CHAPTER III

CONCEPT OF HARD SPHERE FLUID AND ONE-COMPONENT PLASMA FLUID FOR LIQUID METALS

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3.1 Hard Sphere (HS) Theory for Liquid Metals

The pair potential in liquid metals, the so-called effective ion-ion potential, is of a long-range oscillatory type. However, as shown in figure 3.1, the bare ions are only partially screened by the electron gas. Thus the effective interaction distance is larger than the diameter of the bare ion. This situation corresponds to the state of a pseudoneutral atom in metals suggested by Ziman[1]. For this reason, the effective interaction distance in liquid metals is rather close to the atomic diameter.

The simplest possible model of particles with pair interactions is the hard-sphere model whose potential is given by

\[ U(r) = \begin{cases} + \infty & \text{for } r < \sigma, \\ 0 & \text{for } r > \sigma, \end{cases} \]  

(3.1)

where \( \sigma \) is the diameter of the hard sphere, related with the packing density \( \eta \) as \( \eta = \pi \rho \sigma^3/6 \) with \( \rho \) the average number density of atoms. This model is of particular importance since it gives a first useful approximation to the effective short range repulsive interaction which governs the geometrical packing at liquid densities.
Figure 3.1 Schematic diagram of effective ion-ion potential in liquid metals. $\sigma$: effective hard-sphere diameter.
3.1.1 Percus-Yevick Solution for Hard Spheres

The importance of Percus-Yevick approximation in the study of equilibrium properties of simple fluids stems in part from the fact that the particular integral equation can be solved analytically for the important case of a system of hard spheres. The analytic solution was obtained independently by Thiele [2] and Wertheim [3,4]. For hard spheres of diameter \( \sigma \) the obvious condition that

\[
g(r) = 0, \quad r < \sigma \quad (3.2)
\]

On the other hand the density expansion of \( g(r) \) shows that the function

\[
Y(r) = g(r) \exp\left[\frac{U(r)}{k_BT}\right] \quad (3.3)
\]

remain continuous of \( r = \sigma \). In terms of \( Y(r) \) (\( Y(r) \) is the total correlation function), the Percus-Yevick (PY) approximation can be written as

\[
C(r) = Y(r) f(r) \quad (3.4)
\]

which in hard sphere case reduces to

\[
C(r) = -Y(r) \quad r < \sigma \quad (3.5)
\]

\[
C(r) = 0 \quad r > \sigma
\]

Further using equations (3.2), (3.5) and well known Ornstein and Zernike (OZ) relation, the result leads to an integral
equation for \( Y(r) \):

\[
Y(r) = 1 + \rho \int_{r'<\sigma} Y(r') \, dr' - \rho \int_{|r-r'|>\sigma} Y(r') \, Y(|r-r'|) \, dr'
\]

\[
1 + \rho \int_{r'<\sigma} Y(r') \, dr' - \rho \int_{|r-r'|>\sigma} Y(r') \, Y(|r-r'|) \, dr'
\]

(3.6)

Thiele [2] and Wertheim [3,4] have solved equation (3.6) taking its Laplace transform; the final result for \( C_{py}(r, \sigma) \) is

\[
C_{py}(r, \sigma) = \begin{cases} 
\alpha + \beta (r/\sigma) + \gamma (r/\sigma)^3, & (r < \sigma) \\
0, & (r > \sigma)
\end{cases}
\]

(3.7)

where

\[
\alpha = -(1 + 2\eta)^2/(1 - \eta)^4
\]

\[
\beta = 6\eta(1 + \frac{1}{2}\eta)^2/(1 - \eta)^4
\]

\[
\gamma = -\frac{1}{2} \eta(1 + 2\eta)^2/(1 - \eta)^4
\]

(3.8)

with \( \eta \), the packing fraction.

Fourier transform of this result gives[5]

\[
C_{py}(q, \sigma) = (4\pi q^3)(aI_0 + \beta I_1 + \gamma I_2)
\]

(3.9)

where

\[
I_m = \frac{1}{(\sigma q)^m} \int_{0}^{\sigma} x^m \sin x \, dx
\]

and the structure factor

\[
S_{py}(q, \sigma) = [1 - \rho C_{py}(q, \sigma)]^{-1}
\]

(3.10)

immediately follows from the well known OZ relationship.
The function $Y(r)$, defined by equation (3.3), is also of importance for general theoretical purposes. It is given by

$$Y(r) = Y_{py}(r) = \begin{cases} -C(r), & (r < \sigma) \\ g(r), & (r > \sigma) \end{cases} \quad (3.11)$$

The equation (3.7) is used to solve the 'compressibility' and 'virial' equation of states $[2-4]$. The resulting equations are

$$\frac{\beta p^c}{\rho} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \text{ (compressibility equation)} \quad (3.12)$$

and

$$\frac{\beta p^v}{\rho} = \frac{1 + \eta + \eta^2 - 3\eta^3}{(1 - \eta)^3}, \text{ (virial equation)} \quad (3.13)$$

