Analytic fit to the one-component-plasma structure factor

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We use a nonlinear least-squares-fitting program to find an analytic fit to the one-component plasma fluid structure factor $S(q,\Gamma)$ over the ranges $0 \le q \le 21.75$ and $1 \le \Gamma \le 225$. The $S(q,\Gamma)$ function is generated as a table from the solution of the modified hypernetted chain integral equation. The table is fitted with polynomials in q and Γ, using a total of 175 coefficients. The overall fit is good, suggesting that the fitting method might be applied successfully to other distribution functions.

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I. INTRODUCTION

In the theory of fluids, extensive use is made of the two-particle distribution functions $g(r)$ (the radial distribution function) and $S(k)$ (the structure factor) [1]. These functions represent the structural properties of the fluid measured by x-ray diffraction, and from them thermodynamic numbers such as internal energy and pressure may be obtained. Since the late 1960's, the distribution functions of simple model fluids with one coupling parameter have also been used as reference functions for variational models of more complex fluids [1]. This variational theory has been developed into a very accurate method for determining thermodynamic functions and phase transitions in simple materials [2,3].

Among the reference fluids commonly used are the hard-sphere [4], inverse-twelfth [2], and one-component plasma (OCP) [5] models. Each of these models requires an accurate representation of the free energy and of either $g(r)$ or $S(k)$. For fluids with stiff intermolecular repulsions, such as the liquid phases of Ar, N_2, Al, and Fe, the hard-sphere and inverse-twelfth fluids are appropriate. For metals with softer repulsions such as Na and K, and for dense plasmas, the OCP is the appropriate reference fluid.

A recurrent problem with these calculations has been that the distribution function requires a complicated analytic or tabular representation. In the case of hard spheres, the analytic Percus-Yevick approximation to $g(r)$ is commonly used, even though this is a rather poor approximation. A correction by Verlet and Weis has improved the accuracy of this function [6]. For the inverse-twelfth and OCP fluids, tables generated by approximate integral equations, together with interpolation look-up schemes, have been used [2,7]. Although these tables are accurate, they are cumbersome to use in the variational theory.

In this paper, we discuss the reduction of a larger, recently calculated table for the OCP $S(k)$ to a short computer subroutine based on a careful analytic fit to the table. Our hope is that this will be a much more efficient method for calculating fluid thermodynamics than the table, and that this fitting procedure may be extended eventually to more complex fluid distribution functions.

II. ONE-COMPONENT-PLASMA FLUID

The OCP model is the simplest representation of a many-body Coulomb system [8]. In the OCP fluid, positively charged particles with charge Ze move in a uniform neutralizing background. The coupling parameter is $\Gamma = Z^2e^2/akT$, where $a = (3V/4\pi N)^{1/3}$ is the ion-sphere radius. Computer simulations [9] have shown that the OCP has a fluid-solid transition at $\Gamma \simeq 178$. A metastable fluid state with much larger Γ may be simulated, however.

Extensive Monte Carlo simulations have yielded accurate values of the excess Helmholtz free energy $F(\Gamma)/NkT$ and of the two-body distribution functions $g(x,\Gamma)$ and $S(q,\Gamma)$, where $x = r/a$ and $q = ka$, over the fluid range [10,11]. Simple analytic fits [12] to the excess internal energy and configurational free energy from the Monte Carlo (MC) data are

$$\frac{U}{NkT} = A\Gamma + B\Gamma^s + C \tag{1}$$

and

$$\frac{F}{NkT} = A\Gamma + \frac{B}{s}\Gamma^s + (3+C)\ln\Gamma - \left[A + \frac{B}{s} + 1.1516\right], \tag{2}$$

where $A = -0.8992$, $B = 0.596$, $s = 0.3253$, and $C = -0.268$. Any accurate theory of the OCP must match these results closely.

