Lawrence Livermore Laboratory

EQUILIBRIUM STATISTICAL MECHANICS OF STRONGLY COUPLED PLASMAS BY NUMERICAL SIMULATION

Hugh E. DeWitt

November 1, 1977

Lectures given at the NATO Summer Institute on Strongly Coupled Plasmas, Orleans-la-Source, France, July 7-23, 1977

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EQUILIBRIUM STATISTICAL MECHANICS OF STRONGLY
COUPLED PLASMAS BY NUMERICAL SIMULATION*

Hugh E. Dewitt
Lawrence Livermore Laboratory
Livermore, CA 94550

ABSTRACT

Numerical "experiments" using the Monte Carlo method have led to systematic and accurate results for the thermodynamic properties of strongly coupled one-component plasmas and mixtures of two nuclear components. These talks are intended to summarize the results of Monte Carlo simulations from Paris and from Livermore. Simple analytic expressions for the equation of state and other thermodynamic functions have been obtained in which there is a clear distinction between a lattice-like static portion and a thermal portion. The thermal energy for the one-component plasma has a simple power dependence on temperature, $(kT)^{3/4}$, that is identical to Monte Carlo results obtained for strongly coupled fluids governed by repulsive $1/r^n$ potentials. For two-component plasmas the ion-sphere model is shown to accurately represent the static portion of the energy. Electron screening is included in the Monte Carlo simulations using linear response theory and the Lindhard dielectric function. Free energy expressions have been constructed for one and two component plasmas that allow easy computation of all thermodynamic functions.

*Work performed under the auspices of the Department of Energy under contract W-7405-Eng-48.

I. INTRODUCTION

The intent of these lectures is to give a summary of theoretical understanding and computer simulation results for the equilibrium thermodynamic properties of fully ionized light elements at high density. Matter in this state is a "dense" plasma or "strongly coupled" plasma because of the strength of the Coulomb interaction among the point nuclei. At the extreme densities found in white dwarf stars the Coulomb interactions can be so strong that the nuclei are localized into lattice sites, i.e. a Coulomb solid. Most of these lectures, however, will deal with lower densities in which the nuclei form a strongly correlated fluid. Real matter in this state may be considered to be a mixture of two fluids: the fluid of point nuclei governed by pairwise Coulomb interactions with classical mechanics, and a neutralizing fluid of electrons which is degenerate due to Fermi statistics. In real physical systems such as stellar interiors, interiors of large planets (Jupiter), and laser fusion compression experiments, the two fluids interact with each other chiefly by means of the electron screening effect due to some increase of electron density in the neighborhood of each nucleus. A large fraction of the matter in the universe is in the strongly coupled plasma state, and consequently the physics of this state of matter is of great importance.

It will be useful at the beginning of these talks to specify the appropriate form of the Coulomb coupling parameters. In usual laboratory plasmas at low density or weak coupling the appropriate parameter is normally taken as the inverse of the number of particles in the Debye sphere; for ions this is:

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION STATEMENT OF DOCUMENT NO. 84

$$\epsilon = \frac{1}{4\pi\lambda_D^3} = \frac{Z^2\beta e^2}{\lambda_D} = 2\pi^{1/2} Z^3 e^3 n^{1/2} / (kT)^{3/2} \quad (1)$$

where Z is the nuclear charge, $\beta = 1/kT$, $n = N/V$, the ion number density, and λ_D is the Debye screening length. Weak coupling means $\epsilon \ll 1$. This usual plasma parameter can be used to characterize dense plasmas for which $4\pi n \lambda_D^3 < 1$, however the concept of Debye length is no longer useful or appropriate when $\epsilon \gg 1$. It is more convenient to use the form:

$$\Gamma = Z^2\beta e^2 \left(\frac{4\pi}{3} n\right)^{1/3} = Z^2\beta e^2 / \bar{r} \quad (2)$$

where $\bar{r} = \left(\frac{4\pi}{3} n\right)^{-1/3}$ is the ion sphere radius. Note the relation:

$$\epsilon = \sqrt{3} \Gamma^{3/2}$$

$$\Gamma = \frac{\epsilon^{2/3}}{3^{1/3}}$$

An ionized gas is strongly coupled when $\Gamma \gtrsim 1$. At temperatures and densities for strong coupling the plasma is a fluid with properties similar to liquids, and consequently the description used here will use liquid state physics terminology.

The main advances in understanding of the properties of the strongly coupled Coulomb fluid in the last few years have come from Monte Carlo simulations, or numerical "experiments" from Prof. Hansen and his co-workers in Paris and from the group at Livermore. Both groups were inspired by the 1966 pioneering Monte Carlo study of the Coulomb fluid by Brush, Sahlin, and Teller at Livermore.¹ Typically these Monte Carlo simulations compute the

However, if the electrons are treated as a fluid rather than point particles, the energy of the system can be written as:

$$\begin{aligned} E = \langle H \rangle &= \langle K_e \rangle + \langle K_i \rangle + \langle U_{ee} \rangle + \langle U_{ii} + U_{ei} \rangle \\ &= \frac{3}{2} NkT + N_e \left(\frac{3}{5} \epsilon_F + \epsilon_{ex} + \epsilon_{corr} \right) + U \end{aligned} \quad (4)$$

where the brackets indicate an ensemble average, and U is the internal energy of the nuclear Coulomb interactions ensemble averaged in the presence of the electron fluid. The term $\frac{3}{2} NkT$ is obviously the ideal gas kinetic energy of the nuclei. The electron term includes the average kinetic energy, $\frac{3}{5} \epsilon_F$, the exchange energy, and correlation energy, assuming complete electron degeneracy. A second parameter is needed to describe the electron terms and the electron screening effect, namely:

$$r_s = \bar{r}_e / a_0 \quad (5)$$

where $a_0 = \hbar^2 / m_e c^2$, and $\bar{r}_e = \left(\frac{4\pi}{3} n_e \right)^{-1/3} = \bar{r}/Z^{1/3}$ is the electron ion sphere radius, and $n_e = \bar{Z}n$. The Coulomb energy of ions in Eq. 4 may be written as a function of the two parameters, Γ and r_s :

$$\begin{aligned} U &= \left\langle \sum_{i < j}^N \frac{(ze)^2}{r_{ij}} + \text{background} \right\rangle \\ &= NkT f(\Gamma, r_s) \end{aligned} \quad (6)$$

Numerical simulation methods, Monte Carlo and molecular dynamics give U/NkT directly.

where $m = \infty$ is the hard sphere system and $m = 1$ is the Coulomb system. Since inverse power fluids have similar behavior⁴ in strong coupling and go into a lattice at high enough density, it seems useful to include a discussion of the inverse power fluids in these lectures.

The modern understanding of the equilibrium properties of strongly correlated plasmas, at least the OCP, began with the Monte Carlo work of Brush, Sahlin and Teller (BST).¹ In their simulation of the canonical ensemble average of the OCP internal energy they adopted the Metropolis procedure⁵ and they handled the long range of the Coulomb interaction by replicating the basic three dimensional cell containing N point charges in all directions to infinity. The interactions among charges and with image charges were summed with the Ewald method.⁶ Numerical results were obtained for U/NkT , C_V , and $g(r)$ by averaging over about 10^5 configurations of $N = 108$ charges for values of Γ from 0.1 (weak coupling) up to 125. Because of numerical inaccuracies for large Γ the BST results for the thermal energy, heat capacity, and location of the fluid-lattice transition are not too reliable.

In 1971 Hubbard and Slattery applied the BST methods to the calculation of the properties of the dense ionized hydrogen in Jupiter.⁷ The BST program was extended to include electron screening effects for non-zero values of r_s by means of linear response theory and the Lindhard dielectric function for completely degenerate electrons. Their code can also handle arbitrary mixture of two nuclear components so that they could compute the thermodynamic properties of mixtures of light elements, assumed to be fully ionized.⁸ Their first published results were of limited accuracy because computer time

1. The fluid internal energy is a sum of a static energy resembling the energy of particles in a lattice plus a well defined thermal energy:

$$U = U_0(n) + U_{th}(n, kT)$$

$$C_V = \frac{dU_{th}}{dT} .$$

2. Certain integral equations give this qualitative feature, namely the hypernetted chain (HNC) equation and the mean spherical approximation.
3. For arbitrary mixtures of different nuclear charges the ion-sphere charge averaging largely determines the thermodynamic properties so that a one fluid model can be used with

$$r = z^{5/3} \bar{z}^{-1/3} r_0$$

$$r_0 = Re^2/\bar{E} .$$

4. The direct correlation function for distances less than the nearest neighbor distance ($r < 1.7\bar{r}$) has a simple algebraic form dominated by a linear term:

$$c(r) = -\Gamma(a_0 - a_1 x), \quad x = r/\bar{r}$$

and this form determines the ion fluid structure factor, $S(k)$.

