outside range of application.

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Table II. Variation of the Reduced Heat Capacity C_V/Nk for a Bose Ideal Gas as a Function of λ^3/v

	λ^3/v										
	0	0.1037	0.2159	0.3383	0.4734	0.6248	0.7982	1.0031	1.2586	1.6144	2.2714	2.6124
$(C_V/Nk)_{ex}$	3/2	1.5139	1.5291	1.5460	1.5650	1.5869	1.6124	1.6436	1.6838	1.74251	1.8598	1.9257
(C_V/Nk)[L, M]	3/2	"	"	"	"	"	"	"	"	"	"	1.9256
$(C_V/Nk)_{Rob}$]	3/2	—	—	—	1.5923	1.5014	1.6215	1.6497	1.6879	1.7452	1.8613	01.9257

$(C_V/Nk)_{ex}$, direct calculation with all exact digits; (C_V/Nk)[L, M], all Padé approximants except for explicit references; $(C_V/Nk)_{Rob}$, Robinson's estimation; —, mean outside range of application.
Except $(C_V/Nk)[3, 1] = 1.8599$.
Except $(C_V/Nk)[3, 1] = 1.9257$.

Table III. p_i and q_i Coefficient for the Approximants Deduced from the EOS of the Bose Ideal Gas

	[4, 0]	[3, 1]	[2, 2]	[1, 3]	[0, 4]
$p_1 \times 10$	−1.7678	−2.0859	−2.0622	−1.9695	
$p_2 \times 10^3$	−3.3001	2.3237	1.8250		
$p_3 \times 10^6$	−111.29	−6.3058			
$p_4 \times 10^6$	−3.5404				
$q_1 \times 10^2$		−3.1813	−2.9444	−2.0174	17.678
$q_2 \times 10^5$			−7.9893	−26.627	3455.0
$q_3 \times 10^6$				−2.3570	6802.3
$q_4 \times 10^3$					1.3397

The Padé approximants can now be generated from these expressions. All the approximants, except the [0, 4] for Z, agree perfectly with the reference values for both Z and C_V/Nk. Consequently, the results are presented as tables. Tables I and II show the results, while the coefficients are given in Tables III and IV.

[3, 1], [2, 2], and [1, 3] approximants for Z show a pole on the real axis with a value between 31 and 32. The corresponding radius of convergence ρ_R of the series exceeds to those obtained by other authors [7, 8]. This value is also somewhat greater than the Fuchs limit [9]. Unfortunately the [0, 4] approximant gives a worse agreement which is reflected with $\rho_R \approx 5$, corresponding to a pole: $-4.2405 \pm 3.1492i$.

In relation to the approximants for C_V/Nk, the radius of convergence ρ_R has the value 15.31.

Table IV. p_i and q_i Coefficient for the Approximants Deduced from the Reduced Heat Capacity of the Bose Ideal Gas

	[4, 0]	[3, 1]	[2, 2]	[1, 3]	[0, 4]
$p_1 \times 10^2$	8.8388	4.2941	−2.1778	−1.2239	
$p_2 \times 10^4$	66.001	25.831	6.8219		
$p_3 \times 10^5$	38.951	8.9558			
$p_4 \times 10^5$	1.7702				
$q_1 \times 10^2$		−4.5447	−11.017	−10.063	−8.8388
$q_2 \times 10^3$			3.8195	2.2941	1.2124
$q_3 \times 10^5$				7.1863	8.6701
$q_4 \times 10^6$					1.0611

3. FERMI IDEAL GAS

The relation which serves as a starting point for the EOS is now [6]

$$\frac{P}{kT}=\frac{g}{\lambda^3}f_{5/2}(z)=\frac{g}{\lambda^3}\sum_{l=1}^{\infty}(-1)^{l-1}\frac{z^l}{l^{5/2}} \tag{10}$$

where z is determined again by means of

$$\frac{N}{V}=\frac{1}{v}=\frac{g}{\lambda^3}f_{3/2}(z)=\frac{g}{\lambda^3}\sum_{l=1}^{\infty}(-1)^{l-1}\frac{z^l}{l^{3/2}} \tag{11}$$

Here g is a weight factor that arises from the "internal structure" of the particles (such as spin). In the ordinary case ($s=1/2$) $g=2$. However, we present our results without a previous assignment for the value of g. Furthermore, z can be any positive real number, in contrast to the case of free bosons.

