Can an Attractive Potential Increase the Pressure of an Ideal Electron Gas?

George A. Baker, Jr.[1]

We examine the intuitive, classical idea that an interactive system involving commonly used attractive potentials should always have a pressure which is less than that of an ideal Fermi gas. We find that quantum effects are of crucial importance and that, while this idea is normally correct, under certain circumstances, the pressure can exceed that of the ideal Fermi gas.

1. INTRODUCTION AND SUMMARY

It is well known that a neutral system of ions and electrons has an energy which is less than that of the corresponding non-interacting system. This result can be deduced simply by noting first that the expectation value of the Hamiltonian using any wave function is an upper bound. We choose the expectation value of the interactions using the ideal Fermi gas wave function. The upper bound on the energy shift is just the e^2 term in the Matsubara perturbation series. This term is of fixed negative sign. See, for example, ref. 1. One might suppose intuitively, that an attractive potential would also reduce the pressure that the system exerts on its container. The idea is that the attractive potential would cause the particles to clump together and thus behave effectively like a smaller number of particles. Hence they would exert less pressure. In this paper we will see that the situation is more subtle than the above argument might suggest. While this argument might be valid in the classical case, where $p\Omega/NkT$ was shown[2] to depend only on a single variable proportional to $T^3\Omega$, it is well known

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[1] Theoretical Division, Los Alamos National Laboratory University of California, Los Alamos, New Mexico 87545; e-mail: gbj@lanl.gov

that the classical case does not exist. The reason is that in it the energy is not lower semi-bounded. We denote the pressure by p, the volume by Ω, the number of ions by N, Boltzmann's constant by k and the temperature by T. The role of quantum mechanics is crucial. We will see that, under certain circumstances, it does seem to be possible that the electron pressure can exceed that of an ideal gas, even though the ion-electron potential is attractive. The type of electron-ion potential that can cause this effect is of the same character as the one use in the Thomas–Fermi theory of the equation of equation of state. This theory[3–8] and its derivative theories, e.g., the Thomas–Fermi–Dirac theory[9, 10] are perhaps the theories in most general use today.

In order to lay the basis for our investigation, we show in the second section, that the exact solution for the pressure of an ideal Fermi gas can be reformulated in terms of the normal statistical mechanical formulæ as applied to the quantum mechanical solution in a Wigner–Seitz cell[11] of a Bravais lattice, when integrated over the first Brillouin zone.[12] This reinterpretation amounts to a reorganization of the integrals which appear in the exact solution for the ideal Fermi gas. Following Wigner and Seitz,[11] the computations will be simplified by changing the shape of the cell to a sphere. It is pointed out that Baker[13] has studied previously the error in the pressure for the ideal gas resulting from the use of a spherical cell. This error is at most only a few percent.

In the third section, we focus on the low temperature limit of a moderately dilute, spherical, cellular model. The potential used is that of Hydrogen near the ion, but drops more rapidly than the normal Coulomb potential as the distance from the ion increases. We find that in cases of this character, the pressure, although rather small, can exceed that for the ideal Fermi gas by a substantial factor. We outline in a simple case an analytic calculation by means of perturbation theory which demonstrates that the pressure can increase above that for an ideal Fermi gas. We also demonstrate numerically this effect by a direct computation of the pressure in the spherical cellular model approximation.

2. CELLULAR VERSION OF THE IDEAL FERMI GAS

The text book formulation of the pressure of an ideal gas is basically as follows. Consider a large cube of edge L with periodic boundary conditions. The eigenvalues of the Schrödinger equation are

$$\frac{\hbar^2 (2\pi)^2 (i^2 + j^2 + k^2)}{2mL^2}. \tag{2.1}$$

The i, j and k are all integers (positive, negative or zero). The grand partition function is given as

$$\mathcal{Z}(\Omega, T) = \sum_{N=0}^{\infty} \exp[N\mu(\Omega, T)/(kT)] \, Q_N(\Omega, T)$$

$$= \sum_{N=0}^{\infty} \sum_{\substack{\{n_j\} \\ \sum n_j = N}} \exp\left[\sum_j (\mu(\Omega, T) - \epsilon_j) \, n_j/(kT)\right]$$

