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Asymptotic Form of the Mean Spherical Approximation for the Internal Energy of the Classical One-Component Plasma

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The mean spherical approximation for the internal energy U of the classical one-component plasma is solved exactly in the limit $\Gamma \gg 1$, where Γ is the usual Coulomb coupling parameter. The result $\beta U/N = -\frac{9}{10}\Gamma + {}^1/_6\sqrt{3}\Gamma^{1/2} + \Gamma^{1/6}/15\sqrt{3}\, 2^{1/3} + O\,(\Gamma^{-1/6})$ is consistent with DeWitt's empirical analysis of the mean spherical approximation.

KEY WORDS: Mean spherical approximation; classical one-component plasma; strong coupling.

1. INTRODUCTION

DeWitt[(1)] has found that the equilibrium thermodynamic properties of the classical one-component plasma[2] (OCP) satisfy simple functional forms in the "dense" fluid state. The main result of his least squares analysis of the Monte Carlo (MC) calculations of Hansen[(2)] is that the fluid potential energy U can be fitted accurately by the empirical form[(1)]

$$\beta U/N = -0.89461\Gamma + 0.8165\Gamma^{1/4} - 0.5012, \qquad \Gamma > 1 \tag{1}$$

where the dimensionless parameter Γ is defined by[3]

$$\Gamma = \beta e^2/a \tag{2}$$

with $a = (3/4\pi n)^{1/3}$. The form (1) fails in the weak coupling limit $\Gamma \ll 1$, for which the leading contribution to $\beta U/N$ is $O(\Gamma^{3/2})$, and at the fluid–lattice

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[3] The OCP is an electrically neutral system of charged classical particles of one species embedded in a uniform background of opposite charge.

[4] We adopt the usual notation: N is number of particles, n is number density, T is absolute temperature, k_B is Boltzmann's constant, $\beta = (k_B T)^{-1}$, and e is electron charge.

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transition, which is estimated[3,4] to be in the range $\Gamma \sim 144$–158. DeWitt's interpretation of (1) is that it represents the asymptotic form of the internal energy for the strongly coupled or dense OCP in the fluid state. The main characteristics of (1) are the separation of U/N into a dominant static energy portion, $-\alpha e^2/2a$, which is identical in form to the lattice energy at $T = 0$, and a thermal energy portion which varies as $T^{3/4}$. The constant α is 0.15% higher than the bcc lattice sum. The form (1) implies that a strongly coupled OCP may be described as a disordered lattice and that the essential difference between the fluid and solid states is that the leading T dependence of U/N is $T^{3/4}$ rather than T.

Theoretical calculations of the equilibrium static properties of the OCP have been mainly limited to numerical solutions of integral equations for the pair distribution function $g(r)$. Ng[5] has solved the hypernetted chain (HNC) equation for $20 \leqslant \Gamma \leqslant 7000$ and has obtained very accurate numerical results for $\beta U/N$ which are in good agreement with the MC results. DeWitt's analysis of Ng's results yields the form

$$\beta U_{\mathrm{HNC}}/N = -0.9005\Gamma + 0.2688\Gamma^{1/2} + 0.0720 \ln \Gamma + 0.0538 \tag{3}$$

The other integral equation of interest is the mean spherical approximation (MSA) to be discussed in this paper. The numerical solutions of Gillan[6] for $1 \leqslant \Gamma \leqslant 130$ have been analyzed by DeWitt[4] with the empirical result

$$\beta U_{\mathrm{MSA}}/N = -0.9005\Gamma + 0.2997\Gamma^{1/2} + 0.0007 \tag{4}$$

The main characteristics of (3) and (4) are the separation of U into a fluid static energy and a thermal energy portion which is dominated by a $\Gamma^{1/2}$ rather than a $\Gamma^{1/4}$ dependence as in (1).

