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The Pauli Principle and the Restricted Primitive Model

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The restricted primitive model is an electrically neutral, classical model consisting of hard spheres charged either $+q$ or $-q$. We show that, by appropriately selecting the diameter of the hard spheres, the pressure when $q=0$ can be made equal to that for a fluid of Maxwell–Boltzmann point ions and an ideal Fermi gas of electrons. We compare the series expansion of these classical and quantum systems and find that, except for intermediate de Broglie density and moderate to strong electrical interaction strength, the restricted primitive model gives a reasonable representation of the pressure of the corresponding quantum system. Much of the current interest, however, has been focused on the above, excepted region.

KEY WORDS: Equations of state; primitive model; quantum perturbation theory; classical perturbation theory; hydrogen.

In the theory of ionic solutions,$^{(1)}$ the restricted primitive model seemed a reasonable way to approximate the true many-body quantum problem.$^{(2)}$ In its original form, we have a classical, hard-sphere gas. One half of the spheres are charge $+q$ and the other half are charged $-q$. Stell and Lebowitz$^{(3)}$ derived an expansion in powers of the charge about the hard-sphere gas limit. This expansion was further studied by Stell and Wu.$^{(4)}$ It has also been simulated by Monte Carlo methods.$^{(5)}$ It is our view that, over an appropriate range of conditions, the hard sphere is a means of simulating classically the repulsion of the Pauli principle of quantum

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mechanics. A further word should be said about the interaction between the positively and negatively charged particles. After all, there is clearly no Pauli exclusion between them. Never-the-less, we know that in the quantum mechanical treatment that the eigenspectrum is lower semi-bounded. In turn, there is a lower bound on the average separation (depending on the pressure, for example) between these two types of particles. Thus the restricted primitive model is not wholely unsatisfactory to model the interaction in the oppositely charged case. In this case, the words Pauli principle in the title are a compact metaphor for the effective quantum repulsion.

Just because a model might be thought to be primitive or crude does not mean it is uninteresting. Consider, as an example, the Ising model. It is certainly primitive and crude, but its study through the years has been very illuminating. The restricted primitive model has, in recent years, been the subject of considerable study(6) with regard to consideration of the nature of the critical point in various ionic fluids amongst other aspects.

As far as we have been able to tell, not much study has been given to the question of the appropriate choice of the diameter of the hard sphere.(6) In this study, we will consider the restricted primitive model with ions of charge $+e$ and electrons of charge $-e$. All of these particles will be represented by hard spheres of the same diameter c. The more realistic problem of the charged hard-sphere/point-ion mixture(7) could be studied by the same methods we employ here, but we will not do so. The Stell and Lebowitz(3) expansion results include the restricted primitive model where $\sum_{\nu} z_{\nu}^{l} \rho_{\nu} = 0$ for all odd l.

It is well known that a system of hard spheres can not be compressed beyond a certain density. On the other hand a system of point ions and point electrons can be compressed to an arbitrarily high density. (We are not however thinking of compressions so high as to force protons and electrons to combine into neutrons.) The criterion that we will use to select the diameter of the hard spheres is to make the pressure of the reference system, i.e., the uncharged, hard-sphere system, equal to the actual pressure of the uncharged quantum system.

Baker *et al.*(8) have reviewed the classical hard sphere fluid. They use the virial expansion,

$$\frac{P\Omega}{2NkT} = \Theta(x) = 1 + 2.961921959x + 5.483113556x^2 + 7.456350520x^3 + 8.485568085x^4 + 8.868x^5 + 9.250x^6 + \cdots \tag{1}$$

as computed by Kratky.(9) Here Ω is the volume, k is Boltzmann's constant, T is the absolute temperature, N is the number of ions, and also the number of electrons. We use x as the density divided by the density of close packing. That is,

$$0 \leqslant x \equiv \rho/\rho_0 \leqslant 1, \qquad \rho_0 \equiv \sqrt{2}/c^3, \tag{2}$$