$$= \prod_j \{1 + \exp[(\mu(\Omega, T) - \epsilon_j)/(kT)]\}, \tag{2.2}$$

for the case of Fermi statistics as $n_j = 0, 1$ only. The parameter μ is determined by N, the expected number of Fermions in the cube. By taking the partial derivative of $\log \mathcal{Z}$ with respect to the parameter μ, we can obtain in the usual manner,

$$N = \sum_j \frac{1}{\exp[(\epsilon_j - \mu)/kT] + 1}. \tag{2.3}$$

Using this value of μ, we may deduce the Helmholtz free energy from the logarithm of the partition function as

$$A(\Omega, T) = N\mu(\Omega, T) - kT \sum_j \ln\{1 + \exp[(\mu(\Omega, T) - \epsilon_j)/(kT)]\} \tag{2.4}$$

The presure is also determined in the usual way as

$$p\Omega = -\Omega \left.\frac{\partial A}{\partial \Omega}\right|_T = -\sum_j \frac{\Omega \left.\dfrac{\partial \epsilon_j}{\partial \Omega}\right|_T}{\exp[(\epsilon_j - \mu)/kT] + 1}. \tag{2.5}$$

Since each eigenvalue is inversely proportional to L^2, and the volume Ω is just L^3, $\Omega \partial \epsilon_j / \partial \Omega = -\frac{2}{3}\epsilon_j$, which leads to the usual result, $p\Omega = \frac{2}{3}U$, where U is the internal energy. In the limit of infinite box size ($L \to \infty$) Eq. (2.3) becomes,

$$\zeta = \frac{N}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}} = f_{\frac{3}{2}}(z) = \frac{2}{\sqrt{\pi}}\int_0^{\infty} \frac{zy^{\frac{1}{2}}e^{-y}\,dy}{1 + ze^{-y}}, \tag{2.6}$$

where ζ is the de Broglie density which measures the importance of quantum effects, and $z = \exp(\mu/kT)$. The leading factor of $\frac{1}{2}$ arises because

we are considering spin $\frac{1}{2}$ Fermions, e.g., electrons. In this limit, Eq. (2.5) becomes

$$\frac{p\Omega}{NkT} = \frac{f_{\frac{5}{2}}(z)}{f_{\frac{3}{2}}(z)}, \tag{2.7}$$

where,

$$f_{\frac{5}{2}}(z) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{z y^{\frac{3}{2}} e^{-y} \, dy}{1 + z e^{-y}}, \tag{2.8}$$

Let us select $a^3 = \Omega/N$, so that the volume is exactly filled by N small cubes of edge a. The structure of the N small cubes is just a portion of a simple cubic lattice. The reciprocal lattice to this lattice is also a simple cubic lattice and the edge of a primitive cell is $2\pi/a$. If we make the change of variables, $y = \hbar^2 (\vec{k})^2 / (2mkT)$, then (2.6) may be rewritten as,

$$1 = \frac{2a^3}{(2\pi)^3} \iiint_{-\infty}^{\infty} \frac{z \exp\left(-\dfrac{\hbar^2 k^2}{2mkT} \right) d\vec{k}}{1 + z \exp\left(-\dfrac{\hbar^2 k^2}{2mkT} \right)}. \tag{2.9}$$

If we now divide the range of integration of $\vec{k}$ up according to the primitive cells of the reciprocal lattice we obtain the equation for μ as,

$$1 = 2 \sum_{j_1=-\infty}^{+\infty} \sum_{j_2=-\infty}^{+\infty} \sum_{j_3=-\infty}^{+\infty} \left(\frac{a}{2\pi} \right)^3 \iiint_{-\pi/a}^{\pi/a} \frac{d\vec{k}}{1 + z^{-1} \exp\left[\dfrac{\hbar^2}{2mkT} \left(\vec{k} + \dfrac{2\pi}{a} \vec{j} \right)^2 \right]}, \tag{2.10}$$

where the steps in the sums of the j_i are just unity. The corresponding formula for the pressure is just,

$$\frac{p\Omega}{NkT} = \frac{4}{3} \sum_{j_1=-\infty}^{+\infty} \sum_{j_2=-\infty}^{+\infty} \sum_{j_3=-\infty}^{+\infty} \left(\frac{a}{2\pi} \right)^3 \iiint_{-\pi/a}^{\pi/a} \frac{\dfrac{\hbar^2}{2mkT} \left(\vec{k} + \dfrac{2\pi}{a} \vec{j} \right)^2 d\vec{k}}{1 + z^{-1} \exp\left[\dfrac{\hbar^2}{2mkT} \left(\vec{k} + \dfrac{2\pi}{a} \vec{j} \right)^2 \right]}, \tag{2.11}$$