These four general conclusions are of course all related and are mainly a consequence of the apparent fact that a strongly coupled plasma may be described as a disordered lattice. The static energy, $U_0(n)$, represents the average energy of the system with the strong interparticle correlations keeping

With classical mechanics the kinetic energy portion of the OCP Hamiltonian is easy to separate from the interaction portion. Including the neutralizing uniform background the interaction Helmholtz free energy of the OCP is obtained from:

$$\beta F_I = \ln \int \dots \int \frac{\prod_{i=1}^N d^3 r_i}{V^N} \exp(-\beta) \left\{ \sum_{i < j}^N \frac{(ze)^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{N}{V} \sum_{i=1}^N \int d^3 r \frac{ze^2}{|\mathbf{r}_i - \mathbf{r}|} + \frac{N^2}{2V^2} \iint d^3 r d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \quad (9)$$

In principle we would like to evaluate this partition function analytically for all values of Γ . In practice so far the analytical evaluation has been limited to weak coupling ($\Gamma \ll 1$) and intermediate coupling ($0.3 \lesssim \Gamma \lesssim 1$). For potentials that fall to zero faster than $1/r^3$ at large distance a virial expansion in powers of density is possible. In the case of the Coulomb potential the virial coefficients as usually defined from the Mayer cluster expansion all diverge, and a rearrangement of the expansion is necessary to obtain convergent results. This procedure was worked out in 1959 by Abe¹³ with the result:

$$\beta F_I = N \left\{ -\frac{1}{3} (\sqrt{3} \Gamma^{3/2}) + S_2(\Gamma) + S_3(\Gamma) + \dots \right\} \quad (10)$$

The first terms in Eq. (10) is the sum of the ring diagram, and is equivalent to the Debye-Huckel theory. The higher order terms, S_2 , S_3 , etc. are functions of Γ , and not coefficients of powers of n . These integrals involve interactions among clusters of particles as in the Mayer expansion, but the Debye screened potential appears:

when there is no electron screening ($r_g = 0$). One notes that in weak coupling, $\Gamma \ll 1$, that the leading contribution is $O(\Gamma^{3/2})$ or $O(\epsilon)$, thus from Eqs. 10, 12 and 13 we have $\beta F_I/N = -\frac{1}{3}\epsilon$, $\beta U/N = -\frac{1}{2}\epsilon$, and $C_V/Nk = \frac{1}{4}\epsilon$ which are the well known Debye-Huckel results. The addition of the Abe cluster term in Eqs. 10, 12, and 13 simply reduces the $O(\Gamma^{3/2})$ contribution as Γ increases. In fact it has been shown¹⁵ that as $\Gamma \rightarrow \infty$ that the sum of the Abe integrals identically cancels the $O(\Gamma^{3/2})$ term leaving $O(\Gamma)$ as the leading term. Lower bounds on the interval energy are useful and important. The known lower bounds are:

$$\beta U/N = -\frac{1}{2} (\sqrt{3} \Gamma^{3/2}), \quad \Gamma \ll 1 \quad (15)$$

$$= -\frac{9}{10} \Gamma, \quad \Gamma \gg 1 \quad (16)$$

as will be discussed by Prof. Choquard. The change in character of the functional dependence on Γ , i.e. $O(\Gamma^{3/2})$ changing to $O(\Gamma)$, occurs in the region $0.3 \lesssim \Gamma \lesssim 0.75$, and in this intermediate coupling region the Abe expansion is numerically useful for computing values of the thermodynamic functions. The transition value, $\Gamma_t = 0.75$, is an approximate lower limit of the strong coupling regime, this is simply value of Γ where the static energy of the OCP fluid, the $O(\Gamma)$ term becomes apparent in the Monte Carlo data.

For the present discussion a strongly coupled plasma will be taken to mean a coupling parameter range, $\Gamma_t < \Gamma < \Gamma_c$, for which there seems to be a well defined separation of the potential energy into two parts: $U = U_0 + U_{ch}$. This region might also be called the asymptotic Coulomb fluid region since

For the Coulomb solid the Monte Carlo data indicated the expected harmonic vibrations with a small anharmonic correction, namely $g(\Gamma) = 3/2 + 3500/T^2$. The fluid data, however, indicated a very different form, namely $g(\Gamma) = b\Gamma^s - c$, where s is a small power between 0.2 and 0.3. A non-linear least squares fitting procedure for both the energy and heat capacity data established the best value to be $s = 0.25$. The total energy was found to be:¹²

$$U/NkT = -0.89461\Gamma + 0.8165\Gamma^{1/4} - 0.5012, \quad 0.75 < \Gamma < 40. \quad (18)$$

The static energy constant obtained by fitting the fluid data is about 0.15% higher than the Madelung constant for the bcc lattice, $a_{\text{bcc}} = 0.895929$. This formula must obviously fail at small Γ , and presumably there must be corrections to this asymptotic formula that are inverse powers of Γ . It has not been possible with the present data to find a believable correction to the above result. For the data with $\Gamma > 40$ in the fluid phase the same kind of fitting formula applies, however, the values of the three coefficients are slightly different. Also it was not possible to establish the exponent in the thermal energy to be precisely $s = 1/4$ as was the case for the data in the region $1 < \Gamma < 40$. The nature of the data suggested a slight systematic error, although this may be an artifact due to the finite number of particles used in Hansen's simulations, $N = 128$. Hansen's three values obtained with $N = 250$ particles for $\Gamma = 70, 100$, and 140 were all closer to Eq. 18 than his $N = 128$ data. Also it should be mentioned that Hansen's data for a very small number of particles, $N = 16$, showed a van der Waals loop in the region, $40 < \Gamma < 140$. Some evidence of this apparent van der Waals loop is also evident in his data for $N = 54$. It is possible that the accuracy of U/NkT for large Γ will be increased by going to much larger systems.

An asymptotic form of the interaction Helmholtz free energy is readily found by integration:

$$\begin{aligned}
 P_I/NkT &= \int_{\Gamma_1}^{\Gamma} d\Gamma \frac{(U/NkT)}{\Gamma^2} + \frac{\bar{E}_I(\Gamma_1)}{NkT_1} \\
 &= -a\Gamma + 4b\Gamma^{1/4} - c \ln \Gamma + d
 \end{aligned}
 \tag{21}$$

where the entropy constant is found to be $d = -2.809$ by comparison with the Mc cluster expansion evaluated at $\Gamma = 1$. Since the potential energy is negative (meaning the Coulomb interaction energy) the pressure due to the Coulomb interactions is also negative. For the OCP the interaction pressure is given exactly by the virial theorem, $PV/NkT = (1/3)U/NkT$. The negative pressure of the Coulomb interactions among the ions is, of course, more than balanced by the large positive pressure of Fermi degenerate electrons for real systems. Similarly the compressibility from the Coulomb interactions alone is negative for the OCP. Working from the Coulombic pressure the compressibility is found to be:

$$\left(\frac{-P}{\Gamma} \right)_{\Gamma} = -\frac{4}{9} a\Gamma + \frac{13}{36} b\Gamma^{1/4} - \frac{c}{3} .
 \tag{22}$$

This result for the compressibility is of considerable importance since it appears in the OCP structure factor¹⁷ as:

$$S(k) = \frac{1}{1 + \frac{3\Gamma}{K} + \left(\frac{36P}{\Gamma} \right)_{\Gamma}} , \quad K = k\bar{r}
 \tag{23}$$

$$\begin{aligned} \beta u(r) &= \beta \epsilon (\sigma/r)^m = \beta \epsilon (\sigma/\bar{r})^m (\bar{r}/r)^m \\ &= \Gamma/x^m, \quad x = r/\bar{r} \end{aligned} \quad (24)$$

where

$$\Gamma = \beta \epsilon (\sigma/\bar{r})^m \propto \frac{n^{m/3}}{kT} \quad (25)$$

is the generalization of the OCP strong coupling parameter. The inverse power potential has a particularly useful scaling property which is apparent from the virial theorem:

$$E = E_0 + U \quad (26)$$

$$PV = P_0 V + \frac{m}{3} U$$

where

$$U = \left\langle \sum_{i < j} u(r_{ij}) \right\rangle = \frac{Nn}{2} \int d^3r \, u(r) \, g(r) \quad (27)$$

and $E_0 = \frac{3}{2} NkT$ for the ideal gas term. The $m/3$ factor follows from the virial expression for the pressure:

$$(P-P_0)V = \frac{Nn}{6} \int d^3r \, \left(-r \frac{du(r)}{dr} \right) g(r) \quad (28)$$

For low densities the pressure and energy have an expansion in powers of density, the cluster expansion, and the strong coupling parameter Γ is inappropriate. (Recall in the OCP case that weak coupling expressions

phase. The f_{cc} lattice has the lowest energy for $m > 3$; the bcc lattice is lowest for the OCP. The remaining piece, $br^S - c$, is the fluid thermal energy, U_{th}/NkT .