where c is the diameter of the hard spheres. This series is rigorously known to converge for $|x|$ less than or about equal to 0.026.$^{(10)}$ One would expect that a fluid phase would exist for $x \leqslant x_0$, where x_0 is the density of random close packing. Scott and Kilgour$^{(11)}$ have found the empirical value $x_0 = 0.8597$. (See also, Visscher and Bolsterli.$^{(12)}$) Baker *et al.*$^{(8)}$ have found that the [2/4] and the [3/3] Padé approximants$^{(13)}$ reproduce this empirical value to two digit accuracy. We find it convenient to use the [3/3] which diverges at $x = 0.8622$. It is,

$$\Theta(x) \approx \frac{1 + 0.61965799x + 0.62970656x^2 - 0.040053014x^3}{1 - 2.3422639x + 2.0841961x^2 - 0.82673025x^3}. \tag{3}$$

This result gives us a very convenient analytic representation for the pressure of the hard-sphere-gas, reference system.

The corresponding quantum system is hydrogen, which for our case is an ideal Fermi gas of electrons plus a Maxwell–Boltzmann gas of ions. The results for the ideal Fermi gas are well known$^{(14)}$ to be,

$$\frac{P\Omega}{NkT} = \frac{f_{5/2}(z)}{f_{3/2}(z)} = g(\zeta), \tag{4}$$

where ζ is the de Broglie density

$$\zeta = \frac{N}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} = f_{3/2}(z) \tag{5}$$

and

$$f_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{zy^{n-1}e^{-y}\,dy}{1 + ze^{-y}} = \sum_{l=1}^{\infty} \frac{(-1)^{l+1}\,z^l}{l^n}. \tag{6}$$

The function $g(\zeta)$ is obtained by solving Eq. (5) for $z(\zeta)$ and then substituting in Eq. (4). Baker and Johnson$^{(15)}$ give the handy representation

$$g(\zeta) \approx \left[\frac{1 + 0.62094880\zeta + 0.12660436\zeta^2 + 0.0091177644\zeta^3}{1 + 0.080618739\zeta}\right]^{1/3}, \tag{7}$$

which is accurate to within 0.1%. Thus the total pressure for the corresponding quantum system is,

$$p = \frac{NkT}{\Omega}\,[1 + g(\zeta)]. \tag{8}$$

We may now select the appropriate diameter by equating the pressures found in Eqs. (1) and (8). Therefore,

$$2\Theta(x(\zeta)) = 1 + g(\zeta). \tag{9}$$

By use of the representation Eq. (3), Eq. (9) becomes a cubic equation in x, which we may solve by means of Cardan's method.(16) The coefficients are such that there is just one real root. It is positive and lies between 0 and 0.8622. For $\zeta = 0$ we find $x = 0$, and as $\zeta \to \infty$ we have $x \to 0.8622$. From $x(\zeta)$ we may deduce that

$$c = \left[\frac{x(\zeta)}{\sqrt{2}\rho}\right]^{1/3} = \sqrt{\pi}\left[\frac{x(\zeta)}{\zeta}\right]^{1/3}\left(\frac{\hbar^2}{mkT}\right)^{1/2}, \tag{10}$$

where the last factor is λ, the "thermal length." When this choice of c is made, we are guaranteed that the pressure of the reference system is equal (within our errors as noted above) to that for the corresponding quantum system. In Fig. 1 we plot $x(\zeta)$ for hydrogen. In Fig. 2 we plot the value of the diameter c of the hard spheres over the thermal length λ again for hydrogen.

