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Modified Hypernetted-Chain Equation for the Screened Coulomb Potential[*]

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A modified form of the hypernetted-chain (HNC) equation is found that is suitable for the calculation of the pair-correlation function of a classical plasma. The changed equation involves only the short-range screened Coulomb potential and uses no further approximations than are involved in the ordinary HNC equation. The pair-correlation function is computed for a variety of one-component classical plasmas in the region of a dense fluid.

INTRODUCTION

All the equilibrium and many of the nonequilibrium properties of a classical system can be derived from the pair-correlation function $g(r)$. In the intermediate region (dense gas to liquid) the best methods for determining g involve integral equations derived from classical statistical mechanics. One such method is the hypernetted-chain (HNC) equation[1] derived from the Mayer cluster expansion.[2] Although the more accurate Monte Carlo (MC) method has now produced results for a single-component plasma, the HNC equation may be used more easily to obtain results for a multicomponent plasma.

For the classical one-component plasma an additional difficulty arises. The long-range nature of the Coulomb potential necessitates either approximate truncation schemes[3,4] or complicated iteration programs to force convergence to a solution.[4] These methods are difficult to extend to the intermediate region, and the latter method has not been applied there.[5] Previous numerical solutions of the Yvon–Born–Green equation[6] have indicated that oscillatory behavior should be seen in the pair-correlation function in the dense-fluid region. No such behavior has yet been seen in solutions of the HNC equation.[5]

In the Mayer cluster expansion these difficulties are overcome by an infinite summation of diagrams. This leads to a replacement of the Coulomb potential by a short-range screened Coulomb potential plus a modification of the rules for diagrams in the cluster expansion.[7] The appropriate analogous modification for the HNC equation is derived in the following sections. Mere replacment of the Coulomb potential by the screened Coulomb potential leads to a severe underestimation of the many-body effects in $g(r)$.

HNC EQUATIONS FOR SHORT-RANGE POTENTIALS

We follow the standard derivation from the Mayer cluster expansion.[8] Assume that the pair-correlation function can be related to the series function $S(r)$ by

$$g(r)=e^{-U(r)/kT+S(r)} . \tag{1}$$

The many-body corrections to the pair-correlation function are contained in the term involving $S(r)$. This latter function can be related to the pair-correlation function and the direct correlation function $T(r)$ by the Ornstein–Zernicke relation,[8] most conveniently expressed in Fourier-transformed variables

$$S(k)=nT(k)G(k) , \tag{2}$$

where n is the number density and

$$G(r)=g(r)-1 , \tag{3}$$

with the direct correlation function obeying

$$T(r)=G(r)-S(r) . \tag{4}$$

Combining Eqs. (2)–(4) one obtains

$$S(k)=n[T(k)]^2/[1-nT(k)] . \tag{5}$$

Note that the relation between the series function

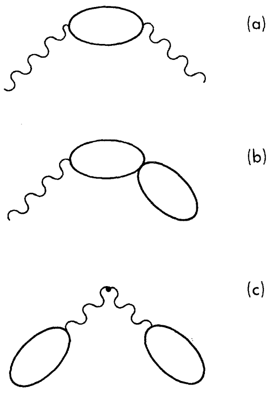

FIG. 1. Diagrams in the Abe nodal expansion.

$S(r)$ and the direct correlation function $T(r)$ [Eq. (5)] is exact. The only approximation involved in the HNC equation is that involved in Eq. (1). This involves neglect of the bridge graphs. Equations (1) and (3)–(5) constitute the HNC equation and can be written as a single integral equation for $g(r)$.[8] In practice, however, the HNC equation is often solved by using the four equations and solving them iteratively using a computer to perform the appropriate Fourier transforms.

MODIFICATION FOR THE SCREENED COULOMB POTENTIAL

The Abe nodal expansion[7] (valid for the screened Coulomb potential) is more complicated than the Mayer cluster expansion. The diagrams for the pair-correlation function consist of two fixed points, corresponding to the positions of the two particles, plus points that are integrated over all space. Between any two points one places any number (zero allowed) of single potential lines, represented by wavy lines, which have a value in k space of

$$-n\beta U_s(k) = -4\pi n\beta e^2/(k^2+1/\lambda_D^2) , \tag{6}$$

where β is $1/kT$ as usual and λ_D is the Debye screening length defined by

$$\lambda_D = (kT/4\pi n e^2)^{1/2} . \tag{7}$$

There are two further rules. Each integrated point must be connected to at least two other points, and no two single potential lines may be connected. Thus the graphs of Figs. 1(a) and 1(b) are acceptable, but the graph of Fig. 1(c) is not allowed.