Although the Monte Carlo calculations yield accurate $g(x,\Gamma)$ and $S(q,\Gamma)$ functions, these functions are not smooth enough to be used directly in look-up tables [5]. We have found that a better procedure is to use thermodynamically consistent integral equations to compute these functions. Rogers and DeWitt have recently solved the Rosenfeld-Ashcroft modified hypernetted-chain (MHNC) equation [13] for the OCP, and this tabular solution is used in our fitting. The details of this MHNC solution will be published elsewhere.

The MHNC table contains $g(x,\Gamma)$ and $S(q,\Gamma)$ for $0 \le q \le 50$ and $0.1 \le \Gamma \le 225$. For each of 49 Γ values there are 1000 q values, so that the interval in q is 0.05. The accuracy of the MHNC solution may be determined

TABLE I. Excess internal energy from Monte Carlo (fitted), MHNC, and analytic fit. The exponent of 10 is shown in square brackets.

Γ	U/NkT		
	MC	MHNC	Fit
1	−5.7120[−1]	−5.7268[−1]	−5.7295[−1]
2	−1.3197[0]	−1.3240[0]	−1.3252[0]
5	−3.7579[0]	−3.7653[0]	−3.8382[0]
10	−7.9995[0]	−8.0096[0]	−8.2355[0]
20	−1.6673[1]	−1.6686[1]	−1.6960[1]
30	−2.5442[1]	−2.5457[1]	−2.5435[1]
40	−3.4257[1]	−3.4273[1]	−3.3783[1]
50	−4.3100[1]	−4.3117[1]	−4.2147[1]
60	−5.1962[1]	−5.1980[1]	−5.0624[1]
70	−6.0838[1]	−6.0857[1]	−5.9257[1]
80	−6.9725[1]	−6.9745[1]	−6.8051[1]
90	−7.8620[1]	−7.8641[1]	−7.6983[1]
100	−8.7522[1]	−8.7545[1]	−8.6024[1]
110	−9.6430[1]	−9.6455[1]	−9.5144[1]
120	−1.0534[2]	−1.0537[2]	−1.0432[2]
130	−1.1426[2]	−1.1429[2]	−1.1353[2]
140	−1.2318[2]	−1.2321[2]	−1.2277[2]
150	−1.3211[2]	−1.3214[2]	−1.3200[2]
160	−1.4103[2]	−1.4107[2]	−1.4121[2]
170	−1.4996[2]	−1.5000[2]	−1.5037[2]
180	−1.5890[2]	−1.5894[2]	−1.5944[2]
190	−1.6783[2]	−1.6787[2]	−1.6840[2]
200	−1.7677[2]	−1.7681[2]	−1.7722[2]
210	−1.8571[2]	−1.8576[2]	−1.8597[2]
220	−1.9465[2]	−1.9470[2]	−1.9477[2]

by comparison with the MC energies. We compute the excess internal energy from the tabular $S(q,\Gamma)$ by the equation

$$\frac{U}{NkT}=\frac{\Gamma}{\pi}\int_0^\infty [S(q,\Gamma)-1]dq \ . \tag{3}$$

The calculated energies are shown in Table I. The agreement between MHNC and MC is excellent.

III. FITTING PROGRAM

There have been a number of attempts to generate $S(q,\Gamma)$ from simple equations or analytic forms. Rather rough fits have been made by Baus and Hansen [14] and by Bretonnet and Derouiche [15] by approximating the direct correlation function $c(x)$. Accurate expressions for the OCP $S(q,\Gamma)$ have been obtained by solving the self-consistent mean-spherical approximation to the Ornstein-Zernicke equation for charged hard spheres [16,17]. However, this approximation requires the solution of complicated transcendental equations. A very accurate analytic expression has been obtained by Singh [18] by a modification of the solution to the mean-spherical approximation, but at the cost of an unphysical discontinuity in the direct correlation function. These expressions also have the disadvantage that the hard-sphere part of the potential gives an unrealistic $g(x,\Gamma)$ for small x, and that solutions are not obtainable for $\Gamma<20$.