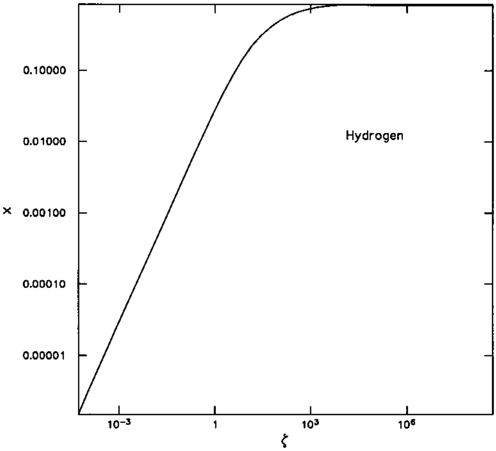

Fig. 1. The density ratio x as a function of the deBroglie density ζ.

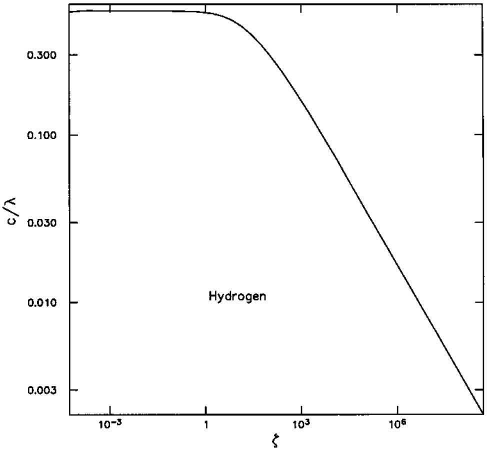

Fig. 2. The ratio of the hard-sphere diameter c to the thermal length λ as a function of the deBroglie density ζ.

Stell and Wu$^{(4)}$ give the excess free energy for the restricted primitive model as an expansion in powers of the electron charge e. If the Helmholtz free energy $\mathscr{A}$ is related to S by $\mathscr{A} = -kT\Omega S$, and S_0 is the result for the reference system, then they give,

$$(S - S_0)\, c^3 = \frac{(\kappa c)^3}{12\pi}\, [A + B\kappa c + C(\kappa c)^2 + D(\kappa c)^3 + \cdots, \tag{11}$$

where

$$A = 1, \qquad B = \tfrac{3}{4} J2, \qquad C = -\tfrac{3}{2} J1, \ldots \tag{12}$$

and

$$\kappa^2 = \frac{4\pi e^2}{kT} \sum_{\nu} Z_{\nu}^2 \rho_{\nu} = \frac{8\pi e^2}{kT}\, \rho \tag{13}$$

for our case. κ is the reciprocal Debye length and ν is the species index. As we will be comparing this result with the corresponding quantum case, we will only carry the computations through order κ^4 as that is as far as those computations go.$^{(17)}$ In order to compare with the quantum case we use the same expansion parameter as is used in the paper of Baker and Johnson.$^{(17)}$ It is

$$y^2 = \frac{e^2}{r_b kT} \qquad \text{with} \quad r_b = \left[\frac{3\Omega}{4\pi N} \right]^{1/3}, \tag{14}$$

where r_b is the Wigner-Seitz, cellular-model radius. The quantity $J2$ is given by Stell and Wu(4) as

$$J2 = \frac{1}{c}\int_0^\infty h_{12}^0\, dr \qquad \text{with} \quad h_{12}^0 = -1 + g_{12}^0, \tag{15}$$

where g_{12}^0 is the radial distribution function for the reference system. They use the approximation formulated, and privately communicated to them, by Rasaiah which is

$$J2^{\mathrm{RI}} \approx -\left(\frac{1 + 0.1156871\rho c^3 + 0.005611\rho^2 c^6}{1 + 0.573836\rho c^3}\right). \tag{16}$$

By Eq. (2) $\rho c^3 = x(\zeta)/\sqrt{2}$, which is a function of ζ only. Putting these results together we get

$$\begin{aligned} -kT\Omega(S - S_0) = {} & -2\sqrt{\frac{2}{3}}\, NkTy^3 \left[1 + \sqrt{6}\left(\frac{3\sqrt{\pi}}{4}\right)^{2/3} \left(\frac{x(\zeta)}{\sqrt{2}}\right)^{1/3} \right. \\ & \left. \times J2\left(\frac{x(\zeta)}{\sqrt{2}}\right) y + \cdots \right]. \end{aligned} \tag{17}$$