Although the form (1) is simple and appealing and confirmed in part by the numerical analysis of the HNC and MSA equations, there exists no firm theoretical basis for (1). We gain some insight by showing in Section 2.1 that an analytic expression for U in the MSA can be found in the limit $\Gamma \gg 1$. Our result is

$$\beta U_{\mathrm{MSA}}/N = -\tfrac{9}{10}\Gamma + \tfrac{1}{6}\sqrt{3}\,\Gamma^{1/2} + \frac{\Gamma^{1/6}}{15\sqrt{3}\,2^{1/3}} + O(\Gamma^{-1/6}) \tag{5}$$

A comparison of (4) and (5) reveals that the form of the static energy and the leading behavior of the thermal energy obtained by DeWitt's numerical analysis over a finite range of Γ is similar to the asymptotic solution for $\Gamma \gg 1$. The MSA result for the static energy per particle, i.e., $U_{\mathrm{MSA}}/N = -9e^2/10a$, is identical to the prediction of the ion-sphere model.[7] Although the coefficients of the $\Gamma^{1/2}$ term in (4) and (5) differ slightly ($\sqrt{3}/6 = 0.2887$), it is remarkable that DeWitt's numerical analysis yield the exact exponent 1/2 of the leading term in the MSA result for the thermal energy.

Another approach to the thermodynamic properties of the OCP is that of Stroud and Ashcroft[8] (SA), who use a variational method based on a hard-sphere reference system. The reference system is assumed to be well approximated by Percus–Yevick theory and the hard-sphere diameter is obtained as a function of Γ by minimizing the free energy. It is shown in the Appendix that U can be determined analytically in the limit $\Gamma \gg 1$ with the result that

$$\beta U_{\mathrm{SA}}/N = -\tfrac{9}{10}\Gamma + \tfrac{2}{3}\left(\frac{\Gamma}{6}\right)^{2/5} + \frac{8}{15}\left(\frac{\Gamma}{6}\right)^{1/5} + O(\Gamma^{-1/5}) \tag{6}$$

Inspection of (6) shows that the method of Stroud and Ashcroft yields the same static energy term as the ion-sphere model, and that the predicted behavior of the dominant term in the thermal energy bears more resemblance to the MC result than the HNC and MSA predictions.

In Section 2.2 we extend DeWitt's least squares analysis of the MSA to higher values of Γ in order to determine the sensitivity of DeWitt's analysis. We discuss in Section 3 some properties of the pair correlation function and show that the usual methods for determining $g(r)$ from its Laplace transform fail. A brief discussion is given in Section 4.

2. THERMODYNAMIC PROPERTIES IN THE MEAN SPHERICAL APPROXIMATION

2.1. Asymptotic Solution for the Internal Energy

The mean spherical approximation (MSA) is based on the assumptions that

$$g(r) = 0, \qquad r < \sigma \tag{7}$$

$$c(r) = -\beta V(r), \qquad r > \sigma \tag{8}$$

where the direct correlation function $c(r)$ is related to $g(r) - 1$ by the Ornstein–Zernike equation. Palmer and Weeks[9] have obtained an exact solution of the MSA for the case of charged hard spheres of radius σ in a uniform neutralizing background. In this case the only approximation is (8). For a system such as the OCP it might be expected that an interpretation of σ as a "distance of closest approach" might be useful, since for $\Gamma \gg 1$ the interparticle potential $V(r)$ prevents particles from approaching each other too closely. Gillan[6] has shown that the static properties of the OCP can be determined from the solution of Palmer and Weeks for hard spheres from the requirement that

$$g(r = \sigma^+) = 0 \tag{9}$$

The above condition is reasonable for a system with a continuous interparticle potential. Gillan solved (9) numerically to determine σ for $1 \leqslant \Gamma \leqslant 130$. The exact result of Palmer and Weeks for the internal interaction energy U in terms of Γ and σ was then used to obtain numerical results for U.

We show in the following that (9) can be solved exactly in the limit $\Gamma \gg 1$ to obtain σ and hence U as a function of Γ within the mean spherical approximation. The exact solution of (7) and (8) with $V(r) = e^2/r$ and arbitrary σ is conveniently given in terms of the dimensionless parameters $\lambda = \sigma/a$, $\eta = \frac{1}{6}\pi n \sigma^3 = (\lambda/2)^3$, and $\kappa = (3\lambda^2\Gamma)^{1/2}$. Some of the relevant results are[9]

$$\beta U/N = -(1/3\lambda^3)\{(1 + \eta - \tfrac{1}{5}\eta^2)\kappa^2 + \kappa\Lambda\} \tag{10}$$