Our approach here is to obtain an accurate table of $S(q,\Gamma)$ from the solution of the MHNC integral equation, and then to fit this table with simple basis functions. This approach does not depend on the specifics of the fluid interaction potential or the availability of analytic solutions of integral equations; it is applicable over any range of Γ; it is equally accurate for $S(q)$ and $g(x)$; and it is suitable for direct evaluation without intermediate calculations. All that is needed is the accurate table. For the task of fitting, we use the SNLS1E Levenberg-Marquardt nonlinear least-squares data fitting subroutine, which is contained in the SLATEC numerical mathematics library on the Livermore CRAY computers.

After much trial and error, we decided to fit the modified direct correlation function $c_s(q,\Gamma)=c(q,\Gamma)+\phi(q,\Gamma)$ instead of $S(q,\Gamma)$. Here $\phi(q,\Gamma)=3\Gamma/q^2$, the Fourier transform of the Coulomb potential. $c_s(q,\Gamma)$ is a monotonic function of q which is more readily fitted with polynomial basis functions than $S(q,\Gamma)$. The two functions are related by the equation

$$S(q,\Gamma)=\frac{1}{1+3\Gamma/q^2-c_s(q,\Gamma)} \ . \tag{4}$$

The structure of the denominator causes the slight oscillations in $c_s(q,\Gamma)$ to be greatly amplified into the oscillations seen in $S(q,\Gamma)$. Accurate representation of $S(q,\Gamma)$ thus requires very accurate $c_s(q,\Gamma)$ fits, but this is more than compensated for by the simple form of the $c_s(q,\Gamma)$ function. For convenience, the function that we actually fit is $-c_s(q,\Gamma)$.

In fitting $-c_s(q)$ for each Γ we have found that by segmenting $-c_s(q)$ into pieces corresponding to the peaks in $S(q)$, we can use polynomials to achieve accurate fits to $-c_s(q)$ and thus to $S(q)$. Our fitting function for each

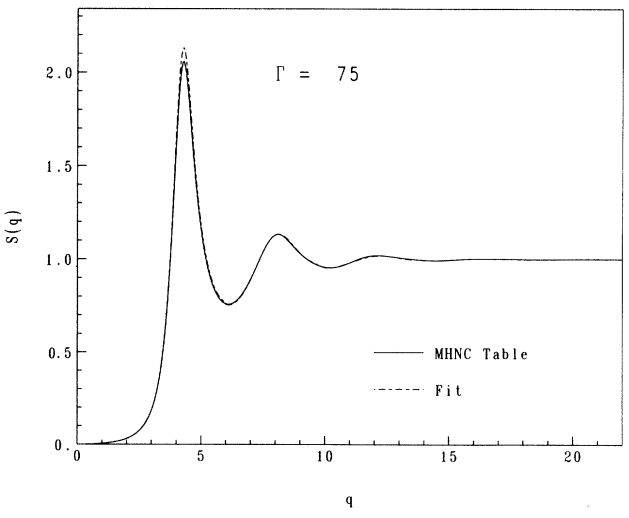

FIG. 1. Comparison of MHNC (solid curve) and fit (dashed curve) $S(q)$'s for $\Gamma=75$.

TABLE II. Coefficients for the analytic fit. For each a_j, the coefficients b_{jm} are given in the order $b_{j00}, b_{j0}, b_{j1}, b_{j2}, b_{j3}, b_{j4}, b_{j5}$. Exponents of 10 are shown in square brackets.