We may now introduce an interpretation of (2.10)–(2.11) in terms of the solution of Schrödinger's equation in a small (Wigner–Seitz) cell. In the

theory of periodic lattices, Bloch's theorem states[12] that any solution for the "one-electron wave function" is of the form $\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\phi(\vec{r})$, where $\phi(\vec{r})$ has the periodicity of the lattice. Following this idea, if we substitute $e^{i\vec{k}\cdot\vec{r}}\phi(\vec{r})$ in the Schrödinger equation, we obtain,

$$\frac{\hbar^2 k^2}{2m}\phi_\lambda(\vec{r}) - \frac{i\hbar^2}{m}\vec{k}\cdot\vec{\nabla}\phi_\lambda(\vec{r}) - \frac{\hbar^2}{2m}\nabla^2\phi_\lambda(\vec{r}) + V(\vec{r})\,\phi_\lambda(\vec{r}) = E_\lambda(\vec{k})\,\phi_\lambda(\vec{r}). \quad (2.12)$$

where for the ideal gas, $V(\vec{r}) = 0$. The boundary conditions required by periodicity are,

$$\vec{n}\cdot\vec{\nabla}\phi_{\text{even}} = 0, \qquad \phi_{\text{odd}} = 0, \quad (2.13)$$

where $\vec{n}$ is the outward pointing normal to the surface of the cell, and "even" and "odd" refer to the parts of the wave function which are even or odd under a reflection operation which maps the cell onto itself. We observe that

$$\phi(\vec{r}) = \exp\left(\frac{2\pi i}{a}\,\vec{j}\cdot\vec{r}\right) \quad (2.14)$$

has the eigenvalues

$$\frac{\hbar^2}{2m}\left(\vec{k} + \frac{2\pi}{a}\,\vec{j}\right)^2. \quad (2.15)$$

Thus, (2.10) and (2.11) are exactly same as if we were to have applied the standard statistical mechanical formulæ to a single small cell, except that instead of the eigenvalues being just a set of discrete values, we must integrate over the first Brillouin zone ($0 \leqslant k_i \leqslant 2\pi/a$).

   If one traces through the above discussion, it is clear that the same construction works for any Bravais lattice. The small cell is then just the Wigner–Seitz cell for that lattice. As the reciprocal lattice of a Bravais lattice is a Bravais lattice,[12] again the results which correspond to (2.10) and (2.11) are just a rearrangement of the integrals. The reciprocal of a body centered cubic lattice is just the face centered cubic lattice, and vice versa. The Wigner–Seitz cells are the truncated octahedron for the bcc lattice and the rhombic dodecahedron for the fcc lattice. They are more nearly spherical than is a cube. This feature suggests, with an eye to the incorporation of a spherically symmetrical potential, the study of a spherical cell (as used by Wigner and Seitz in their original paper[11]). Baker[13] has found that this approximation results in an error for the ideal gas of at most a few percent and the error tends to zero for both very large and very

small values of ζ. A further motivation for the use of the spherical cellular model is the spherical-cell character of the Thomas–Fermi and the Thomas–Fermi–Dirac models.

3. PRESSURE FOR A SPECIAL CASE OF THE SPHERICAL CELLULAR MODEL

In the previous section we saw how the pressure for the ideal Fermi gas could be re-expressed in terms of the eigenvalues of the Schrödinger equation with periodic boundary conditions in a small (Wigner–Seitz) cell. The effect on the ideal gas pressure of using a spherical cell was discussed and found to be small. We will use the spherical cell approximation in this section. In this section we allow $V(\vec{r})$ in Eq. (2.12) to be different from zero. We will consider the case where it is purely attractive. In the study of elements with nuclear charge larger than unity, it is common to consider one-electron states in a screened potential. That is to say, close to the nucleus, the full charge is felt, and as the distance increases, a smaller and smaller central charge is felt.