The actual data for all five available cases, $m = 1, 4, 6, 9, 12$, is shown in Table II. The number quoted in Table II are for $(U_{MC} - U_0)/NkT$ with U_0/NkT taken to be the appropriate lattice value. Thus in this tabulation the constant, a , in Eq. 30, is taken to be exactly the appropriate Madelung constant for the solid phase, rather than being treated as a free parameter. This is an unproved assumption, and one that I regard as questionable. Because of this assumption the U_{th}/NkT data for the OCP as taken from Hansen's paper differ slightly from the U_{th}/NkT data for the OCP in Table I. Recall that Eq. 18 for the fit to Hansen's OCP data for $1 < \Gamma < 40$ used a as a free parameter and it came out slightly higher than the lattice value. The interesting aspect of this thermal energy data for the strongly coupled fluids is the uniformity in behavior and magnitude. Recently Hoover, et al.¹⁹ developed a generalized van der Waals equation of state for liquids, and made a simple fit to the thermal energy data with the assumption in Eq. 40 that $c = 0$ and $s = 1/3$. A more careful analysis with c as a free parameter indicates that the exponent is lower than $1/3$, and is probably close to $1/4$ as in the OCP case.

For the $m = 12$ case the virial expansion with four exactly known coefficients is:

$$U/NkT = \frac{3}{12} (P - P_0)/NkT \quad (31)$$

$$= \frac{1}{4} \{ 3.63\eta^3 + 7.58\eta^2 + 9.94\eta^3 + 8.45\eta^4 + \dots \}$$

1960's the density expansions were powerfully supplemented by integral equations for $g(r)$ which in effect summed to infinity certain kinds of the integrals in the Mayer irreducible clusters. The Percus-Yevick equation was found to give an excellent description of the hard sphere fluid and the PY equation of state was found to be in near quantitative agreement with the molecular dynamics hard sphere data.³ The hypernetted chain (HNC) equation did not work so well for the hard sphere system, but it did appear to be useful for longer range potentials including the inverse power potentials.²⁰

Monte Carlo simulations give presumably nearly exact "experimental" results for the strongly coupled OCP. It is of considerable interest to see what extent integral equations of present day liquid state theory can reproduce the Monte Carlo results. The Percus-Yevick equation has been investigated for the Coulomb potential²¹ and found to be completely inaccurate for large Γ . However, the hyper-netted chain equation (HNC) when solved numerically was found to give results for the total potential energy, U/NkT , for the OCP that are remarkably close to the Monte Carlo results.²¹ Recently Ng has made an extremely accurate numerical solution of the HNC equation,²² and obtained results for U/NkT for the OCP to seven and eight figure accuracy for values of Γ from 20 to 7000. Although $\Gamma = 7000$ is far beyond any conceivable physical situation, these exact numerical results for the HNC equation allow one to find the functional form of U/NkT with respect to Γ without the difficulty presented by the inevitable noise in the Monte Carlo data. To explain simply the HNC equation one notes that the pair distribution function for the OCP may be written generally as:

$$g(r) = h(r) + 1 = \exp \left(-\frac{\Gamma}{x} + S(x) + B(x) \right) \quad (33)$$

The HNC solution is quite continuous for large Γ even up to $\Gamma = 7000$, and consequently it should be interpreted as an approximation for the fluid branch of the OCP equation of state. There is no indication that any known integral equation can give a second solution that would correspond to the equation of state for the solid phase of the OCP. What is remarkable about the above nearly exact analytic result for the fluid phase potential energy is that it clearly shows a separation of the internal energy into a fluid static energy and a thermal energy portion which is dominated by a $\Gamma^{1/2}$ dependence. The HNC fluid static energy comes out remarkably close to the prediction of the ion sphere model which for the OCP would be:

$$(U_0/NkT)_{\text{ion-sphere}} = \left(-\frac{3}{2} + \frac{3}{5}\right) \frac{\beta(ze)^2}{\bar{\epsilon}} = -0.9\Gamma. \quad (37)$$

The HNC equation evidently goes to the ion-sphere result in the limit. The Monte Carlo result for the static energy, namely $U_0/NkT = -0.89461\Gamma$, is very close to the bcc lattice value, which differs from the ion-sphere model by only 0.45%. Since the thermal energy portion is only a small fraction of the total potential energy for large Γ , the close agreement of U_0 for HNC and Monte Carlo insures that the HNC results for U/NkT seem to agree well with the Monte Carlo results. This agreement is deceptive since the HNC thermal energy ($\sim\Gamma^{1/2}$) is very different from the presumed exact thermal energy ($\sim\Gamma^{1/4}$) obtained from the Monte Carlo simulations. Evidently this difference is entirely due to the basic HNC approximation of neglecting the bridge graphs. It is an open question as to whether a more exact integral equation that includes one or more of the lower order bridge graph terms could account for the difference in the HNC and the exact thermal energies. It is, in any

little to distinguish the HNC results from the mean spherical model. It is not even clear whether one approximation is better than the other. Both give a thermal energy in clear disagreement with the thermal energy from the Monte Carlo data. However, the qualitative agreement of the mean spherical model with the "exact" OCP results does indicate that the mean spherical model approximation may well be improved by a better guess for the form of the direct correlation function, $c(r)$. The actual form of $c(r)$ is obtainable from the Monte Carlo simulations and will be discussed later.

V. DENSE PLASMA MIXTURES IN STRONG COUPLING

We consider now arbitrary mixtures of two nuclear species, and for the moment $r_s = 0$. This is simply the extension of the OCP to two components.²⁴ The ion sphere model result, Eq. 37, is easily extended to two components. With the total ion number density as $n = n_1 + n_2$ for charges z_1 and z_2 , the background density of the neutralizing electron is:

$$n_e = z_1 n_1 + z_2 n_2 = \bar{z} n$$

and the radius of a sphere around a charge z_1 of sufficient size to neutralize z_1 is:

$$\bar{r}_1 = \left(\frac{z_1}{\bar{z}} \right)^{1/3} \bar{r} = z_1^{1/3} \bar{r}_e \quad (40)$$

From this result the static energy for a two component mixture according to the ion-sphere prescription is:

this should not be confused with a two component plasma in the sense of fully ionized hydrogen, i.e., charges of opposite sign). The recent Monte Carlo data on mixtures from Livermore also suggests that the thermal energy has the same density and temperature dependence as was found for the OCP, namely $\Gamma_0^{1/4}$. Consequently the internal energy for a two component mixture can be written as:

$$U/NkT = -az^{5/3} \bar{z}^{-1/3} \Gamma_0 + bg(z_1x_1, z_2x_2) \Gamma_0^{1/4} - c \quad (42)$$

where the function $g(z_1x_1, z_2x_2)$ is a charge average for the thermal energy. Clearly for $x_1 = 1$ the value of g is $z_1^{1/2}$ and for $x_1 = 0$ it would be $z_2^{1/2}$. It is tempting to assume a one fluid model for the two component system and to use the ion-sphere charge average for g , namely:

$$g = (z^{5/3} \bar{z}^{-1/3})^{1/4}$$

While this assumption does not give mixture energies that are badly in error, this one fluid model is definitely not correct. Recent Monte Carlo results from both Livermore and Paris for two components indicate that the above assumption for the thermal energy charge average is definitely outside the noise of the Monte Carlo simulations. The Livermore data shown in Table IV can be fitted reasonably well with the form:

$$g = \bar{z}^{1/2} \quad (43)$$

the induced electron density, i.e. the deviation from uniform density, can be written as:

$$\rho_{\text{induced}}(\mathbf{k}) = - \left(1 - \frac{1}{\epsilon(\mathbf{k})}\right) \rho_i(\mathbf{k}) \quad (46)$$