	Segment 1
	$0 \le q \le 3$
a_{00}	0.0,0.0,0.0
a_0	−7.371 59[−3], −3.093 941[−2], 5.775 133[−6]
a_1	−1.785 965[−3], −9.156 094[−3], −5.215 690[−6]
a_2	1.551 919[−3], 1.000 275[−2], 3.407 914[−6]
	Segment 2
	$3 < q \le 5.9$
a_{00}	−2.211 480[−2], −9.281 645[−2], 2.105 917[−5], 1.527 865[−7], −2.511 623[−9], 7.838 556[−12]
a_0	2.970 690[−3], 2.794 343[−2], −8.758 671[−7], −2.009 939[−7], 1.878 432[−9], −4.990 626[−12]
a_1	1.428 655[−3], 4.165 185[−3], −1.643 889[−5], 1.826 357[−7], −1.031 887[−9], 2.195 364[−12]
a_2	−5.537 246[−4], −5.848 738[−3], −8.728 617[−6], 1.076 314[−7], −6.819 082[−10], 1.557 185[−12]
a_3	5.617 672[−5], −2.848 769[−4], −6.427 415[−7], 6.133 415[−8], −6.343 027[−10], 3.021 813[−12], −5.585 550[−15]
a_4	8.484 234[−6], 6.353 313[−4], 2.422 957[−6], −3.388 935[−8], 1.718 468[−10], −3.109 722[−13]
a_5	−2.084 635[−6], −9.537 685[−5], −4.578 476[−7], 4.459 593[−9], −1.674 969[−11], 2.099 074[−14]
	Segment 3
	$5.9 < q \le 9.75$
a_{00}	−1.349 980[−2], −1.178 214[−2], 3.414 967[−5], −1.235 405[−6], 1.525 965[−8], −8.094 505[−11], 1.550 263[−13]
a_0	2.555 060[−3], 2.664 933[−3], −6.691 853[−6], 2.919 678[−7], −3.857 775[−9], 2.114 887[−11], −4.127 568[−14]
a_1	−3.764 923[−4], −1.703 133[−3], 1.295 266[−5], −2.014 016[−7], 1.623 818[−9], −6.486 351[−12], 1.009 608[−14]
a_2	−3.254 136[−5], 1.416 699[−3], 1.207 188[−6], −7.290 296[−8], 1.198 781[−9], −7.296 064[−12], 1.506 339[−14]
a_3	1.485 941[−5], 1.703 860[−5], −7.305 411[−7], −6.153 975[−8], 5.619 353[−10], −2.048 821[−12], 2.735 942[−15]
a_4	−1.211 017[−6], −2.288 448[−4], −6.681 539[−7], 5.033 742[−8], −4.847 156[−10], 2.050 713[−12], −3.298 829[−15]
a_5	6.279 524[−9], 3.944 934[−5], 1.525 661[−7], −7.424 258[−9], 6.856 207[−11], −2.849 071[−13], 4.540 122[−16]
	Segment 4
	$9.75 < q \le 13.65$
a_{00}	−3.662 810[−3], −1.521 862[−3], 8.409 706[−6], −1.124 811[−7], 4.251 699[−10], 3.730 156[−13], −3.686 204[−15]
a_0	6.535 520[−4], 2.852 788[−4], −1.894 213[−6], 3.625 697[−8], −2.316 304[−10], 4.991 858[−13]
a_1	−1.414 461[−4], −6.637 037[−5], −4.604 689[−7], 1.057 214[−7], −1.346 978[−9], 6.856 586[−12], −1.258 136[−14]
a_2	2.153 694[−5], 2.584 947[−4], 2.080 372[−6], −6.118 364[−8], 3.932 223[−10], −8.330 949[−13]
a_3	−2.009 718[−6], −7.529 755[−5], −6.008 686[−7], 1.111 813[−8], −5.850 549[−11], 1.061 405[−13]
	Segment 5
	$13.65 < q \le 17.65$
a_{00}	−1.113 950[−3], −4.092 842[−4], 1.302 525[−6], 1.389 474[−8], −2.263 515[−10], 6.695 408[−13]
a_0	1.804 680[−4], 5.967 425[−5], −3.030 219[−7], −7.034 325[−10], 3.162 043[−11], −1.105 659[−13]

TABLE II. (*Continued*).