Combining Eqs. (10) and (11), we easily find

$$Z=\frac{PV}{NkT}=\frac{f_{5/2}(z)}{f_{3/2}(z)} \tag{12}$$

From simple thermodynamic relations, the reduced heat capacity is expressed as

$$\frac{C_v}{Nk}=\frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)}-\frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} \tag{13}$$

where

$$f_{1/2}(z)=\sum_{l=1}^{\infty}(-1)^{l-1}\frac{z^l}{l^{1/2}}$$

In the "semiclassical" region, i.e., at a low density and/or high temperature, a virial expansion is applicable. This takes the form

$$Z=\frac{PV}{NkT}=\sum_{l=1}^{\infty}(-1)^{l-1}a_l\left(\frac{\lambda^3}{gv}\right)^{l-1} \tag{14}$$

$$\frac{C_v}{Nk}=\frac{3}{2}\sum_{l=1}^{\infty}(-1)^{l-1}\frac{5-3l}{2}a_l\left(\frac{\lambda^3}{gv}\right)^{l-1} \tag{15}$$

where the coefficients a_l are the same as in the case of bosons. The functions $f_n(z)$ have been studied in depth because of their contribution to

many fields of physics. Cloutman [10] has tabulated very extensively values of the functions $F_n(\ln z)$, closely connected with $f_n(z)$ by means of

$$\Gamma(n) f_n(z) = F_{n-1}(\ln z) \tag{16}$$

where $\Gamma(n)$ is the Eulerian gamma function. Substituting into Eqs. (12) and (13), we obtain practically exact values for Z and C_V/Nk.

From Eqs. (14) and (15) we can generate the corresponding Padé approximants. It is clear that the starting expressions become progressively more incorrect as λ^3/gv increases. However, an analytical treatment introduced by Sommerfeld [11] is available for the opposite case with high density and/or low temperature, i.e., for the highly degenerated system. Obviously, we cannot expand around λ^3/gv now because this quantity takes on excessive magnitudes. Instead, we introduce the Fermi energy as ($g = 2$)

$$\varepsilon_F = (h^2/2m)(3\pi^2 n)^{2/3}$$

where $n = N/V$. After brief manipulations, it is found that

$$\frac{\varepsilon_F}{kT} = \left(\frac{9\pi}{16}\right)^{1/3} [f_{3/2}(z)]^{2/3} \tag{17}$$

If we expand around the parameter

$$x = \left(\frac{\pi kT}{\varepsilon_F}\right)^2 = \left(\frac{16\pi^2}{9}\right)^{2/3} [f_{3/2}(z)]^{-2/3} \tag{18}$$

the Sommerfeld expansion contains only even powers in x. This quantity decreases progressively as the system becomes more degenerate, favoring its convergence. The expressions for the chemical potential (Fermi level) μ and the energy E appear in most textbooks on statistical mechanics and solid state physics. Recently Kiess [12] has proposed a straightforward, though tedious, method for obtaining the terms of the expansion. In spite of some shortcomings [13], the expansion is valid and allows more terms to be evaluated.

In this way, the expressions for μ and E were evaluated until the term in x^3. Later, Aguilera et al. [14, 15] found an additional term. From these expressions, we obtain the relations for the compressibility factor Z and the reduced heat capacity C_V/Nk, which we can write as

$$Z = \frac{2}{5}\frac{\varepsilon_F}{kT}\left(1 + \frac{5}{12}x - \frac{1}{16}x^2 - \frac{1235}{36{,}288}x^3 - \frac{10{,}367}{155{,}520}x^4 - \ldots\right)$$

$$= \frac{2}{5}\frac{\varepsilon_F}{kT}\left[1 + \frac{5x}{12}\left(1 - \frac{3}{20}x - \frac{247}{3024}x^2 - \frac{10367}{64800}x^3 - \ldots\right)\right] \tag{19}$$

$$\frac{C_v}{Nk} = \frac{1}{2}\frac{\varepsilon_F}{kT}x\left(1 - \frac{3}{10}x - \frac{247}{1008}x^2 - \frac{10367}{16200}x^3 - \ldots\right) \tag{20}$$