By use of the thermodynamic identity $p\Omega = -\Omega \partial \mathscr{A}/\partial\Omega|_T$ we obtain the pressure from Eq. (17) as,

$$\begin{aligned} \frac{p\Omega}{NkT} = {} & 1 + g(\zeta) - \sqrt{\frac{2}{3}}\, y^3 \left\{ 1 + \sqrt{6}\left(\frac{4\pi}{3}\right)^{1/3} \left(\frac{x(\zeta)}{\sqrt{2}}\right)^{1/3} J2\left(\frac{x(\zeta)}{\sqrt{2}}\right) \right. \\ & \left. \times \left(1 + \frac{d \log x(\zeta)}{d \log \zeta} \left[\frac{1}{2} + \frac{3}{2}\frac{J2'}{J2}\left(\frac{x(\zeta)}{\sqrt{2}}\right) \right] \right) y + \cdots \right\}. \end{aligned} \tag{18}$$

Note is to be taken that Eq. (18) gives an expansion on the right-hand side in powers of y whose coefficients are functions of ζ alone.

The results for the pressure for the corresponding quantum system have been given by Baker and Johnson.(17) Their results are,

$$\frac{p\Omega}{NkT} = 1 + g(\zeta) + G_2(\zeta)\, y^2 + G_3(\zeta)\, y^3 + G_4(\zeta)\, y^4 + \cdots. \tag{19}$$

The $G_i(\zeta)$ are defined by the small y behavior for general ζ by Eq. (19) and the expressions for the G_i are given in full in ref. 17 as well as handy numerical representations. $G_0(\zeta) \equiv 1 + g(\zeta)$. We will not give these formulae here as they are rather lengthy to set out, but will confine ourselves to

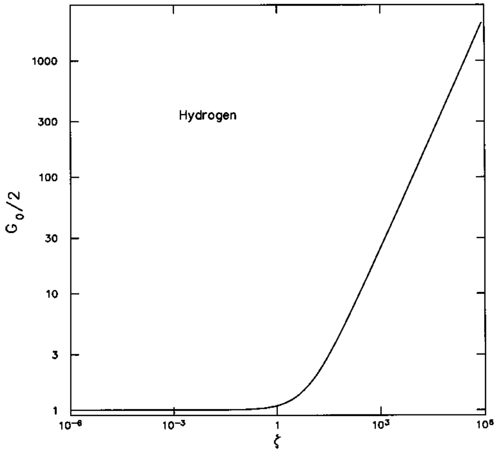

Fig. 3. $[1+g(\zeta)]/2$ for hydrogen.

numerical examples. The behavior of the zeroth order term is illustrated in Fig. 3 for hydrogen.

One obvious difference between the classical and the quantum cases is the fact that the classical case (at least for hydrogen) has no y^2 term and the quantum case does. In Fig. 4 we plot the ratio G_2/G_0, again for hydrogen. This contribution is a purely quantum one and is the exchange correction. We see that it is relatively small.

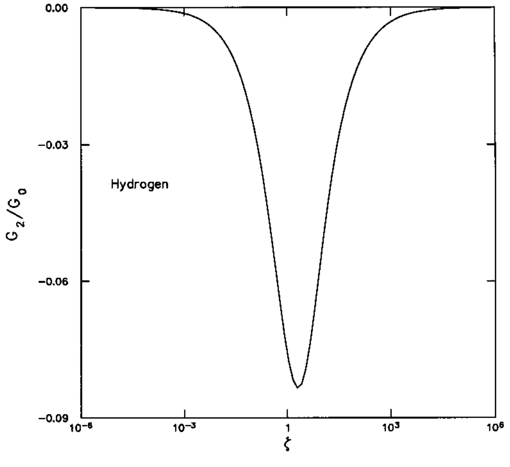

Fig. 4. G_2/G_0 for hydrogen.