a_1	−3.367 708[−5], 3.119 216[−5], −2.722 031[−7], 2.325 234[−8], −1.388 141[−10], 2.497 008[−13]
a_2	4.610 403[−6], 3.458 116[−5], 5.693 294[−7], −1.206 499[−8], 3.339 377[−11]
a_3	−4.014 775[−7], −1.360 860[−5], −1.034 757[−7], 1.002 049[−9]
	Segment 6
	$17.65 < q \leq 21.75$
a_{00}	−3.920 810[−4], −1.705 876[−4], 3.559 208[−7]
a_0	5.697 300[−5], 2.052 896[−5], −6.280 051[−8]
a_1	−8.841 226[−6], 2.420 697[−5], 2.614 085[−7]
a_2	7.427 372[−7], −7.164 052[−6], −8.440 139[−8]

segment i is

$$-c_s(q)=f_0(q,\Gamma)+a_{00}+a_0(q-q_{i-1}) + \sum_{j=1}^{n} a_j(q-q_{i-1})^j(q-q_i) , \quad (5)$$

$$f_0(q,\Gamma)=-\frac{3\Gamma}{q^2+3\Gamma/B_0(\Gamma)} , \quad (6)$$

and

$$B_0(\Gamma)=0.399\,925\Gamma-0.200\,01\Gamma^{0.357\,069} +0.069\,206\,3 , \quad (7)$$

where the q_i are the segment boundaries, $f_0(q,\Gamma)$ is a smooth interpolation between the short- and long-range behaviors of $-c_s(q)$, and $B_0(\Gamma)$ is the OCP bulk modulus, the $q=0$ limit of $c_s(q,\Gamma)$. The polynomial fits the difference between $-c_s(q)$ and $f_0(q,\Gamma)$, and the form of the polynomial guarantees the fitting of the end points of each segment. The terms in $j=1,2$, etc. then fit the deviation from linearity with quadratic, cubic, etc. terms. The end points are at $q=0$, 3.0, 5.9, 9.75, 13.65, 17.65, and 21.75. For $q>21.75$, we set $-c_s(q)=-3\Gamma/q^2$, so that $S(q)=1.0$. The very small oscillations for $q>21.75$ and large Γ are ignored in our fit.

The a_j coefficients in Eq. (5) are determined separately for each Γ value, and so they are functions of Γ. We determine the Γ dependence of the a_j values in the same way as for the $-c_s(q)$ values, namely by a polynomial fit using the nonlinear least-squares program:

$$a_j(\Gamma)=b_{j00}+b_{j0}(\Gamma-1)+\sum_{m=1}^{n} b_{jm}(\Gamma-1)^m(\Gamma-225) . \quad (8)$$

Again, we impose the end points (1 and 225) of the Γ range.

For each Γ, the $-c_s(q)$ function can be fitted with very good accuracy, and the evaluation of the energy yields agreement with the tabular values to within a few hundredths of 1%. The fits to the a_j coefficients are less accurate, because there is a very slight roughness in the MHNC table from one value of Γ to the next. This apparently arises from the numerical methods used in solv-

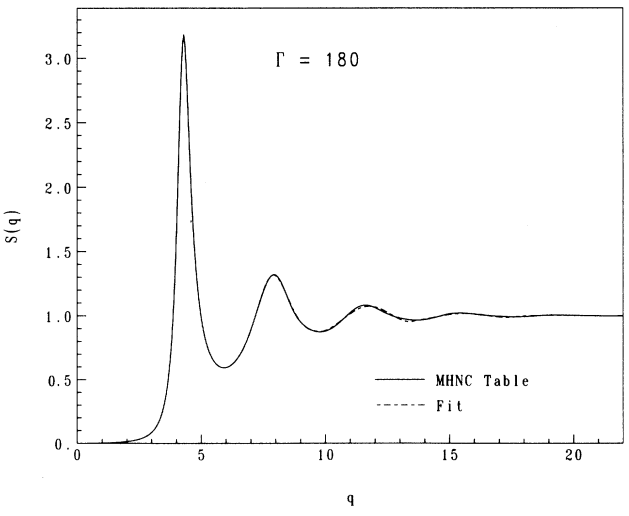

FIG. 2. Comparison of MHNC (solid curve) and fit (dashed curve) $S(q)$'s for $\Gamma=180$.