$$\Lambda = (1 + 2\eta)(1 - J) \tag{11}$$

$$J = [1 + 2(1 - \eta)^3\kappa/(1 + 2\eta)^2]^{1/2} \tag{12}$$

and

$$g(r = \sigma^+) = (1 - \eta)^{-2}[(1 + \eta/2) - \Lambda^2/24\eta] \tag{13}$$

The substitution of (13) into (9) leads to the following equation for λ as a function of Γ:

$$\Lambda^2 = 24\eta(1 + \eta/2) \tag{14}$$

The results of a numerical solution of (14) are shown in Fig. 1; it is seen that σ/a is a monotonic, slowly increasing function of Γ. In order to solve (14) for $\Gamma \gg 1$, we note from (11) and (12) that $\eta \leqslant 1$ for a solution to exist, and Λ increases without bound unless $(1 - \eta)^3\kappa \sim (1 - \eta)^3\Gamma^{1/2}$ approaches a constant. Since the right-hand side of (14) is finite, we conclude that for $\Gamma \gg 1$, $\epsilon \equiv 1 - \eta \sim \Gamma^{-1/6}$ and the limiting value of $\sigma = 2a$. We write

$$\epsilon = \epsilon_1\Gamma^{-1/6} + \epsilon_2\Gamma^{-2/6} + \epsilon_3\Gamma^{-3/6} + \epsilon_4\Gamma^{-4/6} + \cdots \tag{15}$$

expand both sides of (14) in powers of the small parameter ϵ and then in powers of $\Gamma^{-1/6}$, and collect terms of the same order in $\Gamma^{-1/6}$. The results are

$$\epsilon_1 = (18/\sqrt{3})^{1/3}, \quad \epsilon_2 = -\tfrac{1}{3}(18/\sqrt{3})^{2/3}, \quad \epsilon_3 = \frac{5}{18}\sqrt{3}, \; \epsilon_4 = -2^{4/3}/27 \tag{16}$$

The asymptotic dependence of U on Γ is found by combining (10), (14), and (15) and expanding in ϵ:

$$\frac{\beta U}{N} = -\frac{\Gamma}{10}\left(9 + \frac{5}{9}\epsilon^3 + \frac{5}{9}\epsilon^4 + \frac{14}{27}\epsilon^5 + \frac{350}{729}\epsilon^6\right) + \frac{\sqrt{3}}{2}\Gamma^{1/2}\left(1 + \frac{\epsilon^2}{18} + \frac{4}{81}\epsilon^3\right) + \cdots \tag{17}$$

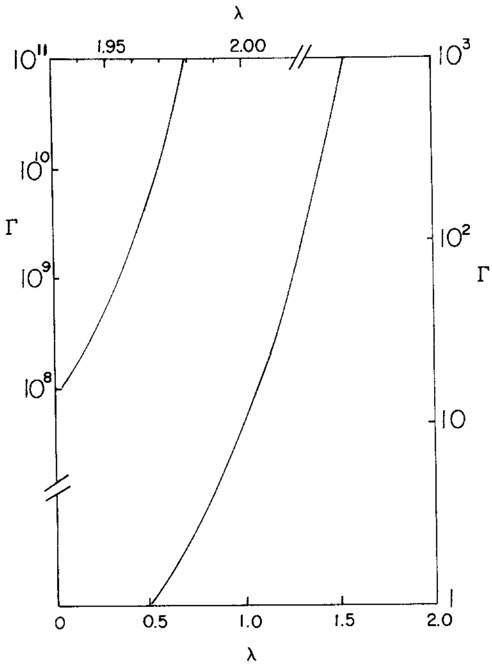

Fig. 1. The Γ dependence of the parameter $\lambda = \sigma/a$ as determined by Eq. (14).

Inspection of (17) shows that it is necessary to retain terms of $O(\Gamma^{-2/3})$ in ϵ in order to obtain $\beta U/N$ to $O(1)$. The substitution of (15) and (16) in (17) yields the asymptotic dependence on Γ for U as given in (5). Note that the form (5) for U is an asymptotic expansion in $\Gamma^{-1/6}$, and that the first correction to the dominant static energy term is $\Gamma^{1/2}$ rather than $\Gamma^{5/6}$.