Equations (3.12) and (3.13) may be integrated to obtain the free energy ($F$). The result is, for compressibility equation of state

$$\frac{F}{Nk_B T} = 3 \ln \lambda - 1 + \ln \rho - \ln(1 - \eta) + \frac{3}{2} \eta \left(\frac{2 - \eta}{1 - \eta}\right) \quad (3.14)$$

and for virial (pressure) equation of state

$$\frac{F}{Nk_B T} = 3 \ln \lambda - 1 + \ln \rho + 2 \ln (1 - \eta) + \frac{6 \eta}{(1 - \eta)} \quad (3.15)$$

where $\lambda = \hbar / (2 \pi k_B T)^{1/2}$. 
The two equations (3.12) and (3.13) give different results because the Percus-Yevick equation is only an approximation: the difference between the two increases with increasing density. Both give the exact second and third virial coefficients, but give different values for higher-order coefficients. The expressions for the virial coefficients obtained by expanding equations (3.12) and (3.13) in powers of density are

\[ \frac{B_n^c}{b^{n-1}} = \left[ 1 + \frac{3}{2} n (n-1) \right] (4)^{1-n}, \tag{3.16} \]

\[ \frac{B_n^v}{b^{n-1}} = \left[ 2 (3n-4) \right] (4)^{1-n}, \tag{3.17} \]

where \( b = B_2 = (2\pi/3) \sigma^3 \). It is interesting to note that Carnahan-Starling (CS) relation is recovered by adding the expressions (3.12) and (3.13) with weights, respectively, of \( \frac{2}{3} \) and \( \frac{1}{3} \):

\[ \frac{\beta_p^{\text{cs}}}{\rho} = \frac{2}{3} \frac{\beta_p^c}{\rho} + \frac{1}{3} \frac{\beta_p^v}{\rho} \]

\[ = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \tag{3.18} \]

The compressibility and virial equations of state obtained by numerical solution of the HNC equation are less accurate than the Percus-Yevick results [6,7], as is clear from figure 3.2; a similar remark holds true for hard sphere results of Born-Green theory.
Figure 3.2 Equation of state of hard spheres from Percus–Yevick and HNC theories; \( c \) stands for compressibility equation and \( v \) for virial equation. The dashed curve shows the "exact" results from the Carnahan-Starling equation, Eqn. (3.18)
The Percus-Yevick radial distribution function can be computed from equation (3.7) and Ornstein-Zernike relation. For $r > \sigma$, it expands as

$$g_{PY}(r, \sigma) = \frac{(1 + \frac{1}{2} \eta)}{(1 - \eta)^2} - \frac{9}{2} \eta \frac{(1+\eta)}{(1-\eta)^3} (\frac{r}{\sigma} - 1) + \frac{3}{2} \eta \frac{(1+2\eta)^2}{(1-\eta)^4} (\frac{r}{\sigma} - 1)^2 + \ldots$$

(3.19)

The PY radial distribution function near crystallization ($\eta = 0.49$) is shown in figure 3.3 together with the "exact" $g(r)$ from a Monte-Carlo calculation (D. Schiff and L. Verlet, Unpublished Results). The Percus-Yevick solution is found to present two major defects.

First, the value at contact, $g(1)$, is too low; in other words the Percus-Yevick approximation underestimates the height of the first peak. The second defect lies in the oscillations of $g(x)$ at larger distances ($x = r/\sigma$); $g(x)$ oscillates slightly out of phase with the computer results and moreover, the amplitude of these oscillations decreases too slowly with $x$, so that the resulting main peak in the structure factor is too high (the maximum reaches the value 3.05 instead of 2.85). Since an accurate knowledge of the hard sphere radial distribution functions at high density is of prime importance in the perturbation theories of simple liquids.

Verlet and Weis [8] have modified the PY radial distribution function so as to reproduce machine results. To do
Figure 3.3 Comparison between "exact" and Percus - Yevick results for the radial distribution function of hard spheres at $\eta = 0.49$. 
this, they introduce the auxiliary parameters \( \eta_w \) and \( \sigma_w \) (\( w = \text{Wertheim} \)) defined in terms of the true packing fraction \( \eta \) and diameter \( \sigma \) by

\[
\eta_w = \frac{\pi}{6} \eta \quad \sigma_w^3 = \eta - \frac{1}{16} \eta^2
\]  

(3.20)

their result is then

\[
g(r, \sigma) = \begin{cases} 
  g_{py}(r, \sigma_w) + (A/r) \exp[-\mu(r-\sigma)] \cos(\mu(r-\sigma)), (r > \sigma) \\
  0, & (r < \sigma)
\end{cases}
\]

(3.21)

where

\[
A/\sigma = (3/4) \eta_w^2 (1 - 0.7117 \eta_w - 0.114 \eta_w^2)/(1 - \eta_w)^4
\]  

(3.22)

and

\[
\mu \sigma = 24 (A/\sigma)(1 - \eta_w)^2/\eta_w (1 + \frac{1}{2} \eta_w)
\]  

(3.23)

Fourier transformation of equation (3.21) gives a structure factor

\[
S(q, \sigma) = S_{py}(q, \sigma_w) + \delta S_1 + \delta S_2
\]  

(3.24)

where (with \( Q = q \sigma / \mu \sigma \))

\[
\delta S_1 = \frac{24(A/\sigma) \eta(2+Q^2)(\sin \mu \sigma Q/Q + Q^2 \cos \mu \sigma Q)}{(\mu \sigma)^2(4 + Q^4)}
\]  

(3.25)

and

\[
\delta S_2 = K_1 \left( \frac{\sigma}{\sigma_w} - 1 \right) + K_2 \left( \frac{\sigma}{\sigma_w} - 1 \right)^2 + \ldots
\]  

(3.26)
The first two terms of equation (3.19) lead to

\[
K_1 = -\frac{24 \eta_w(1 + \frac{1}{2} \eta_w)}{(1 - \eta_w)^2} \sin q \sigma_w \quad (3.27)
\]

and

\[
K_2 = -12\eta_w \left[ \frac{(1 + \frac{1}{2} \eta_w)}{(1 - \eta_w)^2} \cos q \sigma_w + \frac{(1 - 5 \eta_w - 5 \eta_w^2)}{(1 - \eta_w)^3} \right] \sin q \sigma_w \quad (3.28)
\]

which should be sufficient for all practical applications.