The corresponding Padé approximants have also been obtained. Figures 1 and 2 compare the more significant approximants with the exact values for Z and C_V/Nk corresponding to nondegenerate fermions, and Figs. 3 and 4 do the same for highly degenerate fermions.

We conclude that for the EOS, the [0, 3] approximant of the first sequence (nondegenerate fermions) is the best for $\lambda^3/gv < 10.114$, while also the [0, 3] approximant of the second sequence (highly degenerate fermions) is the best for $\lambda^3/gv > 10.114$. The maximum relative error is 0.0278%. The coefficients are $a_2 = 1.7678 \times 10^{-1}$, $q_1 = 1.8668 \times 10^{-2}$, $q_2 = -2.8103 \times 10^{-4}$, and $q_3 = 3.0257 \times 10^{-6}$ for the first case and $a_2 = 4.1667 \times 10^{-1}$, $q_1 = 1.5000 \times 10^{-1}$, $q_2 = 1.0418 \times 10^{-1}$, and $q_3 = 1.8786 \times 10^{-1}$ for the second case.

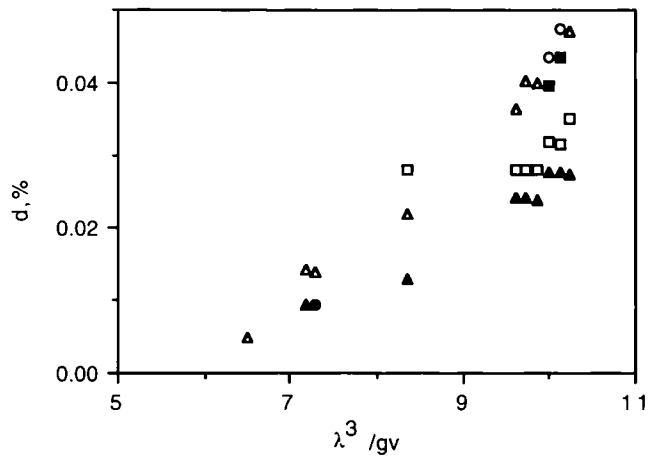

Fig. 1. Percentage deviation: $d = [(Z_{calc} - Z_{tab})/Z_{tab}] \times 100$ for the compressibility factor as a function of λ^3/gv for nondegenerate fermions. Open triangles, global approximant (comprises all approximants not represented explicitly because they are indistinguishable at the scale of the figure); filled triangles, [0, 3] approximant; open squares, [1, 3] approximant; filled squares, [2, 2] approximant; open circles, [2, 1] approximant; filled circles, [0, 3] and [1, 3] approximans.

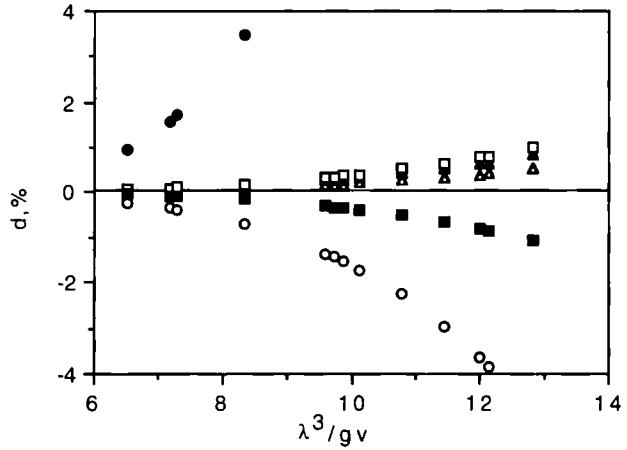

Fig. 2. Percentage deviation: $d = \{[(C_V/Nk)_{calc} - (C_V/Nk)_{tab}]/(C_V/Nk)_{tab}\} \times 100$ for the reduced heat capacity C_V/Nk as a function of λ^3/gv for nondegenerate fermions. Open triangles, [1, 2] approximant; filled triangles, [0, 4] approximant; open squares, [1, 3] approximant; filled squares, [0, 3] approximant; open circles, [3, 1] approximant; filled circles, [4, 0] approximant.