According to the results of the previous section, the ideal gas pressure can be expressed in terms of the results computed in a small cell. Generalizing this formalism to the non-ideal case we obtain,

$$1 = 2 \sum_{\lambda} \left(\frac{a}{2\pi} \right)^3 \iiint_{-\pi/a}^{\pi/a} \frac{d\vec{k}}{\exp[(E_{\lambda}(\vec{k}) - \mu)/kT] + 1}, \tag{3.1}$$

and

$$p\Omega = -2 \sum_{\lambda} \left(\frac{a}{2\pi} \right)^3 \iiint_{-\pi/a}^{\pi/a} \frac{\Omega \left. \frac{\partial E_{\lambda}(\vec{k})}{\partial \Omega} \right|_T d\vec{k}}{\exp[(E_{\lambda}(\vec{k}) - \mu)/kT] + 1}. \tag{3.2}$$

We observe from these equations that when the temperature is small and the lowest eigenvalue is non-degenerate, the principal contributions come from the that eigenvalue alone. Following the ideas expressed at the end of the previous section, we will choose a spherical cell. The radius $r_b = [3\Omega/(4\pi N)]^{\frac{1}{3}}$ insures that there is, on the average, one electron per cell. The first Brillouin zone is $|\vec{k}| \leqslant k_B$, where $k_B = (9\pi/2)^{1/3}/r_b$. We begin with (2.12) and impose the boundary conditions (2.13) where now "even" and "odd" mean the angular momentum l is even or odd respectively. If we choose the potential $V(r) = -(e^2/r)[1 + \omega v(r/r_b)]$, then if $v(x) = 0$, we have the ordinary Coulomb potential for Hydrogen. In this case the lowest

eigenvalue is non-degenerate, and manifestly so if r_b is not small compared to the Bohr radius, a_0.

For the dilute, Coulomb case, we know, except for an error which is exponentially small in the radius of the sphere, that the potential energy in the ground state is minus twice the kinetic energy,[14] and so, as $\Omega \partial E_\lambda / \partial \Omega = \frac{2}{3} \langle \mathcal{T} \rangle + \frac{1}{3} \langle V \rangle$ where $\mathcal{T}$ is the kinetic energy, the pressure contribution from the ground state is just that from the integration over $\vec{k}$ in the first Brillouin zone, We point out that the contribution of the $-i\vec{k} \cdot \vec{\nabla}$ term averages out in the ground state as $l = 0$ there and so there is spherical symmetry. This feature just leaves the k^2 term as the only $\vec{k}$ dependent term. The result for the pressure in this case is thus exactly the same as for the ideal gas at high dilutions and low temperature.

We start out with the simple Coulomb system as our reference system and consider the $v(r/r_b)$ term in the potential, as introduced above, as a modification there unto. As explained above, it will suffice for our present purposes to confine our perturbation theory computations to the case $\vec{k} = \vec{0}$. If we treat ω as a perturbation parameter, then we may write

$$\frac{\partial (p_\lambda \Omega)}{\partial \omega} = -\frac{1}{3} r_b \frac{\partial^2 E_\lambda}{\partial \omega \, \partial r_b} = \frac{2}{3} \frac{\partial E_\lambda}{\partial \omega} - \frac{1}{3} \frac{\partial V_\lambda}{\partial \omega} \tag{3.3}$$

as the contribution to the numerator of the spherical cell version of (3.2) from the state λ. We do not need to consider the first order effects on the denominator, as the spherical cellular model version of (3.1) insures that the changes in $E_\lambda(\vec{0})$, will be compensated by changes is μ. The reason for this feature is that we will in fact only be considering the case where λ denotes the lowest energy state, and we will take the temperature to be low enough so the contributions from the other states will be negligible. The right hand side of (3.3) can be computed straight-forwardly by perturbation theory. First,

$$\frac{\partial E_\lambda}{\partial \omega} = -\left\langle \phi_\lambda \left| \frac{e^2 v(r/r_b)}{r} \right| \phi_\lambda \right\rangle. \tag{3.4}$$

