

CONF-770741-2

PREPRINT UCRL-80222

Lawrence Livermore Laboratory

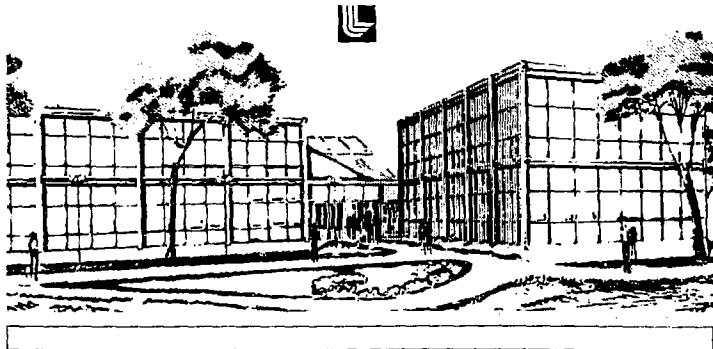
STATISTICAL MECHANICS OF DENSE PLASMAS: NUMERICAL SIMULATION AND THEORY

H. E. DeWitt

October 1977

This paper was prepared for presentation at
NATO Advanced Study 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.



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

STATISTICAL MECHANICS OF DENSE PLASMAS: NUMERICAL SIMULATION

AND THEORY

H. E. DeWitt

University of California Lawrence Livermore Laboratory

P. O. Box 808, Livermore, California 94550

ABSTRACT

Recent Monte Carlo calculations from Paris and from Livermore for dense one and two component plasmas have led to systematic and accurate results for the thermodynamic properties of dense Coulombic fluids. This talk will summarize the results of these numerical experiments, and the simple analytic expressions for the equation of state and other thermodynamic functions that have been obtained. The thermal energy for the one component plasma has a simple power law dependence on temperature that is identical to Monte Carlo results on strongly coupled fluids governed by $1/r^n$ potentials. A universal model for fluids governed by simple repulsive forces is suggested. For two component plasmas the ion-sphere model is shown to accurately reproduce the Monte Carlo data for the static portion of the energy. Electron screening is included using the Lindhard dielectric function and linear response theory. Free energy expressions have been constructed for one and two component plasmas that allow easy computation of all thermodynamic functions.

I. INTRODUCTION

The purpose of this paper is to give a partial summary of current understanding of the equilibrium statistical mechanics of fully ionized light elements at finite temperature and very high density. This state of matter is referred to as a Coulomb fluid or a strongly coupled plasma. The interesting thermodynamic properties are governed by the Coulombic interactions between the nuclei which are treated as charged points. Because

of the relatively large mass of the nuclei as compared with the electron mass the Coulomb fluid is a nearly classical system in contrast with the electron fluid which is highly quantum mechanical. Thus a strongly coupled plasma may be considered as a mixture of two fluids: the fluid of point nuclei governed by pairwise Coulomb interactions in classical mechanics, and a neutralizing electron fluid which because of the high density is degenerate due to Fermi statistics of the electrons. In real physical systems, i.e. stellar interiors, large planetary interiors, and laser-fusion compression experiments, the two fluids interact with each other chiefly by means of an electron screening effect due to some accumulation of fast moving electrons around each nucleus. Since a very large fraction of the matter in the universe, i.e. stellar interiors, is in the strongly coupled plasma state the equilibrium and non-equilibrium properties of the Coulomb fluid are of great interest.

Most of the physics of dense fully ionized plasmas to be discussed will deal with nearly classical Coulombic interactions treated by numerical and analytical statistical mechanics. The main advances in understanding of the strongly coupled system have come in the last five years from Monte Carlo simulations of the Coulomb fluid from Paris and from Livermore. Although the electron fluid at high density dominates the pressure due to the high degree of degeneracy and the large value of the Fermi energy compared with the temperature, $cp \gg kT$, it is assumed that the electron fluid is to a large extent decoupled from the Coulomb fluid of the nuclei. To make this point evident and to define our terms it is useful to first look at the true plasma Hamiltonian for the real two component system: electrons and point nuclei. This Hamiltonian is:

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

where nuclei of mass M have charge z . For a single element electrical neutrality requires

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.