By equation (3.3), for \( r > \sigma \), \( Y(r) = g(r) \) so that the Verlet-Weis \( Y(r) \) is given by equation (3.21) in this regime.

For \( r < \sigma \), Anderson et al [9] have used the empirical formula

\[
Y(r, \sigma) = Y_{py}(r, \sigma_w) + c_0 \exp[c_1 (1 - \frac{r}{\sigma}) + c_2 (1 - \frac{r}{\sigma})^2] \quad (3.29)
\]

where the coefficients

\[
\begin{bmatrix}
c_0 \\
c_1 \\
c_2
\end{bmatrix} = \frac{A}{\sigma}, \quad 1 + \mu \sigma, \quad \frac{1}{2} \left[1 - (\mu \sigma)^2\right] \quad (3.30)
\]

and have been chosen to ensure smoothness at \( r = \sigma \). This formula is not good at \( r = 0 \) [10], but is accurate around \( r = \sigma \).
Differentiating equations (3.12), (3.13) and (3.18) to obtain the bulk modulus respectively, lead to the respective implied infinite wavelength structure factors

\[ S_c(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2} = S_{py}(0) \]  
(3.31)

\[ S_v(0) = \frac{(1 - \eta)^4}{[(1 + 2\eta)^2 + 3\eta^3(\eta - 4)]} \]  
(3.32)

and

\[ S_{cs}(0) = \frac{(1 - \eta)^4}{[(1 + 2\eta)^2 + \eta^3(\eta - 4)]} \]  
(3.33)

The main practical effect of the Verlet-Weis correction to the PY results is to raise the radial distribution function near \( r = \sigma \) and to lower slightly the structure factor around the principal peak. At \( q = 0 \), typically about half the Carnahan-Starling correction (the difference between equations (3.33) and (3.31)) is accounted for.

3.1.2 Hard Sphere Entropy

Entropy is simply a measure of the disorder of molecular motion and can be expressed in disorder parameter by a relation

\[ S = K_B \ln W \]  
(3.34)

where \( K_B \) is the Boltzmann's constant, \( S \) is the entropy of the system and \( W \) is the disorder parameter. The entropy estimated
for the real system contains no contribution from the thermal variation of $\sigma$ [11]. For

$$S = - \left( \frac{\partial F}{\partial T} \right)_\Omega$$

(3.35)

One must always minimize the free energy with respect to $\sigma$ and so obtain the 'best' hard sphere reference system. Accordingly it is to be understood that

$$\left( \frac{\partial F}{\partial \sigma} \right)_{\Omega, T} = 0$$

(3.36)

and the optimizing $\sigma$ is used in all expressions. In particular, this $\sigma$ will define a hard sphere structure factor $S_{hs}(q)$ which is meant to approximate that of the real system.

Consider a one component hard sphere fluid at temperature $T$ with sphere of mass $M$ and diameter $\sigma$, so its volume $w = \pi \sigma^3/6$. If $\Omega$ is the container volume per sphere, the packing fraction is $\eta = w/\Omega$. Carnahan and Starling [12] have proposed a semi-empirical formula for the equation of state of a hard sphere fluid. This leads to an entropy per ion

$$S_{hs} = S_{gas} + S_{\eta}$$

(3.37)

Silbert et al., [13] have suggested that in addition to the two components of hard sphere entropy, there is an additional contribution $S_{el}$ from electrons

$$S = S_{gas} + S_{\eta} + S_{el}$$

(3.38)
where $S_{\text{gas}}$ is the ideal gas entropy written as

$$S_{\text{gas}} = \frac{5}{2} + \ln[\Omega \left(\frac{\frac{M K_B T}{2 \pi \hbar^2}}{3/2}\right)] \quad (3.39)$$

$S_{\eta}$ depends upon the packing fraction $\eta[12]$ expressed as

$$S_{\eta} = 3 - \frac{2}{(1-\eta)} - \frac{1}{(1-\eta)^2} \quad (3.40)$$

and $S_{\text{el}}$ the electronic contribution to entropy [14]

$$S_{\text{el}} = \frac{1}{3} \pi^2 K_B T N(E_F) \quad (3.41)$$

where $N(E_F)$ is the density of state per unit volume at the Fermi energy.

Umar et al [15] pointed out that the entropies of many liquid metals seemed to be explainable at least in a first approximation on the basis of a hard sphere model. Simple and transition metals [16] and also rare earth metals [17] can usually be represented by hard spheres, whose size vary with temperature and volume.

3.1.3 Isothermal Compressibility of HS System

A useful feature of the analytic solution of PY equation for hard sphere of a fluid is that it leads to simple theoretical expression for several physical quantities which can be compared directly with experiments. One such quantity is the liquid structure factor $S(q)$, and Ashcroft and Lekner [18] compared the predictions of the model with reliable
experimental data for a number of liquid metals near the melting point. They found that when a parameter of the model, the packing fraction \( \eta \), was set equal to about 0.45 theoretical and experimental results were in satisfactory agreement over at least for the first peak of the \( S(q) \) curves. One might conclude from this agreement that at least so far as the quantity \( S(q) \) is concerned, considerations of geometrical packing are of primary importance and the actual and complex balance of interatomic forces in the liquid metal can be represented, if there were no attractive forces and the repulsive one were infinite.