where $\epsilon(\mathbf{k})$ is the dielectric function of the electrons. In general $\epsilon(\mathbf{k})$ is a function of the electron temperature, and indeed finite temperature effects may be considerable in the interiors of laser fusion pellets. However, at sufficiently high densities the electron Fermi energy dominates the electron temperature, $kT/\epsilon_F \ll 1$, and the electrons can be treated as a completely degenerate $T=0$ fluid. For $r_s \lesssim 1$ the random phase approximation (RPA) is adequate for the electron dielectric function; at $T=0$ this is given by the Lindhard expression:

$$\epsilon(\mathbf{k}) = 1 + \frac{1}{(k \lambda_{\text{TF}})^2} f(y) \quad (47)$$

where $y = k/k_F$ and k_F is the Fermi momentum wave number, and

$$f(y) = \frac{1}{2} + \frac{1-y^2}{4y} \ln \left| \frac{1+y}{1-y} \right| \quad (48)$$

and

$$\bar{r}/\lambda_{\text{TF}} = \left(\frac{12z}{\pi} \right)^{1/3} r_s^{1/2} = q_{\text{TF}} \quad (49)$$

defines the Thomas-Fermi screening length. Hubbard and Slattery⁷ incorporated the electron screening effect into their Monte Carlo code, and with some minor modifications this code has been operated extensively at Livermore. The effect of the electron screening also changes the form of the ion-ion potential. In $\mathbf{k}$ space this is:

The Monte Carlo results show that for $0 < r_s \leq 0.5$ that $F^{(1)}$ is proportional to r_s times a function of Γ .⁷ This numerical result has been well confirmed by the theoretical analysis of Hansen and Gohm,²⁷ who show that:

$$F^{(1)}/NkT = \frac{1}{3\pi} \int_0^\infty q^2 dq S^{(0)}(q) w(q) \quad (53)$$

$$\text{with } w(q) = \frac{3\Gamma}{q^2} \left(\frac{1}{\epsilon(q)} - 1 \right), \quad q = k\bar{r}$$

and $S^{(0)}(q)$ is the OCP structure factor. Evaluation of the integral numerically and fitting to the same form for U/NkT gives:

$$F^{(1)}/NkT = r_s (.0579\Gamma + .971\Gamma^{1/4} - .343) \quad (54)$$

The energy and pressure are obtained from:

$$\begin{aligned} U/NkT &= \beta \frac{\partial}{\partial \beta} (\beta F/N) \\ &= \Gamma \frac{d}{d\Gamma} (\beta F/N) \\ \beta P/\Gamma &= -V \frac{\partial}{\partial V} (\beta F/N) \\ &= \frac{1}{3} \beta U/N - \frac{r_s}{3} \frac{\partial}{\partial r_s} (\beta F^{(1)}/N) \end{aligned} \quad (55)$$

The explicit results from the Livermore Monte Carlo data are:

$$\begin{aligned} U/NkT &= - (.8946 + .0543 r_s) \Gamma \\ &\quad + (.8165 - .1853 r_s) \Gamma^{1/4} \\ &\quad - (.5012 - .0659 r_s) \end{aligned} \quad (56)$$

fluid, and even the hard sphere $g(r)$. This is another indication that the strongly coupled plasma has properties closely related to more ordinary liquids. The typical oscillations of $g(r)$ about 1 appear when $\Gamma \sim 2.5$. The exact transition value is of some interest, and will be discussed in more detail by Dr. Deutsch. Here I will just point out that the transition value of from monotonic to oscillatory behavior according to the Monte Carlo calculations is definitely less than $\Gamma = 3.08$ at which the OCP compressibility becomes negative (where Eq. 22 gives -1). Although short range order is certainly indicated by the oscillations in $g(r)$, there is no indication of any kind of phase change at $\Gamma \sim 2.5$ or 3.08. The thermodynamic functions are all quite continuous.

A striking feature of the $g(r)$ data is the linear behavior in the screening function in the region below the first peak:

$$g(x) = e^{-\frac{\Gamma}{x} + H(x)} \quad (58)$$

with the screening function as:

$$H(x) = \Gamma(a_0 - a_1 x), \quad .4 < x < 1.8 \quad (59)$$

This empirical feature was first observed in 1973 from the BST data²⁹ and was very useful in calculating the screening enhancement rate of thermonuclear reactions in stellar interiors. Prof. Ichimaru will present a discussion of this linearity in $H(x)$ in relation to the lattice model of the dense plasma, and the use of this relation in more recent estimates of thermonuclear reaction rates. The values of the constants a_0 and a_1 are almost independent of Γ ,

rate calculation) is related to the difference of free energies of two charges before and after reaction (Ref. 29 and also Jancovici's work reported at this meeting). Using Eq. 21 for the OCP free energy one finds that the theoretical value of q_0 is:

$$\Gamma q_0 = (2F_I(\Gamma) - F_I(2^{5/3} \Gamma)) / NkT \quad (64)$$

$$= 1.051\Gamma + 2.172\Gamma^{1/4} - .561 \ln \Gamma = 2.24$$

and this seems to agree with Monte Carlo results as far as it can be checked.

In order to find the OCP structure factor $S(k)$ by Fourier transforming $g(r)$ it is necessary to have an accurate "tail" to extend the MC numerical data for $g(r)$ from $x \sim 2.5$ on to ∞ . This can be done by fitting the solution of the HNC equation on to the MC data with the help of the Ornstein-Zernicke equation. The procedure is described in some detail by Golam and Hansen.²⁷ The assumption of importance here is that the bridge graphs are negligible for $x \gtrsim 2.5$ thus ensuring the validity of the HNC equation. The structure factor is obtained then from:

$$S(k) = 1 + 3 \int_0^\infty x^2 dx \frac{\sin kx}{kx} h(x) \quad (63)$$

where $h(x) = g(x) - 1$. A typical result is shown in Fig. 2. A further check on the accuracy of $S(k)$ so obtained is a direct calculation of the internal energy from

$$H(x) = T(x) + B(x) \quad (68)$$

where

$$T(x) = \int d^3x' c(x') h(|x-x'|) = h-c \quad (69)$$

Since both $H(x)$ and $T(x)$ are now known numerically reasonable results can be obtained for the bridge graph function $B(x)$. This work is in progress.

21. J. F. Springer, M. A. Pokrant, and F. A. Stevens, J. Chem. Phys. 58, 4863 (1973).
22. K. Ng, J. Chem. Phys. 61, 2680 (1974).
23. M. J. Gillan, J. Phys. C: Solid State Physics 7, L1 (1974).
24. E. E. Salpeter, Australian J. Phys. 7, 353 (1954).
25. J. P. Hansen and P. Viellefosse, Phys. Rev. Lett. 37, 391 (1976).
26. J. P. Hansen, G. M. Torrie, and P. Villefosse (to be published).
27. S. Galan and J. P. Hansen, Phys. Rev. 14A, 816 (1976).
28. D. J. Stevenson, Phys. Rev. B12, 3999 (1975).
29. H. E. DeWitt, H. C. Graboske, and M. S. Cooper, Astrophysical J. 181, 439 (1973).

Table II. INVERSE POWER FLUID MONTE CARLO DATA

Hansen
1973

Hoover, et al 1971

$m = 1$		$m = 4$		$m = 12$	
Γ	U_{th}/NkT	Γ	U_{th}/NkT	Γ	U_{th}/NkT
1	.316	.498	.331	.123	.111
2	.473	1.688	.605	1.97	.270
3	.577	4.25	.907	9.98	.476
4	.658	10.72	1.347	31.5	.734
6	.786	18.40	1.644	77.0	1.034
10	.971	27.01	1.887	159.6	1.329
15	1.126	36.37	2.055	219.8	1.506
20	1.252	46.38	2.262	295.7	1.661
30	1.450	56.96	2.412	369.3	1.780
40	1.606	68.06	2.583	432.9	1.870
50	1.703	$\sigma = .013$		504.4	1.956
60	1.821	$m = 6$		$\sigma = .007$	
70	1.909	3.51	.247	$U_{th}/NkT = \Delta a \Gamma + b \Gamma^s - c$ 1) Non-linear 1. sq. (s, b, c) 2) Linear 1. sq. s = .20, .25, .3, .35 (Δa, b, c)	
80	1.986	2.19	.577		
90	2.066	8.77	1.036		
100	2.116	35.09	1.739		
110	2.195	78.96	2.195		
120	2.230	$m = 9$			
125	2.262				
130	2.292	.208	.159		
140	2.34	3.25	.469		
155	2.43	25.98	1.086		
160	2.46	207.9	2.199		