2.2. Least Squares Analysis

Since the asymptotic form of $\beta U/N$ derived in Section 2.1 differs somewhat in form from that found by DeWitt's empirical analysis in the range $1 \leqslant \Gamma \leqslant 130$, it is interesting to attempt to determine the sensitivity of a least squares analysis to the range of Γ. We assume the functional form $\beta U/N = -\frac{1}{2}\alpha\Gamma + b\Gamma^{s} + c$ with $s = 1/2$. The results of our analysis for the coefficients α, b, and c are shown in Table I. It is seen that the coefficients α and b are insensitive to the range of Γ, but that c changes sign. This variation implies that the Γ dependence of the thermal energy portion of U might be more complicated than that assumed by DeWitt. However, it was not possible to determine the nature of the corrections by a least squares analysis.

Table I. Sensitivity of a Least Squares Analysis of the Mean Spherical Approximation to the Energy $\beta U/N = -\frac{1}{2}\alpha\Gamma + b\Gamma^{\frac{1}{2}} + c$ to the Range of Γ

$\alpha/2$	b	c	$\Gamma_{\min}$	$\Gamma_{\max}$	$\Delta\Gamma$	Variance $\times 10^6$
0.9003	0.2977	0.00069	1	130	1	3.40
0.9000	0.2906	0.0433	130	500	10	9.09
0.8999	0.2886	0.0740	5×10^2	10^3	10	1.01
0.9000	0.2920	−0.0168	10^3	4×10^3	50	8.08
0.8996	0.2420	1.7916	4×10^3	10^4	50	8.19

3. CORRELATION FUNCTIONS

The direct correlation function $c(r)$ is given explicitly in the MSA and takes the form[9]

$$\begin{aligned} c(x) &= A + \frac{\Gamma}{2}x^2 + \frac{1}{16}\left(A + \frac{\Gamma\beta U}{\lambda N}\right)x^3 + \frac{\Gamma}{160}x^5, \qquad x < \lambda \\ &= -\Gamma/x \qquad x > \lambda \end{aligned} \tag{18}$$

The value of $c(x = 0) = A$ is given by

$$c(0) = -\frac{(5 + \eta^2)}{60\eta} - \frac{1}{(1 - \eta)^2} - \frac{(1 + \eta)[6\eta(1 + \eta/2)]^{1/2}}{6(1 - \eta)} \tag{19}$$

In the above $x = r/a$ and $\beta U/N$ is given by (10). Qualitative agreement of the MSA values of $c(x)$ with the Monte Carlo values is shown in Table II for $\Gamma = 20$ and $\Gamma = 100$. A direct check on the thermodynamic consistency of the MSA can be obtained by using[10]

$$c(0) = 2\beta U/N - \beta(\partial P/\partial n)_T \tag{20}$$

which follows from the fact that $\int d^3r\,[c(r) + \beta V(r)]g(r) = 0$ [see (7) and (8)]. In (20) P is the pressure and $\beta(\partial P/\partial n)_T$ is the inverse isothermal compressibility. We see from (19) that the leading behavior of $c(0) = -1.2\Gamma$. However, if we determine $c(0)$ from (20) and use (5) and the exact relation $\beta P/n = 1 + \beta U/3N$, we find the leading behavior $c(0) = -1.4\Gamma$. This thermodynamic inconsistency of the MSA is a general feature of approximate integral equations for $g(r)$.

The static pair correlation function $g(x)$ does not appear explicitly in the solution of Palmer and Weeks, but it is given in terms of the Laplace transform $G(s)$. We write

$$g(x) = \frac{\lambda^2}{2\pi i x}\int_{\delta - i\infty}^{\delta + i\infty} ds\, G(s)e^{\lambda s x} \tag{21}$$

Table 2 Comparison of the Mean Spherical Approximation Values for the Direct Correlation Function $c(r)$ with the Monte Carlo Values