This last rule modifies the Ornstein–Zernicke relation and changes Eq. (5). One must distinguish in the diagrams for T between those involving a single potential line and the remainder which is called $t(r)$;

$$t(r) = T(r) + n\beta U_s(r) . \tag{8}$$

These latter diagrams are represented by a bubble as depicted in Fig. 1.

In analogy to Eq. (5), $S(k)$ does not contain the factor $t(k)$ to the first power. Thus the lowest-order term is

$$S(k) + t(k) = [1 - n\beta U_s(k)]^2 t(k) . \tag{9}$$

Note that this term contains the diagram of Fig. 1(a). To obtain higher-order diagrams insert between the bubble and the right-hand side of the diagram either a bubble or a single potential line. However, single potential lines may not touch each other. Thus, single potential lines not at either end of the diagram must be between two bubbles. Thus, one inserts next to any bubble either another bubble or a single potential line followed by a bubble. This yields

$$S(k) = \frac{[1 - n\beta U_s(k)]^2 t(k)}{1 - [1 - n\beta U_s(k)]t(k)} - t(k) . \tag{10}$$

Again this result is exact. For a more detailed derivation of an analogous result with further references to the diagrammatic expansion consult Ref. 9.

Equation (1) is modified easily to

$$g(r) = e^{-\beta U_s(r) + S(r)} . \tag{11}$$

Equations (3), (4), (10), and (11) together constitute the modified HNC equation suitable for the screened Coulomb potential. There are now no longer any long-range terms involved in the problem.

DISCUSSION OF SOLUTIONS

No convergence difficulties were encountered in solution of the modified HNC equations. A step width of smaller than 0.02 was used in the integrations (Simpson's rule), and convergence was found after 7 iterations except at the most dense fluid where 15 iterations were required. The error in computation was less than 0.5%.

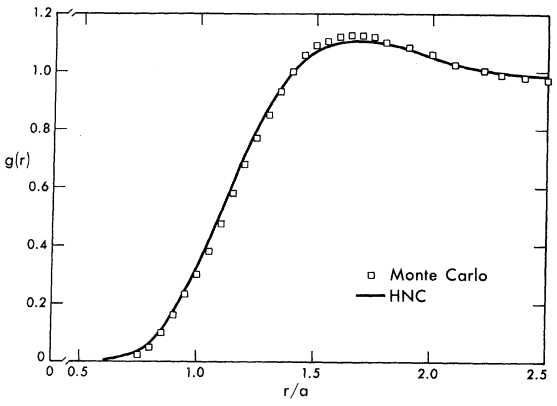

FIG. 2. Pair-correlation function (for $\Gamma = 10$).

TABLE I. Pair-correlation function from HNC equation.