 $\sigma = .007$

Table IV. TWO NUCLEAR COMPONENT PLASMA MIXTURE FLUID DATA FROM LLL

Hansen

LLL

Γ_0	$\tilde{\Gamma}$	(U/NkT)	$(U/NkT)_{zz}$	$(U/NkT)_{1,2}$	$\frac{U_{12} - U_{zz}}{NkT}$	$C_{v,1\tilde{z}}$	$C_{v,1,2}$	$C_{v1,2} - C_{vzz}$
.1875	.3124	-.170	-.135	-.141	-.006	.035	.033	-.002
.375	.6236	-.334	-.323	-.332	-.009	.081	.078	-.003
.6	.9977	-.578	-.579	-.588	-.009	.134	.129	-.005
.75	1.2472	-.754	-.754	-.772	-.018	.161	.147	-.013
1.5	2.2472	-1.707	-1.716	-1.731	-.015	.257	.258	+.001
3.0	4.4944	-3.744	-3.750	-3.779	-.029	.386	.382	-.004
6.0	9.9774	-7.976	-7.980	-8.011	-.031	.601	.586	-.015
12.0	19.9548	-16.627	-16.611	-16.661	-.051	.772	.753	-.019

128 48 36 with $z_1 = 1$
 particles particles
 12 with $z_2 = 2$

$$\tilde{\Gamma} = \overline{z^{5/3}} \bar{z}^{1/3} \Gamma_0 = \tilde{z}^2 \Gamma_0$$

$$(U/NkT)_{\tilde{z}} = OCP \text{ with } \tilde{\Gamma}$$

classical Coulomb interactions between nuclei, and treat the electrons as a neutralizing background. This procedure is possible because at high density the small electron mass results in degeneracy since the Fermi energy is large compared to the temperature, $\epsilon_F \gg kT$. The electron pressure is much greater than the ion pressure, but to a large extent the two fluids are decoupled so that the separate contributions are additive. To make this point more clear one should first consider the real two component system: electrons and point nuclei. The Hamiltonian for this system is:

$$\begin{aligned}
 H &= K_e + K_i + U_{ee} + U_{ei} + U_{ii} \\
 &= \sum_{\alpha=1}^{N_e} \frac{p_{\alpha}^2}{2m_e} + \sum_{i=1}^N \frac{p_i^2}{2M} \\
 &\quad + \sum_{\alpha > \beta}^{N_e} \frac{e^2}{r_{\alpha\beta}} - \sum_{\alpha=1}^{N_e} \sum_{i=1}^N \frac{ze^2}{r_{\alpha i}} + \sum_{i < j}^N \frac{(ze)^2}{r_{ij}} \quad (3)
 \end{aligned}$$

for nuclei of mass M and charge ze . Neutrality for a single element requires

$$N_e = zN$$

and for a fully ionized mixture of elements with z_1 and z_2 the neutrality condition is:

$$N_e = z_1 N_1 + z_2 N_2 = \bar{z}N$$

with $N = N_1 + N_2$. Obviously this system is a quantum mechanical many-body problem which cannot yet be handled by present day computational methods.

Strong coupling usually means densities and temperatures such that $\Gamma > 1$. Debye shielding of the ions by electrons does not apply; to the extent that exponential screening of the nuclei does occur the Thomas-Fermi screening length applies. A few astronomical facts are relevant here. Approximately 80% of the hydrogen in Jupiter is pressure ionized. The Coulomb coupling parameter in the Jovian interior is of the order of 20, and the electron screening parameter is $r_s \sim 1$. For the enormously greater densities in white dwarf stars the two parameters are roughly $\Gamma \sim 100$ to 200 and $r_s \sim 0.01$. Also it should be noted that hydrogenic plasmas in laser fusion pellet compression experiments can include the ranges $\Gamma \sim 0.1$ to 10 and $r_s \sim 0.1$ to 1.

In the limit of $r_s = 0$ the electron density is constant, and electron screening effects disappear. This important limiting situation, classical point charges in a uniform background, is called the one component classical plasma (OCP). Evidently the OCP does not exist in nature, though white dwarf star interiors come close to it. As a mathematical model the OCP has the same importance for real strongly coupled plasmas as the hard sphere fluid has for the understanding of properties of real liquids.^{2,3} The OCP has been the subject of intense research, both theoretical and computational in recent years. It should also be noted that the OCP can be thought of as the extreme limit of the soft sphere fluid in which the particle interactions are described by inverse power potentials:

$$U(r) = \epsilon \left(\frac{r_0}{r} \right)^m \quad (7)$$

limitation required that they use a small number of particles ($N \sim 40$) and average over few configurations (10^4). Later the Hubbard Monte Carlo code was brought to the Livermore Laboratory for use on a larger computer (CDC 7600). At Livermore a large number of runs were made to map out the thermodynamics of one and two nuclear component plasmas including electron screening as functions of Γ and r_s .⁹

In France Prof. J. P. Hansen and his collaborators developed a new and very accurate OCP Monte Carlo code. In 1973 they published results for OCP thermodynamic functions obtained by averaging $N = 128$ particles over 10^6 configurations for values of Γ from 1 to 160 for the fluid state¹⁰ and 150 to 300 for the solid state, the Coulomb lattice.¹¹ Their U/NkT results for the OCP are apparently very accurate and reliable and at the present time they are the standard results available for testing the validity of analytical theories and integral equation results. The Hansen OCP fluid and solid OCP equation of state data can be viewed in the same way as the Alder-Wainwright molecular dynamics data for the fluid and solid hard sphere equation of state in the fluid and solid phases. The numerical experimental data give an accurate mapping of the thermodynamic properties of systems of particles governed by inverse power fluids including the limiting cases, $m = 1$ for the OCP, and $m = \infty$ for the hard sphere system. Empirical relations have been found from the analysis of this data which hopefully will suggest theoretical models for strongly coupled systems.

From the analysis of the data obtained from the Livermore and Paris Monte Carlo strongly coupled plasma equilibrium results a number of general results have emerged:

the ions in positions that resemble a lattice structure. Since the system is a fluid, the average position of the particles changes slowly with correlation. The magnitude of $U_0(n)$ may be expected to be comparable to the energies of simple cubic, face centered cubic, or body centered cubic lattices, but since the strongly coupled fluid is a disordered array, this static energy is expected to be slightly larger than the Madelung energy of the lattice that gives the minimum Helmholtz free energy for the solid, i.e. the bcc lattice for the Coulomb potential.¹¹ In addition to the slow shifts of the average particle positions there are also much more rapid short distance movements of the particles around their average positions. These rapid movements are analogous to the harmonic vibrations that give the thermal energy of a real lattice, and for the fluid these movements give rise to the fluid thermal energy, $U_{th}(n, kT)$. The essential difference of the fluid state as compared with the solid state shows up in the form of U_{th} . The Monte Carlo simulations of the strongly coupled plasma fluid state show that the temperature dependence of the fluid U_{th} per particle is approximately $(kT)^{3/4}$ instead of $(3/2)kT$ for a particle vibrating harmonically around a lattice site.¹²

II. THE OCP IN WEAK AND STRONG COUPLING

The equilibrium properties of the OCP may be rigorously obtained from the canonical partition function for N point charges in a volume V at temperature $\beta = 1/kT$. The thermodynamic limit is assumed:

$$\lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} \frac{N}{V} = n \quad . \quad (8)$$

$$\phi_{\text{eff}}(r) \approx \frac{\beta e^2}{r} e^{-r/\lambda_D} \quad (11)$$

instead of the bare Coulomb potential, $u(r) = e^2/r$. The result for S_2 is:

$$\begin{aligned} S_2 &= \frac{n}{2} \int d^3r \left\{ e^{-\beta u_S} - 1 + \beta u_S - \frac{1}{2} (\beta u_S)^2 \right\} \\ &= \frac{1}{2\epsilon} \int_0^\infty y^2 dy \left\{ e^{-\frac{\epsilon}{y}} e^{-y} - 1 + \frac{\epsilon}{y} e^{-y} - \frac{1}{2} \left(\frac{\epsilon}{y} e^{-y} \right)^2 \right\} \end{aligned} \quad (12)$$

and has the form $O(\epsilon^2 \ln \epsilon)$ or $O(\Gamma^3 \ln \Gamma)$ for $\Gamma \ll 1$. Complicated analytic expansion exist for S_2 and S_3 but they are generally not very useful. A better use of the Abe expansion is simply to numerically evaluate the integrals to sufficient accuracy that numerical derivatives can be taken. The Abe cluster integrals are all monotonic functions of Γ and easy to evaluate for the lower orders.¹⁴ The internal energy and the pressure are found by temperature and volume derivatives respectively of the free energy expression, Eq. 10. One finds:

$$\beta U/N = -\frac{1}{2} (\sqrt{3} \Gamma^{3/2}) + \frac{3}{2} \Gamma \frac{d}{d\Gamma} (S_2(\Gamma) + S_3(\Gamma) + \dots) \quad (12)$$

$$C_V/Nk = \frac{1}{4} (\sqrt{3} \Gamma^{3/2}) - \frac{3}{2} \Gamma^2 \frac{d^2}{d\Gamma^2} (S_2(\Gamma) + S_3(\Gamma) + \dots) \quad (13)$$