The extent to which the model provides a reasonable representation of the actual situation has been tested with reference to the isothermal compressibility \( X_T \), using the formula

\[
S(0) = \rho K_B T X_T \tag{3.42}
\]

where \( \rho \) is the number density of the particles, \( K_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The isothermal compressibility \( X_T \) is defined by

\[
\frac{1}{X_T} = -\Omega \left( \frac{3 \rho \delta}{3 \rho} \right)_T \tag{3.43}
\]

Differentiating equations (3.12), (3.13) and (3.18) we get respective equations of isothermal compressibility.
\[
\frac{1}{x_T^C} = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \rho K_B T,
\]
\[ (3.44) \]
\[
\frac{1}{x_T^V} = \frac{[(1 + 2\eta)^2 + 3\eta^3(\eta - 4)]}{(1 - \eta)^4} \rho K_B T
\]
\[ (3.45) \]
and
\[
\frac{1}{x_T^{Cs}} = \frac{[(1 + 2\eta)^2 + \eta^3(\eta - 4)]}{(1 - \eta)^4} \rho K_B T
\]
\[ (3.46) \]

The compressibilities calculated by setting \( \eta = 0.45 \) in equation (3.44) were compared by Ashcroft and Lekner [18] with experimental values for Na and K by Jarzynski et al [19] for Rb and by Ross [20] more systematically for a series of metals. Of interest is that rather good agreements between the calculated and experimental values of compressibility were obtained for light alkali metals but discrepancies are found for heavy alkali metals and polyvalent metals [21].

3.1.4 Thermal Pressure Coefficient of HS System

Recently, some interesting theoretical calculations have been done for the quantities like thermal pressure coefficient, \( \nu_V \). Ross [20] has investigated systematically the applicability of hard sphere system to the liquid metals by comparing the predictions with experiments on thermal pressure coefficient, \( \nu_V = (\partial p/\partial T)_Q \).

A simple theoretical expression for the thermal pressure coefficient, \( \nu_V \), can be obtained from the results of
Thiele [2] who derived the equation of state for hard sphere model in PY approximation and gave the two expressions for pressure,

\[ \frac{p_c}{\rho K_B T} = \left[ \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \right] \quad (3.47) \]

and

\[ \frac{p_v}{\rho K_E T} = \left[ \frac{1 + \eta + \eta^2 - 3\eta^3}{(1 - \eta)^3} \right] \quad (3.48) \]

It was further modified by Carnahan-Starling [12] as

\[ \frac{p_{cs}}{\rho K_B T} = \left[ \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] \quad (3.49) \]

Thiele [2] states that two different equations of state are obtained because the approximate nature of the solution in PY approximation, and that had an exact solution been used the two relation from which equations (3.47) and (3.48) were obtained would yielded the same equation of state. In order to obtain thermal pressure coefficient equations (3.47), (3.48) and (3.49) can be formally differentiated

\[ \nu_v = \left( \frac{2p_c}{dT} \right)_\rho \]

\[ = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \quad (3.50) \]
\[ \nu_V = \left( \frac{\partial \beta V}{\partial T} \right)_\Omega \]

\[ = \rho K_B \left[ \frac{1 + \eta + \eta^2 - 3\eta^3}{(1 - \eta)^3} \right] \quad (3.51) \]

and

\[ \nu_V = \left( \frac{\partial \rho_{cs}}{\partial T} \right)_\Omega \]

\[ = \rho K_B \left[ \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] \quad (3.52) \]

Thermal pressure coefficient may also be calculated through

\[ \nu_V = \alpha / \chi_T \quad (3.53) \]

Ross [20] found that the hard sphere model gives rather good description of \( \nu_V \) for polyvalent metals but not for alkali metals which is in contrast to the case of \( \chi_T \). Hasegawa [22] has shown that, by introducing temperature dependence of packing fraction, \( \nu_V \) in the hard sphere model can be improved for both alkali and other polyvalent metals. The work of Edward and Jarzynski [11] is also based on the hard sphere model, but more appropriate as the packing fraction and its temperature dependence are determined on the basis of Gibbs-Bogoliubov inequality [23] using realistic pair potential.
3.1.5 Agreement of Hard Sphere Structure Factors with Experimental Results

According to the Ashcroft and Lekner [18], the hard sphere structure factor using Percus-Yevick equation is given by the function of packing density $\eta$. Figure 3.4 shows that the calculated results at three different packing densities. The hard sphere structure factor shows the following features:

(i) The first peak of the structure factor is symmetrical.
(ii) At temperatures just above the melting point, the best agreement with experimental data is found with a packing density $\eta = 0.45$.
(iii) The ratio $(Q_2/Q_1)$ of the position of the second peak $(Q_2)$ to that of the first peak $(Q_1)$ is about 1.86.

Thus the measurement of deviation from the hard sphere structure factor gives useful information in the structural study of liquid metals. As an example, a comparison between the experimental data and the hard sphere structure factor is shown in the figure 3.5 for liquid Al, Zn and Sn near their melting points. The results on the liquid Al satisfy the above features of hard sphere structure factor, but the structure factor of liquid Zn has an asymmetry of the first peak. With respect to the ratio $(Q_2/Q_1)$, both Zn and Sn have large deviation from the value of 1.86. However, Waseda [24] maintains that a random distribution of hard sphere of appropriate diameter is better for a fundamental understanding
Figure 3.4 Hard-sphere structure factors by the Percus Yevick equation. \( \eta \): packing density.
Figure 3.5 Comparison of hard-sphere structure factor with experimental data in the cases of Al, Zn and Sn near the melting point.
of atomic distribution in all liquid metals. In this respect, most metallic elements seem to be consistent with the fact that the characteristic of their crystal structure becomes obscure on melting; then the increase in the freedom of atomic configuration contributes to the construction of universal short-range order, which mainly depends upon the size factor similar to that of hard sphere model. Deviation of this type decreases with an increase of fluid volume arising from the elevation of temperature, and then disappears at temperatures of 300°C to 500°C above the melting point. The liquid structure of Sn type shows such behaviour [24].