r/a	$\Gamma=1$ $g(r)$	$\Gamma=2$ $g(r)$	$\Gamma=3$ $g(r)$	$\Gamma=4$ $g(r)$	r/a	$\Gamma=5$ g(HNC)	$\Gamma=10$ g(HNC)	$\Gamma=10$ g(MC)
0.05					0.35	0.00014	0.0	
0.10	0.00040				0.40	0.00083		
0.15	0.00252				0.45	0.00325		
0.20	0.0172	0.0044			0.50	0.00903	0.00011	
0.25	0.0471	0.0060			0.55	0.0213	0.00067	
0.30	0.0880	0.0094	0.00104	0.00014	0.60	0.0432	0.00219	
0.35	0.136	0.0267	0.00442	0.00086	0.65	0.0739	0.00678	
0.40	0.189	0.0499	0.0126	0.00325	0.70	0.111	0.0180	0.005
0.45	0.278	0.0840	0.0279	0.00920	0.75	0.162	0.0344	0.020
0.50	0.336	0.129	0.0520	0.0215	0.80	0.224	0.0693	0.050
0.55	0.391	0.181	0.0860	0.0419	0.85	0.292	0.109	0.100
0.60	0.448	0.237	0.130	0.0720	0.90	0.368	0.168	0.160
0.65	0.501	0.299	0.182	0.112	0.95	0.445	0.240	0.230
0.70	0.552	0.358	0.240	0.161	1.00	0.530	0.328	0.300
0.75	0.600	0.423	0.303	0.222	1.05	0.592	0.421	0.380
0.80	0.642	0.481	0.370	0.297	1.10	0.668	0.537	0.475
0.85	0.680	0.541	0.436	0.356	1.15	0.727	0.620	0.580
0.90	0.715	0.593	0.501	0.430	1.20	0.785	0.715	0.680
0.95	0.746	0.642	0.563	0.498	1.25	0.836	0.795	0.770
1.00	0.780	0.689	0.623	0.578	1.30	0.877	0.878	0.850
1.05	0.803	0.733	0.678	0.637	1.35	0.916	0.942	0.925
1.10	0.822	0.770	0.728	0.679	1.40	0.950	0.994	0.995
1.15	0.846	0.803	0.772	0.750	1.45	0.973	1.030	1.055
1.20	0.861	0.833	0.812	0.803	1.50	0.991	1.066	1.090
1.25	0.877	0.860	0.847	0.841	1.55	1.006	1.087	1.105
1.30	0.892	0.882	0.877	0.877	1.60	1.017	1.099	1.120
1.35	0.901	0.902	0.903	0.907	1.65	1.024	1.105	1.125
1.40	0.916	0.915	0.925	0.935	1.70	1.028	1.104	1.125
1.45	0.925	0.930	0.943	0.957	1.75	1.031	1.100	1.120
1.50	0.935	0.943	0.958	0.974	1.80	1.031	1.091	1.110
1.55	0.943	0.954	0.970	0.987	1.90	1.030	1.073	1.085
1.60	0.949	0.963	0.980	0.998	2.00	1.023	1.052	1.060
1.65	0.955	0.970	0.987	1.006	2.10	1.018	1.028	1.025
1.70	0.961	0.976	0.993	1.010	2.20	1.012	1.012	1.005
1.75	0.964	0.980	0.998	1.014	2.30	1.007	1.000	0.990
1.80	0.970	0.986	1.001	1.017	2.40	1.004	0.992	0.980
1.85	0.973	0.988	1.003		2.50	1.000	0.988	0.975
1.90	0.977	0.990	1.005	1.017				
2.00	0.981	0.995	1.007	1.016				
2.10	0.986	0.998	1.007	1.013				
2.20	0.989	0.999	1.006	1.009				
2.30	0.992	1.000	1.005	1.007				
2.40	0.993		1.004	1.004				
2.50	0.995		1.003	1.003				
2.75	0.998		1.001	1.0005				
3.00	0.999		1.000	1.000				

One defines a parameter Γ for the strength of the interaction which is $\beta e^2/a$, where a is the average interparticle spacing $(3/4\pi n)^{1/3}$. The results are shown in Table I and in the graph of Fig. 2, where the most dense-fluid system results are compared to those obtained from the MC procedure.[10]

Two major qualitative features emerge from this comparison. The HNC results rise from zero at smaller values of r/a than the MC results. The oscillations that appear in the pair-correlation function for dense fluids are larger for the MC results than for the HNC results. Both of these features are also found in comparisons of HNC and MC results for other potentials.[4,8] Oscillations in the pair-correlation function have not been found in previous calculations using the unmodified form of the HNC equation[5] because of the difficulty of solution in the region of Γ greater than 2.

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[1] E. Meeron, J. Math. Phys. 1, 192 (1960); T. Morita, Progr. Theoret. Phys. (Kyoto) 23, 385 (1960); J. M. J. Van Leeuwen, J. Groenveld, and J. De Boer, Physics 25, 792 (1959).

[2] T. E. Hill, *Statistical Mechanics* (McGraw-Hill, Princeton, N. J., 1960), Chap. 5.

[3] F. Lado, Phys. Rev. 135, A1013 (1964); A. A. Broyles and H. L. Sahlin, Bull. Am. Phys. Soc. 8, 32 (1963); A. A. Broyles, H. L. Sahlin, and D. D. Carley, Phys. Rev. Letters 10, 319 (1963).