114

$$N_e = zN$$

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

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

where $N = N_1 + N_2$. Because of the attractive interaction between electrons and nuclei it is evident that a proper treatment of this many body system requires quantum mechanics since the classical partition function of point charges of opposite sign is divergent. However, if we treat the electrons not as particles but as a neutralizing fluid, the average total energy of the plasma can be written as:

$$E = \langle H \rangle = \langle K_e \rangle + \langle K_i \rangle + \langle U_{ee} \rangle + \langle U_{ii} + U_{ei} \rangle$$

$$= N_e \left(\frac{3}{5} \epsilon_F + \epsilon_{ex} + \epsilon_{corr} \right) + \frac{3}{2} N kT + U$$

where the brackets indicate an ensemble average, and U is the internal energy of the nuclear Coulomb interactions suitably ensemble averaged in the presence of the electron fluid:

$$U = \sum_{i < j} \frac{(ze)^2}{r_{ij}} + \text{background}$$

$$= NkT \Gamma(\Gamma, r_s)$$

where Γ is the classical Coulomb interaction parameter and r_s is the electron screening parameter for complete degeneracy ($\epsilon_F/kT \gg 1$):

$$\Gamma = \frac{z^2 e^2}{kT} \left(\frac{4\pi}{3} n \right)^{1/3} = \frac{z^2 e^2}{kT \bar{r}} \sim \frac{\langle (ze)^2 / r \rangle}{kT}$$

$$r_s = \frac{\bar{r}_e}{a_0}$$

where $a_0 = \hbar^2 / m_e e^2$ and

$$\bar{r}_e = \frac{1}{\left(\frac{4\pi}{3} n_e \right)^{1/3}} = \frac{\bar{r}}{z^{1/3}}$$

since $n_e = \bar{z}n$ with $n = N/V$, the ion number density, and n_e is the electron number density. \bar{r} is a convenient measure of the average

distance between nuclei. Note that the radius of a sphere surrounding a charge z_1 containing sufficient negative charge to neutralize z_1 , the ion-sphere radius is:

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

The two parameters, Γ and r_s , are sufficient to specify the thermodynamic properties of the system. Hence the internal energy in the form, U/NkT , is a function of Γ and r_s . Strong coupling generally means that $\Gamma > 1$, and for the high density or low temperature required, the concept of Debye length does not enter the description of the plasma; the length \bar{r} is more appropriate. Also the screening due to degenerate electrons is not Debye screening but much more like Thomas-Fermi screening. For the pressure ionized hydrogen found in the interior of Jupiter the Coulomb coupling parameter is of the order of 20, and the electron screening parameter is $r_s \sim 1$. For the enormously higher densities in white dwarf stars the value of the two parameters are roughly $\Gamma \sim 100$ to 200 and $r_s \sim 0.01$.

The limit of $r_s = 0$ gives a very useful and important mathematical abstraction, the classical one component plasma (OCP) which evidently does not exist in nature, though white dwarf star interiors come very close to it. The OCP as a mathematical model has the same importance for real strongly coupled plasmas as the hard sphere fluid has for the theory of real liquids. In fact the OCP may be considered as the extreme limit for the "soft" sphere system described by inverse power potentials:

$$u(r) = \epsilon \left(\frac{\sigma}{r}\right)^m$$

For $m = \infty$ one obtains the hard sphere potential for spheres of diameter σ , namely $u(r) = \infty$ for $r \leq \sigma$ and $u(r) = 0$ for $r > \sigma$. The OCP is obtained for $m = 1$ with $\epsilon\sigma = (ze)^2$. Extensive computer simulations of the strongly coupled soft sphere systems¹ are now available ($m = 1, 4, 6, 9, 12$, and $m = \infty$ for hard spheres²), and remarkable similar features are found all the way from the extreme soft sphere case, the Coulomb system for $m = 1$, to the hard sphere fluid for $m = \infty$. All of these fluid systems go into a lattice at appropriately high values of the coupling parameter; the fluid thermal energy has an apparently universal form for the soft sphere systems; and the pair distribution function, $g(r)$, has the same oscillatory structure. Because of the regular features observed in the computer simulations of the soft sphere fluids it is reasonable to consider the OCP as a fluid governed by a very soft potential, $1/r$, and make use of what is known from liquid state theory.³