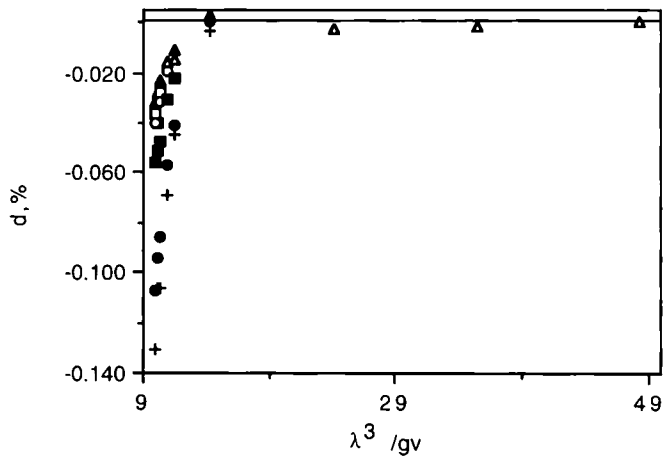

Fig. 3. As in Fig. 1 but as a function of λ^3/gv for highly degenerate fermions. Open triangles, global approximant (as in Fig. 1); filled triangles, [0, 3] approximant; open squares, [1, 3] approximant; filled squares, [0, 4] approximant; open circles, [3, 0] approximant; filled circles, [1, 2] approximant; plus (cross), [2, 1] approximant.

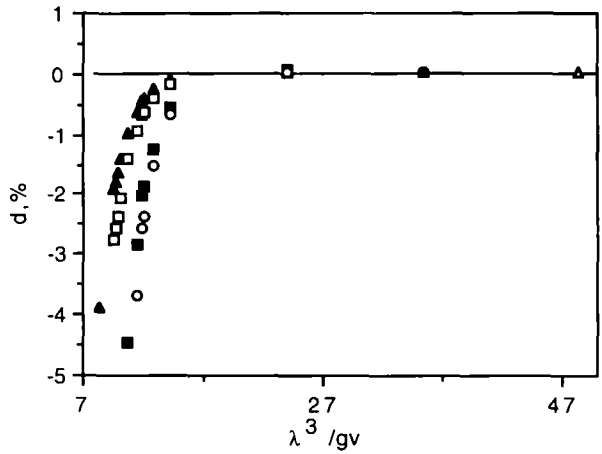

Fig. 4. As in Fig. 2 but as a function of λ^3/gv for highly degenerate fermions. Open triangles, global approximant (as in Fig. 1); filled triangles, [0, 3] approximant; open squares, [3, 0] approximant; filled squares, [1, 2] approximant; open circles, [2, 1] approximant; filled circles, [1, 2] and [2, 1] approximants.

With respect to C_V/Nk, the division is established for $\lambda^3/gv = 12$. For lower values of λ^3/gv the [1, 2] approximant of the first sequence is the best choice, while for higher values of λ^3/gv, the [0, 3] approximant of the second sequence is the most adequate. The maximum relative error is now 0.410%. The respective coefficients are $a_2 = -8.8390 \times 10^{-2}$, $p_1 = 3.5504 \times 10^{-2}$, $q_1 = 1.1018 \times 10^{-1}$, and $q_2 = 3.8201 \times 10^{-3}$ for the first case and, for the second case [coefficients derived from the terms inside parentheses in Eq. (20)]: $q_1 = 3.0000 \times 10^{-1}$, $q_2 = 3.3504 \times 10^{-1}$, and $q_3 = 8.1396 \times 10^{-1}$.

In summary, the agreement is completely satisfactory. Therefore, the introduction of more complicated approximants makes no sense.

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