	$\Gamma = 20, \lambda = 1.10$		$\Gamma = 100, \lambda = 1.32$	
x	$c(x)_{MC}$	$c(x)_{MSA}$	$c(x)_{MC}$	$c(x)_{MSA}$
0.00	−25.9012	−25.5812	−132.485	−122.747
0.008	−25.8996	−25.5806	−132.456	−122.743
0.25	−25.3428	−25.0137	−128.837	−119.910
0.50	−23.8092	−23.5377	−119.511	−112.518
0.75	−21.6401	−21.4800	−107.130	−102.084
0.999	−19.1089	−19.1481	−93.5919	−89.8140
1.249	−16.1448	−16.0128	−80.2928	−80.0640
1.499	−13.2787	−13.3422	−67.2661	−66.7111
1.749	−11.2396	−11.4351	−56.4657	−57.1755
1.999	−9.8794	−10.0050	−49.5032	−50.0250
2.249	−8.8207	−8.8928	−44.1782	−44.4642
2.499	−7.9686	−8.0032	−39.8882	−40.0160
2.748	−7.2627	−7.2780	−36.3465	−36.3901
2.998	−6.6699	−6.6711	−33.3612	−33.3555

where

$$G(s) = \frac{\lambda s L(s)}{12\eta[L(s) + S(s)e^{\lambda s}]} \tag{22}$$

$$L(s) = 12\eta(P\lambda s + \kappa) \tag{23}$$

and

$$S(s) = (\lambda s)^4 + R(\lambda s)^3 + \tfrac{1}{2}R^2(\lambda s)^2 + 12\eta(\kappa - P)\lambda s - 12\eta\kappa \tag{24}$$

In the limit $\Gamma \gg 1$, $R \sim \Gamma^{1/6}$, $\kappa \sim \Gamma^{1/2}$, and $P = \kappa/2$. The path of integration in (21) is to be taken to the right of all poles of the integrand. The poles of $G(s)$ can be determined numerically for arbitrary Γ and are found to be in the left-half plane[4] and to shift toward the imaginary axis with increasing Γ. This behavior is consistent with the fact that $G(s)$ is the Laplace transform of a well-behaved function and that the system is disordered. In the limit $\Gamma \gg 1$ the poles lie on the imaginary s axis and are given by the simultaneous solutions to the transcendental equations

$$1 - s \sin 2s - \cos 2s = 0 \tag{25a}$$

$$s + s \cos 2s - \sin 2s = 0 \tag{25b}$$

[4] In addition to the double pole at $s = 0$.

The above equations can be combined to give $2s - s^2 \sin 2s = \sin 2s$ if spurious solutions are omitted. The first few poles are $\pm is = 4.4934, 7.7252, 10.9041, 14.0662, 17.2208, 23.5194$. For large, integer m the poles are given by $\pm is_m = (2m + 1)\pi - (4/\pi)(2m + 1)^{-1}$. The determination of the poles of $G(s)$ allows us to explicitly close the contour in (21) in the left-hand plane and obtain an explicit representation of $g(x)$. However, the residues are all order unity, so that this representation does not appear to be useful.

The usual method[11] for determining $g(x)$ is to write (21) as

$$g(x) = \frac{\lambda^3}{24\pi i\eta x} \sum_{n=1}^{\infty} \int_{\delta - i\infty}^{\delta + i\infty} ds\, s \left[\frac{L(s)}{S(s)}\right]^n e^{s(x - \lambda n)} \tag{26}$$

If $S(s)$ has no zeros in the right-hand plane, then the contour can be closed in the right-hand plane and explicit expressions can be obtained for $g(x)$ in the ranges $\lambda n \leqslant x \leqslant \lambda(n + 1)$. However, for the MSA in the limit $\Gamma \gg 1$, the roots of $S(s)$ can be simply determined to be $s_1 = 1.0$, $s_2 = -6.079\Gamma^{1/6}$, $s_{3,4} = (-3.728 \pm i1.083)\Gamma^{1/6}$. Since s_1 lies on the right-hand plane, this procedure is not applicable.