Second, the computation of $\partial \langle V \rangle / \partial \omega$ involves $\partial \phi / \partial \omega$. As it turns out that the boundary conditions for $\partial \phi / \partial \omega$ are the same as those for ϕ, we may expand $\partial \phi / \partial \omega$ in terms of the eigenfunctions ϕ_ν. The result is,

$$\frac{\partial \phi_\lambda(\vec{r})}{\partial \omega} = \sum_{\nu \neq \lambda} \frac{\left\langle \phi_\nu \left| \frac{e^2 v}{r} \right| \phi_\lambda \right\rangle}{E_\nu - E_\lambda} \phi_\nu(\vec{r}). \tag{3.5}$$

Combining these ingredients, we obtain from (3.3) the result,

$$\frac{\partial(p_\lambda\Omega)}{\partial\omega} = -\frac{1}{3}\left\langle \phi_\lambda \left| \frac{e^2 v(r/r_b)}{r} \right| \phi_\lambda \right\rangle - \frac{2}{3}\sum_{\nu\neq\lambda} \frac{\left\langle \phi_\lambda \left| \frac{e^2}{r} \right| \phi_\nu \right\rangle \left\langle \phi_\nu \left| \frac{e^2 v(r/r_b)}{r} \right| \phi_\lambda \right\rangle}{E_\nu - E_\lambda}.$$

$$(3.6)$$

The ideas of the independent electron model, and the ideas of the Thomas–Fermi model suggest that a potential where $v(r/r_b)$ is negative and decreases from zero at $r = 0$ is of interest. One such potential, which is simple to deal with, is $v(x) = -x$. When we substitute this case in (3.6) we get just,

$$\left.\frac{\partial(p_\lambda\Omega)}{\partial\omega}\right|_{\omega=0} = \frac{e^2}{3r_b} > 0. \tag{3.7}$$

This result shows under the right circumstances, since the pressure in the reference system is, except for an exponentially small error, equal to the ideal gas pressure, that the ideal electron gas pressure can be exceeded, even when using a purely attractive potential. Physically this effect seems to be related to the considerable increase in the kinetic energy when the electron is caught in the right sort of deep potential well.

From the thermodynamic point of view, any density dependent potential, such as the ones with which we are concerned, lowers the chemical potential in a non-trivial way and thus may effect the pressure and the internal energy. In the simple case we consider here, this behavior is easily seen as it results from a simple additive, but density dependent, term to the energy.

I have computed an example numerically for a density of about 5.8×10^{-4} grams per cubic centimeter, and $\omega = 1$. Neither the formation of molecules nor the possibility of phase transitions are considered in these numerical computation. I used a modification of the computer program used by Baker.[13] Germane to our application, one starts with a spherical Heitler–London atom. Adjustments are made for exchange corrections, and there are semi-classical corrections for the electron-electron and ion-ion repulsions. The procedures described at the beginning of this section are then followed to derive numerically the pressure. Results for the above mentioned choice of $v(x)$ are given in Table I. I have also computed the corresponding pressures for the cellular model of Hydrogen. At the lowest temperature reported, the pressures are very nearly at their zero temperature values. It is to be observed that for the case of Hydrogen, the pressure

Table I. Cellular Model Pressure Results

T (ev)	p (bars)	p/p_{ideal}	p_{H} (bars)	$p_{\text{H}}/p_{\text{ideal}}$
0.5	411.9	1.438	35.48	0.1238
0.2	362.3	2.924	54.60	0.4406
0.01	340.6	8.374	36.74	0.9034

stays below that for the ideal Fermi gas. (It is not thermodynamically forbidden for the pressure to increase as the temperature decreases. An example is water in the approximate range of 0 to 4 °C, where $\partial v/\partial T|_p < 0$, which implies by mechanical stability and elementary thermodynamics that $\partial p/\partial T|_v < 0$.) Also, we see that the pressure with the modified potential rises well above the ideal gas value. This last observation is the *raison d'être* of this paper.

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