The present understanding of the physics of strongly coupled plasmas, in particular, the OCP, began with the pioneering Monte Carlo simulation work of Brush, Sahlin, and Teller (BST).⁴ They were able to adapt the Monte Carlo method of Metropolis, et al.⁵ for the calculation of canonical ensemble averages of fluid internal energies to handle the long range of the Coulomb potential by replicating the basic cell of N charges with images to infinity and summing the interactions of charges and image charges with the Ewald method.⁶ In most of their computer runs they used $N = 108$ charges and averaged over 10^5 configurations with values of Γ ranging from 0.1 (in the weak coupling or Debye region) up to $\Gamma = 125$ at which point their code indicated a transition from the Coulomb fluid to the Coulomb lattice. They obtained strong coupling results for U , $g(r)$, and excess heat capacity C_V . Because of numerical inaccuracies for large Γ their results for the thermal energy and heat capacity as well as the fluid-lattice transition Γ are not reliable. The next development in the application of the Monte Carlo method to strongly coupled plasmas occurred in 1971 when Hubbard and Slattery recognized that the OCP results of BST could be applied to the interior of Jupiter if the screening effects of electrons were included.⁷ They modified the BST Monte Carlo program to include the electron fluid screening effect for non-zero values of r_s by means of linear response theory and the Lindhard dielectric function. They also generalized their code to handle two nuclear components⁸ so that the thermodynamic functions of arbitrary mixtures of light elements, such as fully ionized hydrogen and helium, could be calculated. Because of computer time limitation at the University of Arizona they could make Monte Carlo runs with only a small number of charges $N \approx 40$, and only about 10^4 configurations. Thus their initial results were not very accurate. The Hubbard Monte Carlo code was next revised for use on the larger computers at the Livermore Laboratory, and a large number of runs were made to map out the thermodynamics of one component plasmas with electron screening and mixtures of two nuclear components with screening as functions of Γ and r_s .⁹

Independently of the Monte Carlo dense plasma work in the United States J. P. Hansen and his collaborators in Paris developed a new and very accurate OCP Monte Carlo code and in 1973 they published results for OCP thermodynamic functions obtained with $N = 128$ charges and averaged over 10^6 configurations for values from 1 to 160 for the fluid state¹⁰ and from 150 to 300 for the Coulomb lattice.¹¹ Their results for U/NkT for the strongly coupled OCP are apparently very accurate and reliable and can be considered as the standard results for testing the validity of analytical theories and integral equation results. Thus the Hansen fluid and solid OCP equation of state data can be viewed in the same manner as the Alder-Wainwright molecular

dynamics data for the hard sphere equation of state in the fluid and solid phases. In the respective limits, $m=1$ for the soft sphere system, and $m=\infty$ for the hard sphere system, one has an accurate set of numerical experimental data that rap out the thermodynamic properties. This data can be analyzed to look for empirical relations and fitting functions that 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:

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:

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

$$C_V = \quad dU_{th}/dT \quad .$$

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

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

$$\Gamma_0 = 8e^2/\bar{r} \quad .$$

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 the ions in positions that resemble a lattice structure. Since the system is a fluid, the average position of the particles changes slowly with time, unlike the real lattice that appears with still stronger

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 hcc 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 of 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

For the present discussion a strongly coupled plasma will be taken to mean a coupling parameter range, $\Gamma_t < \Gamma < \Gamma_f$, for which there seems to be a well defined separation of the potential energy into two parts: $U = U_0 + U_{th}$. This region might also be called the asymptotic Coulomb fluid region since 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 $\Gamma_f = 155$. The lower limit Γ_t is somewhat ill-defined but may be estimated as $\Gamma_t \sim 0.75$, as the lower limit of accuracy of the asymptotic formula for the energy of the strongly coupled fluid. For $\Gamma_t = 0.75$ the potential energy may be obtained accurately with a few terms of the Abe cluster expansion.¹³ The genuine weak coupling limit means $\Gamma \ll 1$ for which the Debye theory is valid.