The interaction contribution to the pressure, $P_I = P - P_0$ with $P_0 = NkT$, is by the virial theorem:

$$(P - P_0)/n = \frac{1}{3} \beta U/N \quad (14)$$

a very simple analytic expression gives the equation of state and leads to all other thermodynamic functions. The upper limit is clearly the fluid-lattice transition which is indicated to be from the Pollock and Hansen Monte Carlo work as $\Gamma_f = 155$. For $\Gamma_c = 0.75$ the potential energy may be obtained accurately with a few terms of the Abe cluster expansion.¹⁴

The most accurate Monte Carlo data on the potential energy for the strongly coupled Coulomb fluid that is available at the present time is that of Hansen¹⁰, and some of this data is shown in Table I. In a separate column the values of the thermal energy are given for each Γ value. A striking feature of the Coulomb fluid data is that the thermal energy is only a small fraction of the total potential energy for large Γ ; U_{th}/NkT at $\Gamma = 155$, the fluid-lattice transition, is only 2% of the total energy. The Monte Carlo process necessarily gives U/NkT and not U_{th}/NkT so that it is necessary to obtain U/NkT with great accuracy in order to get dependable results for the thermal energy. Hansen used $N = 128$ particles and averaged over 10^6 configurations to obtain his results. A statistical analysis of this data indicated that up to Γ of 40 the results are consistent. For $\Gamma > 40$ the data indicate a possible small systematic error. Also it was found that the second moment of $g(r)$ did not satisfy the Stillinger-Lovett condition.¹⁶ Consequently the data for Γ in the range from 1 to 40 was used to deduce the quantitative results for the thermal energy. The total energy is written as:

$$\begin{aligned} U/NkT &= (U_0 + U_{th})/NkT \\ &= -a\Gamma + g(\Gamma). \end{aligned} \tag{17}$$

The $\Gamma^{1/4}$ behavior of the thermal energy appears to be quite definite. It is possible, of course, that Eq. 18 is only a fortunate fitting function. However, the clear appearance of the exponent $s = 0.25$ is suggestive of some underlying mechanism governing the thermal energy of the Coulomb fluid. It is a very interesting theoretical challenge to find a theoretical model that can explain the $\Gamma^{1/4}$. It is my opinion that this result for U_{th}/NkT is a fundamental result deduced from valid numerical "experimental" data.

An independent Monte Carlo calculation of the heat capacity should in principle give additional information about the functional form of U_{th} . Both BST and Hansen obtained results for C_V using:

$$C_V/Nk = \beta^2 (\langle U^2 \rangle - \langle U \rangle^2) / N \quad (19)$$

Unfortunately the numerical data for C_V so obtained are less accurate than the data for U/NkT because the computer must work with the difference of very large numbers, $\langle U^2 \rangle$ and $\langle U \rangle^2$. This calculation of C_V is further complicated by the fact that the CCP fluid static energy $U_0/NkT = -a\Gamma$ is so much larger than U_{th}/NkT . From Eqs. 17 and 18 a simple expression for the heat capacity is readily found:

$$\begin{aligned} C_V/Nk &= -\Gamma^2 \frac{d}{d\Gamma} \{g(\Gamma)/\Gamma\} \\ &\approx \frac{3}{4} b \Gamma^{1/4} - C \end{aligned} \quad (20)$$

This result agrees well with Hansen's numerical data for C_V/Nk .

for the small k limit of $S(k)$. Compressibility results have been obtained from Hansen's values for $S(k)$, and at least for the $\Gamma < 40$, the results are in good agreement with the above result for $(\partial P/\partial n)$.

The various results quoted in this section completely specify the equilibrium thermodynamic functions for the OCP. The $r^{1/4}$ form appearing in U_{th}/NkT indicates that the thermal energy itself varies as $T^{3/4}$ in contrast to $\frac{3}{2} NkT$ for the thermal energy observed in the solid phase due to harmonic vibrations around lattice sites. It is not surprising that the thermal energy of the OCP fluid differs from the solid thermal energy. An understanding of the underlying mechanism to account for the $T^{3/4}$ behavior in the fluid state would be most helpful for dense plasma theory.

III. STRONG COUPLING RESULTS FOR INVERSE POWER FLUIDS

Fluids governed by repulsive $1/r^m$ potentials (Eq. 7) may at first glance seem remote from plasma physics. This may seem particularly so for the $m = 12$ case which describes the repulsive part of the Lennard-Jones 6-12 potential used for describing interaction among molecules of ordinary gases and liquids. However, the Monte Carlo calculation of U/NkT for the cases of $m = 4, 6, 9$, and 12 indicate a basic similarity to the OCP Monte Carlo results.⁴ One sees the same kind of change of functional form in the internal energy from weak to strong coupling as is seen in the plasma case. In weak coupling, however, there is a virial expansion in powers of density unlike the weak coupling plasma case. The strong coupling parameter for the inverse power potentials can be defined in a manner analogous to Eq. 2 for the $1/r$ potential. The general inverse power potential can be written as:

behaved linearly with $\epsilon \sim \Gamma^{3/2}$. It is convenient to express the density coupled with the appropriate power of temperature as:

$$\begin{aligned}\tilde{n} &= \frac{n\sigma^3}{\sqrt{2}} \frac{\epsilon}{kT}^{3/m} \\ &= \frac{3}{4\pi\sqrt{2}} \Gamma^{3/m}\end{aligned}\quad (29)$$

As with the OCP all thermodynamic quantities are functions of Γ (or equivalent of $\tilde{n}$). The virial expansion in powers of $\tilde{n}$ gives exact results for weak coupling (low density or high temperature) and strong coupling results are available from the Monte Carlo studies of Hoover, et al.⁴ The interaction internal energy has the form:

$$\begin{aligned}U/NkT &= \frac{3}{m} (P - P_0)/nkT \\ &= \frac{3}{m} (\tilde{B}_2\tilde{n} + \tilde{B}_3\tilde{n}^2 + \tilde{B}_4\tilde{n}^3 + \dots) \\ &= a\Gamma + (b\Gamma^S - c), \quad \Gamma_t \leq \Gamma < \Gamma_f\end{aligned}\quad (30)$$

The virial expansion is convergent for the entire fluid phase, but at present time only a few of the dimensionless virial coefficients ($\tilde{B}_2$, $\tilde{B}_3$, etc.) have been evaluated; seven are known for the hard sphere fluid, $m = \infty$.¹⁸ The Monte Carlo strong coupling data for $m = 4, 6, 9$, and 12 can all be fitted with the second form of Eq. 30. As described in OCP case the $a\Gamma$ term is the static energy of disordered system, U_0/NkT , and the constant a is expected to be close to or perhaps identical to the Madelung constant for the lattice

and for large Γ the result is:

$$U/NkT = .00493\Gamma + (.516\Gamma^{1/4} - .49), \quad (32)$$

$$200 \lesssim \Gamma < 538$$

where $a = .00483$ is the fcc Madelung constant for the $1/r^{12}$ potential, $\Gamma_f = 538$ is the value of the coupling parameter when the fluid freezes. $\Gamma_t \sim 200$ is an estimate of the point at which the asymptotic strong coupling form appears. Γ_t for $m = 12$ is far larger than in the OCP case ($\Gamma_t \sim .75$ for $m = 1$) because of the far shorter range of the $1/r^{12}$ potential. In general it will be true that

$$\lim_{m \rightarrow \infty} \frac{\Gamma_f - \Gamma_t}{\Gamma_f}$$

and for the hard sphere gas there is no static lattice energy and no thermal energy. Table III gives the strong coupling fits to the data for the five known cases assuming that a = Madelung constant, and $s = 1/4$. For this investigation a non-linear least squares fitting routine was used with a , b , c , and s as free parameters. The value of the exponent as $s \approx 1/4$ appeared best for $m = 1$ and $m = 12$. There are too few data points for $m = 4$, 6 , and 9 to assert confidently that in all cases that $s = 1/4$. However, the results do strongly suggest a universal form of the thermal energy, namely $\Gamma^{1/4}$, for all the inverse power fluids.