Contrary to the results for liquid metals of the Zn and Sn types, the temperature variation of the structure of Al type metals shows the simple features. The main effect of temperature variation [24] is the change in the amplitude of the oscillations in the structure factor. Namely, a decrease around the peak and an increase elsewhere are observed. In order to obtain a simple expression for the effect of temperature on the structure factor of liquid metals, the temperature dependence of the packing density $\eta$ may be approximated by the exponential function

$$\eta = A \exp(-BT) \quad (3.54)$$

where $T$ is the absolute temperature. $A$ and $B$ are two parameters with uncertainty of $\pm 0.005$ and $0.003$ respectively.
A good hard sphere behaviour occurs in Mg, Al, In and Pb [25], the alkaline earths [26], the noble and transition metals [27-30] and in a number of rare earths (Y. Waseda, Private communication). A slight skewness of the first peaks occurs in Zn and Cd [25] but otherwise these metals are also well described by hard spheres. However, in Ga, Si, Ge, Sn, Sb, Bi and (to a very modest extent) in Tl there is a shoulder on the high angle side of the principal peak which can not be described by hard sphere alone. For the most part, there are the cases which do not form close packed solids. Heine and Weaire [31] have shown that the Coulomb forces favour close packing and that other cases may be explained by special circumstances. The implications that bumps and dips of \(g(r)\) will be less pronounced is borne out on Fourier transformation of the observed structure factor \(S(q)\) for such cases [25]. The completely typical result for Bi may be contrasted with those for Na and Al [16].

Turning to the low angle region, the very general results are obtained [32-34]

\[
S(0) = \rho K_B T K_T
\] (3.55)

The right hand side of equation (3.55) may be evaluated using observed data for the melting point and for hard sphere with \(\eta = 0.45\), the agreement is poor for polyvalent metals [34]. Further, the poorer results of \(C_p\) find for Sn, Bi and Pb [35].
might be attributable to the inadequacy of hard sphere reference system. From the structure factor evidence it can already be inferred that the hard sphere model is deficient though still remaining semi-quantitative meaning. Clearly, either more works need to be done on this reference system or another suitable reference system should be adopted.

For polyvalent metals hard sphere system remains the better reference system but it is found that for alkali metals one-component plasma (OCP) reference system seems to be superior to HS reference system because the effective interaction potential is softer for alkalis than for polyvalent metals [36]. The thermodynamic properties and the structure factor of this reference system (OCP) have been calculated by using the Monte-Carlo simulation [37-39]. More recently, the Gibbs-Bogoliubov variational approach to investigate the thermodynamic properties of alkali metals using OCP reference system have been the subject of interest [40-43] because it presents the advantage to supply a free energy lower than the hard sphere results.

3.2 Concept of One-Component Plasma (OCP)

Under the pressure and temperature conditions characteristic of degenerate stellar matter (e.g. in white dwarfs or the outer layers of neutron stars) and of the interior of the heavy planets, the lighter elements are generally assumed to be completely ionized. The remaining
nuclei can, to a good approximation be considered as point charges, whereas the electrons are strongly degenerate and in first approximation play the role of a rigid uniform background [37]. If the nuclei of one element predominate, the physical situation can be reasonably well described by the simple model of the classical one-component plasma (OCP), which may also be relevant for the description of super-dense matter in the laser-driven fusion experiments.

The equilibrium properties of the OCP depend only on the single dimensionless parameter \( r = (Ze)^2/a \), where \( Ze \) is the charge of the ions and 'a' is the ion sphere radius.

Since the degenerate electrons play the role of the rigid uniform background, the thermodynamic properties (internal energy, pressure etc.) of the zero temperature electron gas must be added to the corresponding ionic properties of the OCP. The former depend only on dimensionless parameter \( r_s \)

\[
    r_s = a/(a_o Z)^{1/3}
\]

where \( a_o \) is the electronic Bohr radius (\( a_o = 0.529 \) Å). Such a treatment of the electron gas is only valid if the degeneracy condition is satisfied, i.e. \( K_B T/ \varepsilon_F << 1 \) [40]. Here \( \varepsilon_F = h^2 (3\pi^2 n)^{2/3}/2m \), where \( n \) is the number density of degenerate electron system and \( m \) is the mass of an electron. This condition is well fulfilled in most astrophysical situations.
The ions on the other hand, can be treated classically because of their considerably higher mass [44].

3.2.1 Specification of OCP Model

The model treated for the study consists of a system of identical point charges immersed in a uniform background; the continuous charge density of the background is chosen equal and opposite to the average density of the point charges, so that system as a whole is electrically neutral. In the discussion of the physical application it is assumed that the point charges represent the positively charged nuclei of a heavy element and the background represents approximately the effect of free electrons.