[4] A. A. Broyles, S. U. Chung, and H. L. Sahlin, J. Chem. Phys. 37, 2462 (1962); A. A. Broyles, *ibid.* 33, 546 (1960).

[5] D. D. Carley, Phys. Rev. 131, 1406 (1963); J. Chem. Phys. 43, 3489 (1965).

[6] C. W. Hirt, Phys. Fluids 10, 565 (1967).

[7] R. Abe, Progr. Theoret. Phys. (Kyoto) 22, 213 (1959); E. Meeron, Phys. Fluids 1, 139 (1958); H. F. Friedman, Mol. Phys. 2, 23 (1959); 2, 190 (1959).

[8] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965), Chap. 2.

[9] F. Del Rio and H. E. DeWitt, Phys. Letters 30A, 337 (1969); Phys. Fluids 12, 791 (1969).

[10] S. G. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. 45, 2102 (1966).

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Phase-Amplitude Method in Atomic Physics. II. *Z* Dependence of Spin-Orbit Coupling[*]

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The spin-orbit interaction for p electrons is shown to occur in the K shell for all atoms and to vary with atomic number Z according to $\Delta\mu \propto H\alpha^2(0,\ Z)/Z$, where $\Delta\mu$ is the difference in quantum defect between the fine-structure levels evaluated at the series limit, $\alpha(0,\ Z)$ is the amplitude function for a nonrelativistic zero-energy p wave at $r=0$, and H is a relativistic correction factor. The quantity $\Delta\mu$ is evaluated and found to vary as $Z^{2.33}$, which is in remarkable agreement with experiment. In addition to this gross behavior, the variation of $\alpha^2(0,\ Z)/Z$ exhibits a structure tied to the Periodic Table. This structure derives from the influence of the valence region of the atomic potential, which affects the spin-orbit interaction through the normalization factor $\alpha(0,\ Z)$. Neither inner screening effects, embodied in Casimir's $\sigma(Z)$ parameter, nor deviations of the atomic potential from Zr^{-1} in the interaction region appear very relevant to this problem.

I. INTRODUCTION

The study of spin-orbit (SO) interaction is a very old subject, historically dealing with the analysis of the optical spectra of particular atomic configurations. A recent advance[1] employing quantum-defect theory (QDT) has led to an empirical law by which the strength of SO interaction of p electrons for all atoms can be expressed approximately as a power law in Z, the atomic number. In the present paper, the phase-amplitude method (PAM)[2] is used to show that the SO interaction for p electrons can be expressed as the product of two factors. One factor originates from a *purely hydrogenic* interaction that takes place within the atomic K shell in the field of the *unscreened* nucleus and the other factor depends on the spin-independent potential outside the K shell. This latter factor is the amplitude function of the PAM and constitutes an electron optical transmission function that connects the amplitude of a radial wave function at $r=0$ to that in the ionic field beyond the valence region of the atom. This application of PAM to the Z dependence of SO interaction is a prototype for applications to other inner-shell phenomena, such as K-shell photoabsorption, which can be usefully separated into a factor arising from interactions localized near the nucleus and a normalization factor that depends on transmission properties of the entire atomic field.

Before proceeding, we will review briefly the aspect of the PAM to be exploited here. As shown in an earlier paper,[2] hereafter referred to as I, the radial wave function $P(r)$ for an electron in the field of an ion can be conveniently expressed in terms of an amplitude function $\alpha(r)$ and a phase function $\delta(r)$:

$$P(r)=\alpha(r)\{f\cos[\delta(r)]-g\sin[\delta(r)]\}, \qquad (1)$$

where (f,g) are independent Coulomb functions defined in I. The utility of the amplitude function derives from the fact that $\delta(r)$ depends solely on the range $[0,r]$ whereas $\alpha(r)$ depends on the entire range $[r,\infty]$. Hence, for an interaction taking place at small r, the part of Eq. (1) in braces is characteristic of a purely Coulomb field and should scale with atomic number in a simple way. Therefore, all nonhydrogenic behavior is isolated in the factor $\alpha(r)$, which we will show depends strongly on the field in the valence shells of atoms. This