IV. INTEGRAL EQUATION RESULTS

Until about 20 years ago most calculations of the equation of state of dense gases and liquids had to rely on the virial expansion with the cluster integrals evaluated for assumed intermolecular potentials. In the

where $g(r)$ is the pair distribution function, $h(r) = g(r) - 1$ is the total correlation function, $S(x)$ indicates the sum of all convolution or series of graphs in the cluster expansion of $g(r)$, and $B(x)$ is the sum of all bridge graphs. $h(r)$ is related to the direct correlation function, $c(r)$, by the Ornstein-Zernike equation:

$$h(r) = c(r) + n \int d^3r' c(r') h(|\underline{r} - \underline{r}'|) . \quad (34)$$

The HNC integral equation is obtained from the above relations by the approximation of neglecting the bridge graph contributions, i.e. assuming $B(x) = 0$. The resulting equation is non-linear for $h(r)$ but may be solved with computers to any desired accuracy, and the OCP internal energy is obtained from the integral:

$$\begin{aligned} U/NkT &= \frac{n}{2} \int d^3r \frac{8e^2}{r} (g(r) - 1) \\ &= \frac{3\Gamma}{2} \int_0^\infty x^2 dx \frac{1}{x} h(x) \end{aligned} \quad (35)$$

Some of Ng's HNC results for U/NkT are given in Table I to show a comparison with the Monte Carlo results of Hansen for U/NkT . Since Ng's results are of high accuracy and span an extremely wide range in Γ it was possible to find the functional dependence on Γ ; the result is:¹²

$$(U/NkT)_{\text{HNC}} = -0.90047\Gamma + 0.26883\Gamma^{1/2} + 0.0720 \ln \Gamma + 0.0538. \quad (36)$$

case, significant that the simple approximation of the HNC equation is sufficient to give the basic qualitative feature of the fluid phase OCP internal energy, namely a division into a static portion and a thermal portion.

Another widely used approximation in liquid state theory is the mean spherical approximation which states that:

$$\begin{aligned} c(r) &= -\beta u(r), \quad r < \sigma \\ h(r) &= -1, \quad r < \sigma \end{aligned} \tag{38}$$

where σ is an equivalent hard sphere radius, and $c(r)$ and $h(r)$ are connected by the usual Ornstein-Zernike equation. Gillan²³ has solved the mean spherical model for the OCP by using a judicious choice of σ so that $g(r)$ does not go negative. He obtains $g(r)$ and computes values of U/NkT some of which are shown in Table I. As is the case with the HNC numerical results the absolute values of U/NkT obtained from the mean spherical model are in moderately good agreement with the Monte Carlo results. The functional form obtained from Gillan's numbers is:

$$(U/NkT)_{MS} = -0.9005\Gamma + 0.2997\Gamma^{1/2} + 0.0007. \tag{39}$$

As with the HNC results there is a clear separation of the potential energy into a static portion, U_0 , that is very close to the ion-sphere result, and a thermal energy that is dominated by $\Gamma^{1/2}$. In a numerical sense there is

$$\begin{aligned}
 (U/NkT)_{\text{ion-sphere}} &= -\frac{9}{10} (x_1 z_1^{5/3} + x_2 z_2^{5/3}) \bar{z}^{-1/3} \beta e^2 / \bar{r} \\
 &= -\frac{9}{10} \frac{\bar{z}^{5/3}}{\bar{z}^{1/3}} \bar{z}^{-1/3} \Gamma_0
 \end{aligned}
 \tag{41}$$

where

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2}$$

and

$$\Gamma_0 = \beta e^2 / \bar{r}.$$

Thus the ion-sphere model gives a characteristic simple charge averaging prescription for mixtures of ions, namely $\bar{z}^{5/3} \bar{z}^{-1/3}$, that is very different from the $\bar{z}^2$ charge averaging that appears in the Debye result for weak coupling. In view of the remarkable agreement of the OCP ion-sphere result with both the Monte Carlo and the HNC results for the static energy, it is reasonable to expect that the ion-sphere result will be equally good for the static energy for the ion mixtures. Indeed this is the case. The two nuclear component Monte Carlo data from Livermore⁹ agree perfectly with the ion-sphere charge averaging prescription. More recent (unpublished) and much more extensive Monte Carlo for a variety of mixtures for $z_1 = 1$, $z_2 = 2$ and $z_1 = 1$, $z_2 = 3$ also completely agree with the ion-sphere charge average prescription. Also Hansen and Viellefosse have solved the coupled hyper-netted chain equations for two nuclear components,²⁵ and have found that for the HNC approximation that again the ion-sphere charge averaging is satisfied. (Hansen and Viellefosse use the term "Two-Component Plasma" or TCP in their paper, and of course, mean two components of the same sign;

although it should be noted that this form has no theoretical justification at the present time. Hansen and Vielliefosse note that the ion sphere charge average is strictly additive when the electron density remains constant. Their solution of the HNC equations for two components suggest that this additive property also holds true for the thermal energy. Thus they suggest that the two component energy is:

$$U/NkT = \{x_1 U(z_1^{5/3} \Gamma_0^{-1}) + x_2 U(z_2^{5/3} \Gamma_0^{-1})\}/NkT \quad (44)$$

where $\Gamma_0^{-1} = z^{-1/3} \Gamma_0$. Very recently they have two component Monte Carlo results which indicate the same additivity.²⁶ The Livermore and Paris Monte Carlo results for mixtures are so close in numerical agreement and also close to the noise level, that at the moment it is difficult to give a final answer for the thermal energy for mixtures. The precise form will probably not be clear until there is a good theoretical model for the $\Gamma^{-1/4}$ thermal term.

VI. SCREENING CORRECTIONS

So far in these lectures the electron background has been treated as a rigid neutralizing background with no properties other than the constant densities. This is obviously unrealistic for applications to the interior of Jupiter and stellar interiors. In order to treat the electrons as a responding background the linear response theory has been used to describe the increase in electron density near each ion. With the ion charge density given by:

$$\rho_i(\underline{r}) = ze \sum_{i=1}^N \delta(\underline{r} - \underline{r}_i) \quad (45)$$

$$u(k) = \frac{4\pi(ze)^2}{k^2 \epsilon(k)} \quad (50)$$

and in r space:

$$u(r) = \frac{(ze)^2}{r} g(r/\lambda_{TF}) \quad (51)$$

$$\sim \frac{(ze)^2}{r} e^{-r/\lambda_{TF}}, \quad r < \lambda_{TF}$$

The r space representation is not readily useful since the screening function, $g(r/\lambda_{TF})$, exhibits Friedel oscillations for large r . The simple exponential screening is apparent only at short distances. The k space form, Eq. 50, however, can be adapted into the calculation of the Ewald potential needed to describe the image charges for the plasma Monte Carlo calculation.

The Monte Carlo code gives results for U/NkT and P/NkT as functions of Γ and r_s . Note that the simple virial theorem factor of $1/3$ relating the energy and pressure no longer applies since the ion-ion potential, Eq. 51, is no longer pure Coulomb. It is more general and useful to discuss the results by starting with the Helmholtz free energy which can be written as:

$$\beta F/N = \beta(F^{(0)}(\Gamma) + F^{(1)}(\Gamma, r_s))/N \quad (52)$$

with $F^{(0)}(\Gamma)$ given by Eq. 21 for the OCP. A two component version of $F^{(0)}$ can also be easily worked out using the charge averaging results given in the previous section. The entropy constant for the two component mixture is given in Ref. 9. Our interest here is in the screening correction, $F^{(1)}$.

and for the pressure:

$$(P-P_0)/n_kT = \frac{1}{3} (U^{(0)}/NkT) + .185 r_s^{-1/4} \quad (57)$$

Similar numerical results are available for mixtures of two elements in Ref. 7. but will not be quoted here. The two ionic component results are being done now more accurately, so that the free energy of a mixture (e.g. fully ionized hydrogen and helium) can be used for locating the condition for phase separation.²⁸

The largest numerical effect of electron screening is on the static portion of the energy, but even this is only a few percent at $r_s \sim .5$. The pressure of the plasma is affected rather little by electron screening. This fact is apparent from the form of $F^{(1)}$ which is proportional to $r_s \Gamma = \beta e^2/a_0$, and hence independent of volume. Consequently the correction due to screening in Eq. 55 comes only from the thermal portion of the free energy.