A dimensionless parameter $\Gamma$ is defined as follows: The unit of distance is taken as the ion sphere radius (the radius of a sphere containing one particle)

$$a = \left(\frac{3}{4} \pi n\right)^{1/3}$$

(3.57)

where $n$ is the number density of system in ions per cubic centimeter. The nearest neighbour particle distance for a simple cubic lattice is $1.6120a$. The potential energy of two particles, divided by $K_B T$, may then be expressed in dimensionless form as

$$\frac{\Phi(x)}{K_B T} = \frac{\Gamma}{x}$$

(3.58)
where $x = r/a$

and

$$\varphi(r) = \frac{(Ze)^2}{r},$$

$$\Gamma = \left[\frac{(Ze)^2}{K_B T}\right]$$

$$= \left[\frac{(Ze)^2}{K_B T}\right] \left[\frac{4\pi n}{3}\right]^{1/3}$$

Thus $\Gamma$ is approximately $2\frac{1}{2}$ times the ratio of potential energy of two ions at their average separation distance 1.6a, to the average ion kinetic energy. For $\Gamma \leq 0.01$, the ratio is about 250, and consequently the system should behave nearly as a perfect gas. On the other hand for $\Gamma \geq 100$, the ratio is approximately $1/40$; under this condition the system could behave as a solid.

However, the picture of considering the electron gas as a perfectly rigid and uniform background is generally a very crude approximation. Even a highly degenerate electron gas will be polarized by the ionic charge distribution and the formation of non-uniform electron "clouds" around each ion will modify the ion-ion interaction. Consequently the bare ion potential between ions must be replaced by an effective screened potential. The importance of electron screening can be quantitatively discussed in terms of Thomas-Fermi (TF) screening length:

$$\frac{\lambda_{TF}}{a} = (\pi/12Z)^{1/3} (r_s^{-1})^{1/2}$$
Since in the crude Thomas-Fermi model the screened interionic potential is

\[ U(r) = \frac{(Ze)^2}{r} e^{-\frac{r}{\lambda_{TF}}} \]  

(3.62)

it is clear that electron screening is negligible only in the high density limit (\( r_s \to 0 \)). In a typical white dwarf (density \( \sim 10^6 \text{ g/cm}^3 \) and predominantly Helium composition), it is found that \( r_s \sim 0.15 \) and \( \lambda_{TF}/a \sim 4 \). In the deep interior of Jupiter (density \( \sim 5 \text{ g/cm}^3 \) and predominantly Hydrogen composition), it is found \( r_s \sim 0.7 \) and \( \lambda_{TF}/a \sim 7 \). Hence it is seen that the screening length is of one or a few interionic spacing, which implies a relatively short-ranged effective interaction compared to the bare Coulomb potential.

3.2.2 Stability Criterion for OCP Fluid

As an application of the Gibbs-Bogoliubov inequality, a necessary condition for stability of the homogeneous phase of the OCP can be derived [45]. It is a generalization to a classical OCP of Ferrell's validity criterion [46] for testing approximations to the degenerate electron gas correlation energy. The Gibbs-Bogoliubov inequality on the Helmholtz free energy \( F \) of the many particle system with the Hamiltonian \( H \) reads

\[ F \leq F_0 + \langle H - H_0 \rangle \]  

(3.63)
where $F$ is the Helmholtz free energy of the many particle system with Hamiltonian $H$, $F_0$ is the free energy of the reference system with the Hamiltonian $H_0$ and $\langle \ldots \rangle_0$ denotes the statistical average over this reference system.

Let the Hamiltonian of the classical OCP be expressed as a sum of the kinetic energy $K$ and the interaction energy $V$. We substitute

$$
H_0 = K + \Gamma V
$$

$$
H = K + (\Gamma + \Delta \Gamma) V
$$

(3.64)

in equation (3.63) and expand the result with respect to $\Delta \Gamma$. The zeroth and first order terms vanish identically by virtue of the following [45]

$$
f(\Gamma) \equiv \frac{F}{NK_BT}
$$

(3.65)

or equivalently,

$$
\frac{df(\Gamma)}{d\Gamma} = \frac{\langle V \rangle_0}{NK_BT}
$$

(3.66)

The second order term of equation (3.63) then yield

$$
\frac{d^2f(\Gamma)}{d\Gamma^2} < 0
$$

(3.67)

This condition thus makes a stability criterion for classical OCP fluid.
3.2.3 Equation of State for OCP System

The variational approach is based on an exploitation of the so-called Gibbs-Bogoliubov inequality which states that if the Hamiltonian for a system is regarded as that for a reference system plus a perturbation then the Helmboltz free energy for the reference system plus the expectation value of the perturbation averaged over the reference system is greater than or equal to the Helmboltz free energy of the actual system.

Let $H = K + V$ be the Hamiltonian of a system of interest and $H_0 = K + V_0$ be that for one-component plasma reference system. An upper bound to the Helmholtz free energy per ion, at fixed temperature and volume is

$$F \leq F_0 + \langle H - H_0 \rangle_0$$

$$F = F_0 + \langle H - H_0 \rangle_0$$

$$= F_0 + \langle V \rangle_0 - V_0$$

(3.68)