II. THE ASYMPTOTIC OCP FLUID POTENTIAL ENERGY

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. 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:

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

For the Coulomb solid the Monte Carlo data indicated the expected harmonic vibrations with a small anharmonic correction, namely $\epsilon(\Gamma) = 3/2 + 3500/\Gamma^2$. 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:

$$U/NkT = -0.89461\Gamma + 0.8165\Gamma^{1/4} - 0.5012, \quad 0.75 < \Gamma < 155.$$

The static energy constant obtained by fitting the fluid data is about 0.15% higher than the Madelung constant for the bcc lattice, $\epsilon_{bcc} = 0.895929$. 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.

Other thermodynamic functions are easily obtained from this asymptotic form of the internal energy. Thus the heat capacity is found by integration to be:

$$C_V/Nk = -\Gamma^2 \frac{d\epsilon(\Gamma)/\Gamma}{d\Gamma} = \frac{3}{4} b\Gamma^{1/4} - c$$

and this result agrees very well with the somewhat less accurate Monte Carlo data for the heat capacity. Similarly the Helmholtz free energy is found by integration to be:

$$\begin{aligned} F/NkT &= \int_{\Gamma_1}^{\Gamma} d\Gamma' \frac{(U/NkT)}{\Gamma'} + \frac{F(\Gamma_1)}{NkT_1} \\ &= -a\Gamma + 4b\Gamma^{1/4} - c\ln\Gamma + d \end{aligned}$$

where the entropy constant is found to be $d = -2.809$ by comparison with the Abe 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:

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

This result for the compressibility is of considerable importance since it appears in the OCP structure factor¹⁵ as:

$$S(k) = \frac{1}{1 + \frac{3\Gamma}{k^2} + \left(\frac{\partial \beta P}{\partial n}\right)_{\beta}}, \quad K = kF$$

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 $\Gamma < 100$, the results are in good agreement with the above result for $\partial \beta P / \partial n$.

The various results quoted above completely specify the equilibrium thermodynamic functions for the OCP. The surprising aspect of these results is the $\Gamma^{1/4}$ term appearing in U_{th}/NkT which indicates that the thermal energy varies as $T^{3/4}$. At the present time there is no theoretical model to explain this result, and it should be taken as a challenge to theoreticians to explain this form which seems to be so basic to strongly coupled plasmas. In the absence of a good theoretical model it may be argued that the $s = 1/4$ power is simply a fortunate accident of fitting a function to the Monte Carlo data or that the result is some unsuspected artifact of the Monte Carlo simulation process. It is the opinion of this author that the result obtained from Hansen's data for U/NkT is a fundamental result that has been deduced from valid numerical "experimental" data.

For weak and intermediate coupling in the OCP, i.e., for $\Gamma \lesssim 100$, the OCP thermodynamic functions may be readily calculated from the Abe cluster expansion; for the Helmholtz free energy this is:

$$U/NkT = -\left\{\frac{1}{3}(\sqrt{3} \Gamma^{3/2}) + S_2(\Gamma) + S_3(\Gamma) + \dots\right\}$$

for which the first term is the Debye result. The internal energy is:

$$U/NkT = -\left\{\frac{1}{2}(\sqrt{3} \Gamma^{3/2}) + \Gamma \frac{d}{d\Gamma} (S_2(\Gamma) + S_3(\Gamma) + \dots)\right\}$$

To connect this "weak" coupling result for the internal energy with the Monte Carlo results for $\Gamma \gtrsim 0.75$, one must use the numerical results for the integrals, S_2, S_3 , etc., as given by Rogers and DeWitt¹⁶. For $\Gamma \gtrsim 0.3$ the S_2 integral has an analytic expansion of considerable complexity which begins with $\Gamma^3(\ln\Gamma+C)$. It is an interesting problem in mathematical analysis to understand how the functional dependence on Γ for U/NkT changes from an expansion for small Γ that begins with $\Gamma^{3/2}$ to the utterly different form beginning with Γ found from the Monte Carlo simulations of the strong coupling plasma. So far the cluster expansion has given no real clue as to how the asymptotic form might be generated from it for large Γ . The same kind of change of functional form in the internal energy for "weak" and "strong" coupling is also seen in the Monte Carlo data for other inverse power potentials as opposed to the virial expansion results. One notes that for the general inverse power potential:

$$BU(r) = B\epsilon\left(\frac{\sigma}{r}\right)^m = B\epsilon\left(\frac{\sigma}{r}\right)^m \left(\frac{r}{\sigma}\right)^{-m} = \frac{\Gamma}{x^m}$$

where the coupling parameter for the m th inverse power potential has the form $\Gamma = B\epsilon(\sigma/r)^m = n^{m/3}/kT$. Four known terms in the virial expansion for the $m = 12$ case¹ give an accurate result for the internal energy for low densities, and the Monte Carlo results are available for high density. The basic results are:

$$U/NkT = \frac{1}{4} \left\{ 3.63 \left(\frac{n\sigma^3}{\sqrt{2}} \left(\frac{\epsilon}{kT} \right)^{1/4} \right) + 7.58 \left(\frac{n\sigma^3}{\sqrt{2}} \left(\frac{\epsilon}{kT} \right)^{1/4} \right)^2 + \dots \right\}$$

for the virial expansion, and the high density or strong coupling result from the Monte Carlo is:

$$U/NkT = 0.00494\Gamma + 0.516\Gamma^{1/4} = 0.49$$

for $200 < \Gamma < 538$. The same form of the thermal energy, namely $\Gamma^{1/4}$, appears for the inverse power potentials as was found for the OCP. These results strongly suggest a universal form for the thermal energy for all the inverse power fluids, namely a $T^{3/4}$ behavior.

III. INTEGRAL EQUATION RESULTS

The Monte Carlo simulations give presumably nearly exact "experimental" results for the strongly correlated plasma thermodynamic functions. It is of considerable interest to see to what extent the integral equations used in present day liquid state theory can account for the Monte Carlo results. It is well known, for example, that the Percus-Yevick equation gives results for $g(r)$ and PV/NkT for the hard sphere system that are remarkably close to molecular dynamics and Monte Carlo results for the hard sphere fluid. The Percus-Yevick equation has been investigated for the Coulomb potential¹⁷ 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.¹⁷ Recently Ng has made an extremely accurate numerical solution of the HNC equation¹⁸, 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:

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

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:

$$h(r) = c(r) + n \int d^3r' c(r') h(|r - r'|)$$

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:

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

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 result¹²

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

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:

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

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 ($\sqrt{\Gamma}^{1/2}$) is very different from the presumed exact thermal energy ($\sqrt{\Gamma}^{1/4}$) 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 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:

$$c(r) = -\beta u(r), \quad r < \sigma$$

$$h(r) = -1, \quad r < \sigma$$

where σ is an equivalent hard sphere radius, and $c(r)$ and $h(r)$ are connected by the usual Ornstein-Zernike equation. Gillan¹⁹ 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:

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

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 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.

IV. MIXTURES OF TWO NUCLEAR SPECIES IN STRONG COUPLING

Consider a dense plasma with two nuclear species with charges z_1 and z_2 and with number densities n_1 and n_2 , and with the usual condition of electrical neutrality so that

$$n_e = z_1 n_1 + z_2 n_2 = \bar{z} n \quad \text{with } n = n_1 + n_2.$$

The ion sphere model applied to two fully ionized elements gives a definite prediction for the static energy of the two component system²⁰. The radius of a sphere around a charge z_1 of sufficient size to contain enough electrons to neutralize z_1 is:

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

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

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

where

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

and

$$\Gamma_0 = B e^2 / r$$

Thus the ion-sphere model gives a characteristic simple charge averaging prescription for mixtures of ions, namely $z^{5/3} z^{-1/3}$, that is very different from the 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 Vieillefosse have solved the coupled hyper-netted chain equations for two nuclear components²¹, and have found that for the HNC approximation that again the ion-sphere charge averaging is satisfied. (Hansen and Vieillefosse use the term "Two-Component Plasma" or TCP in their paper, and of course, mean two components of the same sign; 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:

$$U/NkT = -a z^{5/3} z^{-1/3} \Gamma_0 + b g(z_1 x_1, z_2 x_2) \Gamma_0^{1/4} - c$$

where the function $g(z_1 x_1; z_2 x_2)$ is a charge average for the thermal energy. Clearly, for $x_2 = 1$ 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:

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

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 can be fitted with the form:

$$g = z^{-1/2}$$

although it should be noted that this form has no theoretical justification at the present time. Hansen and Viellefosse 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:

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

where $\Gamma_0^{-1} = z^{-1/3} \Gamma_0$. Very recently they have two component Monte Carlo results which indicate the same additivity^{2c}. 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 $\Gamma_0^{-1/4}$ thermal term.