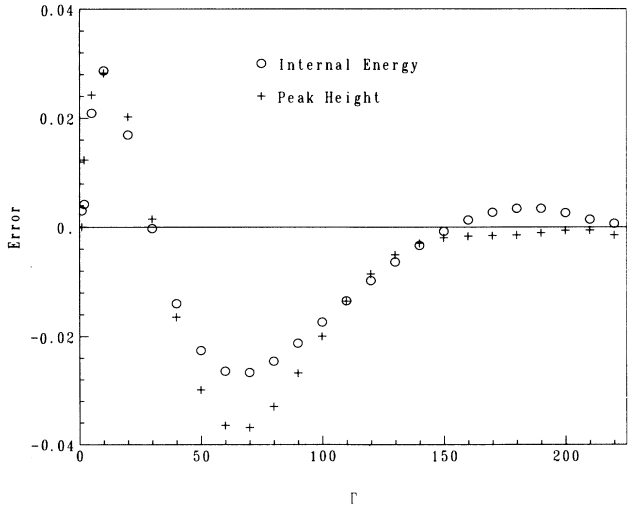

FIG. 3. Errors in the peak height and internal energy of the fitted $S(q,\Gamma)$.

ing the MHNC equation. Because of this roughness, we cannot fit the very important second segment with the highest accuracy, and the average error in the energy rises to about 1%, as shown in Table I.

For the six segments, the maximum j values required for a good fit are 2, 5, 5, 3, 3, and 2. For the preliminary fit to the Γ dependence, we used a maximum value $m=6$ for fitting each a_j coefficient. This gave a global fit with 256 b_{jm} coefficients. By systematically varying m and checking the accuracy of the energy calculations, we were able to reduce the m values for each coefficient to the minimum acceptable value consistent with a good overall fit. This yielded 175 b_{jm} coefficients in the final fit. These coefficients are listed in Table II.

Direct comparison of the tabular and fitted $S(q,\Gamma)$ functions are revealing about the quality of the fit. At low Γ values, near $\Gamma=5$, the fit is poor, because the change in behavior of $S(q,\Gamma)$ at low Γ is not well represented by Eq. (8). Near $\Gamma=85$, where roughness occurs in the tabular function, the fit overshoots the peak of $S(q,\Gamma)$, and the energy is in error by as much as 2.5%. Near the OCP melting point at $\Gamma=180$, the accuracy of the fit is very good, and this is where the function would be most frequently used in variational calculations on liquid metals. These comparisons are shown in Figs. 1 and 2, and the errors in energy and in the first peak of $S(q,\Gamma)$ are shown in Fig. 3.

IV. CONCLUSIONS

We have found that the OCP structure factor $S(q,\Gamma)$ may be fitted with moderately good accuracy using polynomial functions of q and Γ. We are limited in the accuracy that we can achieve by slight roughness in the $S(q,\Gamma)$ table. Further work will be needed to produce a smoother table and to find ways to reduce the number of coefficients needed to fit the table. In the meantime, this fitting procedure may be used to fit other distribution functions with very high accuracy.

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APPENDIX: $S(q,\Gamma)$ SUBROUTINE

We have written a subroutine in standard FORTRAN that returns a value of $S(q,\Gamma)$ for input values of q and Γ. The initial part of the routine determines which segment the input q belongs to and then calls another subroutine to evaluate the fit to that segment. Each segment has a subroutine with a specific data block containing the b_{jm} coefficients.

The subroutine is compact, with 210 code lines. A timing check on the Livermore CRAY XMP shows that the average call time is 33 μs. A copy of this routine may be obtained from H. E. DeWitt either in the form of a diskette or as a data file transmitted by electronic mail. The e-mail address is hedw@ocfmail.ocf.llnl.gov.

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