Here angular brackets denote an appropriate expectation value per atom and $F_0$ is the free energy per ion of the OCP reference system of plasma parameter $\gamma$ with same density $n$ and temperature $T$ as the real system. Equation (3.68) represents Gibbs-Bogoliubov variational method. The OCP free energy per ion is given by

$$F_0 = \frac{3}{2} k_B T + V_0 - T S_0$$

(3.69)
here $V_0$ is the OCP potential energy and $S_0$ is the entropy. $<V_0>$ is the expectation of $V$ averaged over the reference system. Explicitly, we have

$$<V>_0 = \frac{1}{2} n \int V(r) g_0(r/a, r) \, dr \quad (3.70)$$

where $g_0(r/a, r)$ is the reference systems radial distribution function. Alternatively in relation to ideality ($Z = 0$), we may write

$$F_0 = F_{id} + \Delta F_0$$

and

$$S_0 = S_{id} + \Delta S_0 \quad (3.71)$$

equation (3.69) becomes

$$\frac{\Delta F_0}{K_B T} = \frac{V_0}{K_B T} - \frac{\Delta S_0}{K_B} \quad (3.72)$$

where each term in latter depends on $r$ only. Combining equations (3.69) and (3.71), we may write equation (3.68) as

$$F = F_{id} - T \Delta S_0 + <V>_0 \quad (3.73)$$

Here $F_{id}$ is an ideal gas contribution written as

$$F_{id} = \frac{3}{2} K_B T - K_B T \left[ \frac{5}{2} + \ln \left( \frac{M K_B T}{2 \pi n^2} \right)^{3/2} \right] \quad (3.74)$$

and $\Delta S_0$ depends only on $r$ (and not on $\sigma$, $a$ and $T$ separately). In equation (3.68), a choice of $r$ must be made; this is done by
using the variational condition

\[
\left( \frac{\partial F}{\partial \tau} \right)_{n,T} = 0 \quad (3.75)
\]

3.2.3 (i) Entropy

Under these circumstances, the entropy estimate for the real system is obtained as follows:

\[
S = - \left( \frac{\partial F}{\partial T} \right)_n
\]

\[
= - \left( \frac{\partial F}{\partial T} \right)_{n,\tau} - \left( \frac{\partial F}{\partial T} \right)_{n,T} \left( \frac{\partial r}{\partial T} \right)_{n} \quad (3.76)
\]

The final term of equation (3.76) vanishes via equation (3.75) then

\[
S = - \left( \frac{\partial F}{\partial T} \right)_{n,\tau} \quad (3.77)
\]

Thus the equation (3.73) leads to

\[
S = - \left[ \frac{\partial}{\partial T} \left( F_{id} - T \Delta S_o + \langle V \rangle \right) \right]_{n,\tau} \quad (3.78)
\]

\[V \text{ for the metal is non-vanishing to the extent that electron gas is non degenerate; to the first order in } T, \text{ it may be written as}
\]

\[
S = S_{id} + \Delta S_o + S_{el}
\]

\[= S_o + S_{el} \quad (3.79)
\]
3.2.3 (ii) Pressure

A simple expression for pressure can be obtained as follows:

\[ \frac{p}{n^2} = (\frac{\partial F}{\partial n})_T \]

\[ p = n^2 (\frac{\partial F}{\partial n})_T \]

\[ = n^2 [(\frac{\partial F}{\partial n})_T, \Gamma + (\frac{\partial F}{\partial \Gamma})_n, T (\frac{\partial \Gamma}{\partial n})_T] \]  \hspace{1cm} (3.80)

The final contribution of equation (3.80) vanishes due to equation (3.75)

\[ p = n^2 [ (\frac{\partial F}{\partial n})_T, \Gamma ] \]  \hspace{1cm} (3.81)

using equation (3.73) into equation (3.81), we get

\[ p = n^2 \left[ \frac{\partial}{\partial n} \left( F_{id} - T \Delta S_0 + \langle V \rangle \right)_T, \Gamma \right] \]

\[ = n K_B T + 0 + n^2 \left[ \frac{\partial}{\partial n} \left\{ \frac{1}{2} \mathcal{V}(r) g_o (r/a, \Gamma) d(n,r) \right\} \right]_T, \Gamma \]

\[ = n K_B T - \frac{n^2}{2} \mathcal{V}(r) \left( r \frac{\partial V}{\partial r} - 3n \frac{\partial V}{\partial n} g_o (r/a, \Gamma) \right) dr \]  \hspace{1cm} (3.82)

This is the exact equation of state \[21\] for the system described by the (possibly density dependent) interaction.

\[ V = \sum_i \sum_{i<j} V(r_{ij}) \]  \hspace{1cm} (3.83)

but modified in that the exact radial distribution has been
replaced by the reference one.

3.2.4 Internal Energy Formula

With the knowledge of the radial distribution function or the static structure factor, the excess internal energy $U_{\text{ex}}$ of the OCP is calculated according to

$$\frac{U_{\text{ex}}}{NK_B T} = \frac{n}{2K_B T} \int_0^\infty \frac{(Zq)^2}{r} \left[ g(r) - 1 \right] dr$$

$$= \frac{1}{2K_B T} \int_0^\infty \frac{(Zq)^2}{q^2} \left[ S(q) - 1 \right] dq$$  \hspace{1cm} (3.84)

Since the total internal energy $U$ of the system is given by

$$U = \frac{3}{2} N K_B T + U_{\text{ex}}$$  \hspace{1cm} (3.85)

and the pressure by

$$p = n K_B T + \frac{U_{\text{ex}}}{3V}$$  \hspace{1cm} (3.86)

various thermodynamic functions of the OCP can be determined once equation (3.84) is evaluated as a function of $r$.