CONCLUSION

This discussion of the statistical mechanics of the strongly coupled plasma has focused on the results for the idealized system of point charges moving a continuous background since this is the basic system that must be understood before electron screening effects can be computed properly. The discussion of the properties of $g(r)$ and $S(k)$ will be given elsewhere. The main point to emphasize here is that the equilibrium thermodynamic properties of the classical strongly correlated plasma have been accurately obtained over an extremely wide density and temperature range and that these functions are given by very simple and easy to use analytic forms. In a certain sense an analytic solution has been found for a very difficult many body problem by deducing the solution from the Monte Carlo "experimental" data. Now that this work has been more or less completed, it is now possible to use the results profitably for other problems. Thus for the equation of state of the fully ionized hydrogen in the interior of Jupiter one needs electron screening

corrections. These have been computed directly by Monte Carlo simulation at Livermore⁹ and the results agree well with the fluid perturbation theory for screening developed by the Paris group^{22,23}. It should be noted that in the analytic theory of the electron screening, one uses the OCP structure factor, $S(k)$, not the hard sphere structure factor that is commonly used in calculations of most liquid state properties.

The understanding of the equilibrium thermodynamic properties of classical strongly coupled plasmas has developed very rapidly in the last few years, and is now nearing completion. More theoretical understanding of the equilibrium properties is needed, and it is hoped the interesting results obtained so far will suggest further work.

TABLE I
THERMAL EQUATION OF STATE FOR OCP

Γ	MONTE CARLO		HYPER-NETTER CHAIN		MEAN SPHERICAL MODEL	
	U/NkT	U_{th}/NkT	U/NkT	U_{th}/NkT	U/NkT	U_{th}/NkT
1	-0.580	.315	-0.570	.331	-0.607	.294
2	-1.318	.471			-1.377	.424
3	-2.111	.572	-0.2103	.598	-2.180	.522
4	-2.926	.542			-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	2.927
120	-105.284	2.069	-104.713	3.343	-104.775	3.285

REFERENCES

1. W. G. Hoover, S. G. Gray, and K. W. Johnson, J. Chem. Phys. 55, 1128 (1971).
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, Rowlinson and Rushbrooke, eds., North Holland Publishing, Amsterdam 1968.
4. S. Brush, H. L. Sahlén, and E. Teller, J. Chem. Phys. 45, 2102 (1966).
5. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. M. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).
6. E. 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. E. 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. A 8, 3110 (1973).
12. H. E. DeWitt, Phys. Rev. A 14, 1290 (1976).
13. R. Abe, Prog. Theor. Phys. 22, 213 (1959).
14. F. H. Stillinger and R. Lovett, J. Chem. Phys. 49, 1991 (1968).
15. P. Vieillefosse and J. P. Hansen, Phys. Rev. A 12, 1106 (1976).
16. F. J. Rogers and H. E. DeWitt, Phys. Rev. A 8, 1061 (1973).
17. J. F. Springer, M. A. Pokrant, and F. A. Stevenc, J. Chem. Phys. 58, 4863 (1973).

18. Kin-Chue Ng, J. Chem. Phys. 61, 2680 (1974).
19. M. J. Gillan, J. Phys. C: Solid State Phys. 7, L1 (1974).
20. E. E. Salpeter, Australian J. Phys. 7, 352 (1954).
21. J. P. Hansen and Patrick Vieillefosse, Phys. Rev. Lett. 37, 391 (1976).
22. J. P. Hansen, G. M. Torrie and P. Vieillefosse (to be published).
23. S. Galem and J. P. Hansen, Phys. Rev. A 14, E16 (1976).

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.