Where detailed comparisons have been made there is excellent agreement between the Livermore Monte Carlo screening results and the calculation based on Eq. (53) reported by Galam and Hansen. For $r_s \geq .5$ there is an additional $O(r_s^{-3/2})$ contribution which also shows up in the Monte Carlo data.

VII. PAIR CORRELATION AND DIRECT CORRELATION FUNCTIONS

The pair correlation function $g(r)$ is obtainable from the Monte Carlo calculations but only to a distance of approximately half of the size of all containing the N charges. This distance, $x \sim N^{1/3}/2$, is sufficient to show the major structural features of $g(r)$. An example is shown in Fig. 1 for $\Gamma = 40$. The $g(r)$'s for the OCP resemble the $g(r)$ for the inverse power

though a slight but important dependence has been found. a_0 and a_1 have a geometrical relation to the location and height of the first peak in $g(r)$. With the empirical form, Eq. 59, one has:

$$g(x) = e^{\Gamma f(x)} = e^{\Gamma(-\frac{1}{x} + a_0 - a_1 x)} \quad (60)$$

The first peak occurs at $x_m \sim 1.68$, and the height is:

$$g(x_m) = e^{\Gamma \Delta}$$

where Δ is a small number found empirically from the MC data. A little algebra with Eq. 60 shows that:

$$a_1 = \frac{1}{x_m^2} = .39 \quad (61)$$

and

$$a_0 = 2a_1^{1/2} + \Delta = 1.27 + \Delta \quad (62)$$

For large Γ the linear behavior in x of $H(x)$ cannot be seen very far because $g(x)$ is almost zero until $x \sim .8$. For small x a different functional form appears:

$$H(x) = \Gamma(a_0 - a_1 x^2), \quad x \lesssim .4 \quad (63)$$

Recently Prof. Jancovici has shown that a_1 should be $1/4$ rather than $1/2$ as reported in Ref. 29. The constant a_0 (which is crucial for the reaction

$$\begin{aligned}
 U/NkT &= \frac{\Gamma}{\pi} \int_0^{\infty} dk S(k) \\
 &= \frac{3\Gamma}{2} \int_0^{\infty} x dx h(x)
 \end{aligned}
 \tag{64}$$

For each value of Γ the evaluation of the energy from the k integration and x integration come out slightly different, but they closely bracket the Monte Carlo results for U/NkT . An additional check on the accuracy of the $S(k)$ data is the compressibility relation that appears in $S(k)$, Eq. 23.

At least up to $\Gamma = 40$ there is good agreement with Eq. 22.

With $S(k)$ known numerically one also has $\tilde{c}(k)$ from:

$$S(k) = \frac{1}{1 + \tilde{c}(k)} \tag{65}$$

so that $c(r)$ can be obtained with a Fourier transform. For $x \gtrsim 1.8$ the direct correlation function goes over to the Coulomb potential:

$$c(x) \approx -\frac{\Gamma}{x} \tag{66}$$

but for $x < 1.8$ $c(x)$ behaves much like $H(x)$, namely

$$\begin{aligned}
 c(x) &\approx -\Gamma(a_0' - a_1' x), \quad .4 < x < 1.8 \\
 &\approx -\Gamma(\alpha_0' - \alpha_1' x^2), \quad x < .4
 \end{aligned}
 \tag{67}$$

where the constants a_0' , a_1' and α_0' , α_1' are slightly different from the values for $H(x)$. This behavior is shown in Fig. 3. The calculation of $H(x)$ and $c(x)$ allows one also to find the bridge graph function since:

References

1. S. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. 45, 2102 (1966).
2. B. J. Alder and T. E. Wainwright, J. Chem. Phys. 27, 1208 (1957).
3. G. S. Rushbrooke, Equilibrium Theories of the Liquid State in Physics of Simple Liquids, Temperley, Rawlinson and Rushbrooke, eds., North Holland Publishing, Amsterdam 1968.
4. W. G. Hoover, S. G. Gray, and K. W. Johnson, J. Chem. Phys. 55, 1128 (1971).
5. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. M. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).
6. B. R. A. Nijboer and F. W. DeWette, Physica 23, 309 (1957).
7. W. B. Hubbard and W. L. Slattery, Astrophysical J. 168, 131 (1971).
8. W. B. Hubbard, Astrophysical J. 176, 525 (1972).
9. H. E. DeWitt and W. B. Hubbard, Astrophysical J., 205, 295 (1976).
10. J. P. Hansen, Phys. Rev. A8, 3096 (1973).
11. E. L. Pollock and J. P. Hansen, Phys. Rev. A8, 3110 (1973).
12. H. E. DeWitt, Phys. Rev. A14, 1290 (1976).
13. R. Abe, Prog. Theor. Phys. 22, 213 (1959).
14. F. J. Rogers and H. E. DeWitt, Phys. Rev. A8, 1061 (1973).
15. S. G. Brush, H. E. DeWitt, and J. G. Trulio, Nuclear Fusion 3, 5 (1963).
16. F. H. Stillinger and R. Lovett, J. Chem. Phys. 49, 1991 (1968).
17. P. Vieillefosse and J. P. Hansen, Phys. Rev. A12, 1106 (1976).
18. F. H. Ree and W. G. Hoover, J. Chem. Phys. 46, 4181 (1967).
19. W. G. Hoover, G. Stell, E. Goldmark, and G. D. Degani, J. Chem. Phys. 63, 5434 (1975).
20. P. Hutchinson and W. R. Conkie, Mol. Phys. 24, 567 (1972).

Table I. THERMAL EQUATION OF STATE FOR OCP

	<u>MONTÉ CARLO</u>		<u>HYPER-NETTED CHAIN</u>		<u>MEAN SPHERICAL MODEL</u>	
Γ	U/NkT	U_{th}/NkT	U/NkT	U_{th}/NkT	U/NkT	U_{th}/NkT
1	-.580	.315	-.570	.331	-.607	.294
2	-1.318	.471			-1.377	.424
3	-2.111	.572	-.2103	.598	-2.180	.522
4	-2.926	.652			-2.999	.579
6	-4.590	.778				
10	-7.996	.950	-7.9355	1.070	-8.053	.952
15	-12.313	1.106			-12.343	1.165
20	-16.667	1.225	-16.538	1.472	-16.667	1.343
30	-25.429	1.409			-25.373	1.642
40	-34.232	1.552	-33.999	2.020	-34.125	1.895
60	-51.936	1.741	-51.597	2.431	-51.710	2.320
80	-69.690	1.879	-69.264	2.774	-69.360	2.680
100	-87.480	1.981	-86.973	3.074	-87.053	2.997
120	-105.284	2.069	-104.713	3.343	-104.775	3.285

Table III. FLUID THERMAL ENERGY FOR INVERSE POWER POTENTIALS

$$u(r) = \epsilon (\sigma/r)^m$$

Data for $m = 4, 6, 9, 12$ (Hoover, et al) and $m = 1$ (Hansen) all fit the form:

$$U_{th}/NkT = b\Gamma^{1/4} - c, \text{ where } \Gamma = (8\epsilon) (\sigma/\bar{r})^m$$

$$\bar{r} = \left(\frac{1}{\frac{4}{3} \pi N/V} \right)^{1/3}$$

m	$U/NkT = (U_o + U_{th})/NkT$		
1	$-.895929\Gamma$	$+ .8739\Gamma^{1/4}$	$-.5777$
4	1.181978Γ	$+ 1.150\Gamma^{1/4}$	$-.7413$
6	$.205945\Gamma$	$+ .9267\Gamma^{1/4}$	$-.5484$
9	$.0300478\Gamma$	$+ .7067\Gamma^{1/4}$	$-.4913$
12	$.0049258\Gamma$	$+ .5156\Gamma^{1/4}$	$-.4870$

The $\Gamma^{1/4}$ power law appears best for the $m = 1$ and $m = 12$ cases for which there are the most points.

$$C_v/Nk = \frac{3}{4} b \Gamma^{1/4} - c; \text{ Hansen's data checks this result very well.}$$

Figure Captions

- Fig. 1 Monte Carlo $g(r)$ for $\Gamma = 40$ with HNC extension. The insert shows the linear behavior of the screening function.
- Fig. 2 OCP structure factor $S(k)$ for $\Gamma = 40$ obtained by Fourier transform of $g(x)$.
- Fig. 3 OCP direct correlation function for $\Gamma = 40$.

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

NOTICE

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.