Analyzing the Monte-Carlo data obtained by Hansen [38], DeWitt [47] found that a fitting formula

$$\frac{U_{\text{ex}}}{NK_B T} = - (0.89461 \pm 0.00003) \Gamma + (0.8165 \pm 0.0008) \Gamma^{1/4}$$

$$- (0.5012 \pm 0.0016)$$  \hspace{1cm} (3.87)
reproduced the data with good accuracy in the region, $1 \leq \Gamma \leq 40$. DeWitt proposed also a slightly modified formula,

$$
\frac{U_{\text{ex}}}{N K_B T} = - (0.8966 \pm 0.0001) \Gamma + (0.874 \pm 0.009) \Gamma^{1/4}
$$

$$
- (0.568 \pm 0.023),
$$

for $50 \leq \Gamma \leq 140$; the agreement of this formula with MC data was, however, less accurate than that of equation (3.87). This fact led DeWitt to question the accuracy of Hansen's data for large value of $\Gamma$ (i.e., $40 < \Gamma < 160$).

Slattery et al [39] fitted their liquid $\frac{U_{\text{ex}}}{N K_B T}$ data ($1 \leq \Gamma \leq 160$) for 128 particles Monte-Carlo to run to the form

$$
\frac{U_{\text{ex}}}{N K_B T} = -0.89752 \Gamma + 0.94544 \Gamma^{1/4} + 0.17954 \Gamma^{-1/4} - 0.80049
$$

(3.89)

The Helmholtz free energy $F$ of the OCP could then be calculated from the formula

$$
f(\Gamma) = \frac{F}{N K_B T}
$$

$$
= \int_{\Gamma_1}^{\Gamma} \frac{U_{\text{ex}}}{N K_B T} \frac{d\Gamma'}{\Gamma'} + f(\Gamma_1)
$$

(3.90)

The normalized free energy $f(\Gamma)$ at $\Gamma_1 = 1$ was evaluated through integration of $U_{\text{ex}}/N K_B T$ with the Abe formula [48] ($0.0 \leq \Gamma \leq 0.1$), the hypernetted chain (HNC) results
(0.1 \leq r \leq 0.6), and the Monte-Carlo values (0.6 \leq r \leq 1.0).

Slattery et al [39] thus found

\[ f(r) = a r + b r^{1/4} - c r^{-1/4} + (d+3) \ln r \]

\[ - (a + 4b - 4c + 1.135) \]  \hspace{1cm} (3.91)

where

\[ a = -0.89752, \quad b = 0.94544, \]
\[ c = 0.17954, \quad d = 0.80049 \]

3.2.5 Helmholtz Free Energy

Using the OCP model as a reference system, the formula for Helmholtz free energy, \( F \), to be used in the variational calculation can be obtained from the literature [39,42] and is the sum of number of terms, namely,

\[ F = F_{\text{eg}} + F_{\text{ocp}} + F_{\text{M}} + F_{\text{d}} + F_{\text{b}} \]  \hspace{1cm} (3.92)

Here, \( F_{\text{eg}} \) represents the free energy of the electron gas in the metal under consideration, for which the widely used formula [49] has been adopted

\[ F_{\text{eg}} = \left[ \frac{3}{10} k_F^2 - \frac{3}{4 \pi} k_F - (0.0474 + 0.0155 \ln k_F) \right] Z \]

\[ - \frac{1}{2} \left( \frac{\pi k_B}{k_F} \right)^2 T^2 \]  \hspace{1cm} (3.93)

where
\[ k_F = (3\pi^2 Z n)^{1/3} \] and \( Z \) the ionic valence.

\( F_{\text{OCP}} \) is the free energy of the OCP reference system, for which a four parameter fit to the free energy of machine simulations [39] are used, as in [42], i.e.

\[
F_{\text{OCP}}(\Gamma) = \left[ \frac{3}{2} + a \Gamma + 4(b \Gamma^{1/4} - c \Gamma^{-1/4}) + d \ln \Gamma \right] - \left[ a + 4(b-c) + 0.421 \right] K_B T \tag{3.94}
\]

in which \( a = -0.89752 \), \( b = 0.94544 \), \( c = 0.17954 \) and \( d = -0.80049 \), and \( \Gamma = Z^{12}/a_o K_BT \), with \( a_o \) being the radius of the volume occupied by one ion and with \( Z' \) being chosen to yield a minimum approximate \( F \). Hence \( \Gamma' \) is a variational parameter. As regards \( F_M \), arising from the deviation of the Madelung energy from its value in the OCP reference system, it may be written [42]

\[
F_M(\Gamma) = \left[ (\Gamma^* - \Gamma)/\Gamma \right] \left[ a \Gamma^* + (b \Gamma^{1/4} + c \Gamma^{-1/4}) + d \right] K_B T \tag{3.95}
\]

with \( \Gamma^* = \frac{Z_{\text{eff}}^2}{a_o K_BT} \), where \( Z_{\text{eff}}^2 = Z^2 - \rho_d^2 \), \( Z \) and \( \rho_d \) being respectively, the actual ionic valence and the depletion charge (which vanishes when the non-locality of the pseudopotential is omitted, as is done in several applications of the OCP model to variational thermodynamic calculations [41,42]).

\( F_d \) and \( F_b \) in equation (3.92) denote, respectively, the diagonal term and the band structure term, i.e.
\[ F_d = \pi^{-2} \int_{\mathbb{F}} \int_0^1 dk \ k^2 \exp(-ik \cdot r) \Delta \Psi(r) \exp(ik \cdot r), \]  
\[ F_b(r) = -\left(\frac{Z_{\text{eff}}^2}{\pi}\right) \int_0^\infty dq \ F_N(q) \ S_{\text{ocp}}(q,r) \]  

(3.96)
(3.97)

where \( S_{\text{ocp}}(q,r) \) and \( F_N(q) \), respectively, stand for the OCP structure factor and the normalized energy-wave number characteristic.
3.3 References