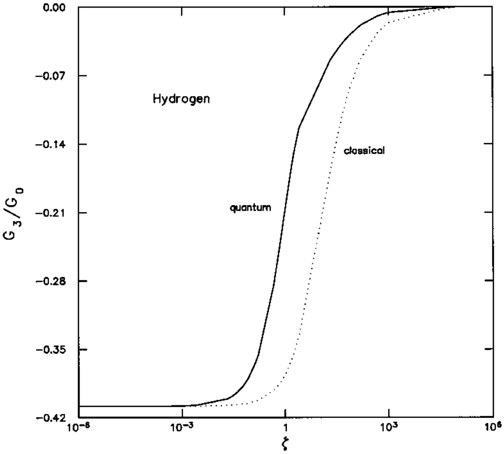

Fig. 5. G_3/G_0 for hydrogen in the classical and the quantum cases.

We next turn to the consideration of the y^3 term. It is called the Debye–Hückel term,$^{(18)}$ after their discovery of it in the theory of ionic solutions. We show it in Fig. 5 for hydrogen. For hydrogen, the shapes of the classical and the quantum curves are very similar, but they are offset in ζ by about one order of magnitude.

For the fourth coefficient, we notice a marked difference between the quantum results and the classical case. These results are illustrated in Fig. 6 for hydrogen. Most obviously, these curves are of different signs for the classical and the quantum cases! The magnitude of the classical coefficient

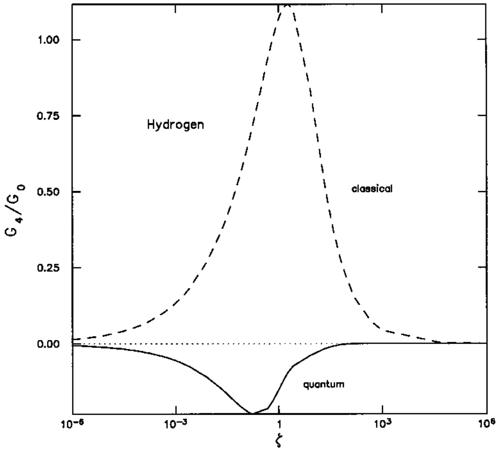

Fig. 6. G_4/G_0 for hydrogen in the classical and the quantum cases.

is larger than that of the quantum coefficient. This term in the quantum case involves the "second exchange correction" and the next term in the expansion of the Debye–Hückel term. In both the classical case and the quantum case, four-particle correlations are involved.

From these comparisons, at least in the area of plasma physics, we can conclude that both for low deBroglie density (classical limit) and for high deBroglie density (degenerate quantum gas limit) that the restricted primitive model does reasonably well in representing the pressure. For intermediate deBroglie densities and weak coupling, that is smallish y, it will also do reasonably well. However for moderate to strong coupling and intermediate deBroglie density, the discrepancies in the third and fourth coefficients indicate that the detail behavior in this region will vary between the two models. This is not too surprising when one remembers that condensation into atoms, and atoms into molecules(19) occurs here, and that the effects of quantum mechanics are very considerable.

It is, of course, not surprising that when the interaction is weak $(y \ll 1)$ that the kinetic energy dominates and so both the quantum and the classical systems reduce to the ideal gas. Likewise, at very high deBroglie densities, $\zeta \gg 1$, the electron pressure due to the Pauli exclusion principle becomes dominant and again the quantum system and our modified, restricted, primitive model tend to the same values. It might have been the case that a miracle occurred and the modified, restricted, primitive model was also accurate in the intermediate regions, but such is not the case. We provide *quantitative* results to enable one to put limits on the region where a given accuracy can be expected for the modified, restricted, primitive model.

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