4. DISCUSSION

We have seen that the asymptotic solution of the mean spherical approximation for the internal energy is consistent with that found by DeWitt's least square analysis of the numerical solution. This agreement gives some additional support to the form (1) adopted by DeWitt from his analysis of the Monte Carlo data. DeWitt[4] has also made a preliminary analysis of the potential energy for repulsive potentials of the form $V(r) = \epsilon(\sigma/r)^m$ for $m = 4, 6, 9$, and 12. The Monte Carlo data[12] are fitted to the form $\beta U/N = \frac{1}{2}\alpha\Gamma + b\Gamma^s + c$ for $\Gamma \gg 1$, with $\Gamma = \beta\epsilon(\sigma/a)^m$. There is an insufficient number of data points for $m = 4, 6$, and 9 for us to be confident of the results. The result for $m = 12$ suggests that $\beta U/N = 0.00493\Gamma + 0.516\Gamma^{1/4} - 0.49$, $200 \leqslant \Gamma \leqslant 538$; the coefficient $\alpha/2$ is close to the fcc Madelung constant 0.00483 of the $1/r^{12}$ potential. It would be of much interest to extend the Monte Carlo calculations for $1/r^m$ potentials to additional values of m and Γ. However, DeWitt's results suggest that there is a universal form of the leading behavior of the thermal energy, i.e., $\Gamma^{1/4}$ for all strongly coupled inverse-power fluids.

The origin of the conjectured universal behavior presents a challenging problem to theory. From this point of view the long-range nature of the $1/r$ potential is an irrelevant complication to a theoretical analysis. The analysis of the mean spherical approximation presented here shows that some simplifications occur in the strong coupling limit, and suggests that it might be possible to obtain explicit asymptotic solutions of the mean spherical approximation or hypernetted chain equations for the internal energy of inverse-power fluids. However, it is doubtful that much insight into the origin of the $\Gamma^{1/4}$ dependence of the thermal energy can be gained from the investigation of integral equations for the pair distribution function $g(r)$. As an example of the difficulty of such an investigation, the bridge graphs which are neglected in the hypernetted chain equation contribute to $g(r)$ only for $r/a \leqslant 2.5$. Yet the contribution of the bridge graphs to U must be of the form $\beta U/N = -0.2688263\Gamma^{1/2} + 0.8165\Gamma^{1/4}$, so that the $\Gamma^{1/2}$ dependence in (3) is exactly canceled. A more fruitful approach might be one that attempts to isolate the physical mechanisms important for strong coupling and in particular mechanisms important near the fluid–solid transition.

APPENDIX

We consider briefly two other approaches to the OCP that lead to explicit results for U in the limit $\Gamma \gg 1$. The variational approach of Stroud and Ashcroft based on the hard-sphere reference fluid is based on the inequality

$$\beta f \leqslant \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} - 3\eta^{2/3}\frac{1 - \eta/5 + \eta^2/10}{1 + 2\eta}\Gamma \tag{A1}$$

where f is the deviation of the free energy per particle from its ideal gas value. The parameter $\eta = \frac{1}{6}\pi n \sigma^3$, and σ is the hard-sphere diameter. A lowest upper bound for f is obtained by minimizing the right-hand side of (A1) with respect to η. The result for η is expressed as

$$\Gamma = 2\eta^{1/3}\frac{2 - \eta}{2 + \eta}\frac{(1 + 2\eta)^2}{(1 - \eta)^5} \tag{A2}$$

Note that at $\Gamma = 155$, $\eta = 0.52$ according to (A2), in comparison to $\eta = 0.31$ according to its MSA value. Equation (A2) can be solved for $\epsilon = 1 - \eta$ using the same method as in Section 2.1, with the result that

$$\epsilon = 6^{1/5}\Gamma^{-1/5} - \frac{6^{2/5}}{15}\Gamma^{-2/5} - (46/225)\, 6^{3/5}\,\Gamma^{-3/5} + \cdots \tag{A3}$$

To obtain U we use the relation $U = f + Ts$ and recognize that the first term in (A1) is the negative of $-Ts$. The asymptotic result (6) for U then follows.

The basis of the approach of Ref. 13 is a linear-closure procedure for the BBGKY hierarchy. The procedure leads to a second-order differential equation for $g(r)$ which can be solved analytically in the limit $\Gamma \gg 1$. The result for U is

$$\beta U/N = -0.6771\Gamma + 3/14 + \cdots \tag{A4}$$

It is remarkable that this simple approximation gives the leading term proportional to Γ, but the numerical coefficient and the thermal energy portion are in disagreement with (1).

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