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A thermodynamically consistent analytical approximation for the structure factor of one-component classical plasma

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Abstract. A simple and accurate analytical approximation for the structure factor of the one-component classical plasma (OCP) is proposed, based on the work of Chaturvedi and co-workers. The exact solution of the hard-core OCP model in the generalised mean-spherical approximation is used to construct the Padé approximants for the packing fraction η and Yukawa tail parameter λ from the conditions of thermodynamical consistency of the OCP structure factor and recent Monte Carlo simulations. The model provides the OCP structure factor in closed analytical form which is in a very good agreement with the Monte Carlo simulations of Galam and Hansen when the OCP coupling constant is in the region $\Gamma > 20$. The thermodynamic properties of liquid sodium near the melting point have been calculated with the OCP as a reference system in the variational method (called the OCPV method) and compared with the results of the hard-sphere variational method and the very accurate Weeks–Chandler–Andersen thermodynamic perturbation theory. The accuracy of the OCPV method appears to be sufficiently high for calculations of liquid metal properties under pressure.

1. Introduction

The calculation of thermodynamic properties for sp-bonded and transition liquid metals using the one-component classical plasma (OCP) as a reference system have been discussed in recent years in [1–5] and in other works. The precision of the Gibbs–Bogolubov variational method used in the above-mentioned papers depends essentially on the accuracy of the description of the structure factor S_k and the thermodynamic properties of the reference system [6]. A stringent test on the structure factor of the reference system is its consistency with thermodynamic properties. This constraint can be taken into account for the OCP in the so-called generalised mean-spherical approximation (GMSA) from the analysis of the long-wavelength limit of the model structure-factor [7, 8]. In § 2 we shall briefly re-derive some GMSA results (Equations 5, 6, 12, 15) obtained in [8] to clarify presentation and discussion. The problem is reduced to two coupled transcendental equations whose solutions we approximate with simple Padé approximants to get a useful explicit formula for the OCP structure-factor.

2. One-component classical plasma (OCP) in the generalised mean-spherical approximation (GMSA)

In the GMSA, the OCP soft core is replaced by a hard core with some diameter d [6–9]. Then the radial and direct correlation functions $h(r)$ and $c(r)$ obey the following conditions

$$h(r) = -1 \quad r < d \tag{1a}$$

$$c(r) = -\beta z^2 e^2 / r - \beta B_0 \exp(-\lambda_0 r) / r \quad r > d \tag{1b}$$

where ze is the OCP charge and $\beta = 1/T$ is the inverse temperature. The core region cannot be reached by particles in the GMSA. The $c(r)$ and $h(r)$ are related by the known Ornstein-Zernike equation.

The free parameters d , B_0 and λ_0 should be found from the fitting to the thermodynamic properties as discussed below. It is convenient to use dimensionless coordinate $x = r/d$ and momentum $k = qd$, so we rewrite (1) in the form

$$\begin{aligned} h(x) &= -1 & x < 1 \\ c(x) &= -\lim_{\mu \rightarrow 0} [\gamma \exp(-\mu x) / x] - B \exp(-\lambda x) / x & x > 1 \end{aligned} \tag{2}$$

where $\gamma = z^2 e^2 / d = \Gamma / 2\eta^{1/3}$, the OCP coupling constant is equal to $\Gamma = z^2 e^2 / \bar{a}$, $\bar{a} = (3\Omega / 4\pi)^{1/3}$ is the mean distance between particles and $\eta = \pi d^3 / 6\Omega = (d/\bar{a})^3 / 8$ is a packing fraction. Following [10] we can factorise the Fourier transform of the direct correlation function (in the text below all Fourier transforms are indicated by a lower case subscript)

$$1 - c_k = Q_k Q_{-k}. \tag{3}$$

The function Q_k have the known analytical properties [11] which lead to the following expressions [8]

$$Q_k = 1 - 12\eta \int_0^\infty dx \exp(ikx) q(x) \tag{4}$$

$$q(x) = F(x) + \lim_{\mu \rightarrow 0} [A \exp(-\mu x)] + b \exp(-\lambda x) \quad x > 0 \tag{5}$$

$$F(x) = [p_0 + p_1 x + p_2 x^2 + p_3 x^3 + w \exp(-\lambda x)] \theta(1 - x). \tag{6}$$

Here $\theta(x) = 1$ when $x > 0$ and $\theta(x) = 0$ when $x < 0$. The supplementary relations for unknown coefficients should be found from Baxter’s equation [11]

$$-q(x) + J(x) - 12\eta \int_0^1 dt q(t) J(|x - t|) = 0 \tag{7}$$

where $J(x) = \int_x^\infty dt th(t)$.

The condition of thermodynamical consistency can be introduced in the following manner. The structure factor of the system can be written in the form

$$S_k = 1 / (1 - c_k) = 1 / |Q_k|^2. \tag{8}$$

In the long-wavelength limit we have [12]

$$\lim_{k \rightarrow 0} (1/S_k) = \kappa^2 / k^2 + \chi_T^0 / \chi_T \tag{9}$$

where $\kappa^2 = 24\eta\gamma$ is the square of the Debye inverse screening length, χ_T is the OCP

compressibility and $\chi_T^0 = T/\Omega$ is the ideal gas compressibility. The OCP internal energy U in GMSA can be found from the equations

$$\beta U = 12\eta\gamma I \quad I = \int_0^\infty dx xh(x). \tag{10}$$

The OCP equation of state in GMSA is given by

$$p/p^0 = 1 + 4\eta g(1) + \frac{1}{3}\beta U \tag{11}$$

where $g(x) = 1 + h(x)$ and $p^0 = T/\Omega$. Consequently we have the following conditions of self-consistency [8]:

$$\beta U = 12\eta\gamma I = (\beta U)_{MC} \tag{12a}$$

$$\chi_T^0/\chi_T = 4p_2^2 - 2\kappa(p_1 - \kappa I) = (\chi_T^0/\chi_T)_{MC} \tag{12b}$$

$$g(1) = p_1 + 2p_2 + 3p_3 - \lambda w \exp(-\lambda) = 0. \tag{12c}$$

The subscript MC indicates the results taken from the Monte Carlo simulation in [13]. Constraints (12a) and (12b) give the proper equation of state for the OCP. From [13] we have

$$(\beta U)_{MC} = a_s + b_s\Gamma^{1/4} + c_s\Gamma^{-1/4} + d_s \tag{13}$$

$$(\chi_T^0/\chi_T)_{MC} = 1 + \frac{4}{3}a_s\Gamma + \frac{13}{36}b_s\Gamma^{1/4} - \frac{11}{36}c_s\Gamma^{-1/4} + \frac{1}{3}d_s$$

where $a_s = -0.897744$, $b_s = 0.95043$, $c_s = 0.18956$ and $d_s = -0.81487$. After straightforward but tedious algebra one can obtain from (7) the linear system for coefficients A , b , p_0 , p_1 , p_2 , p_3 and w . Excluding these coefficients we get two transcendental equations for η and λ as functions of Γ .

The numerical solution of these equations were fitted by Padé approximants

$$\eta = (c_1\Gamma + c_2\Gamma^{3/4} + c_3\Gamma^{1/2} + c_4)/(\Gamma + c_5\Gamma^{3/4} + c_6\Gamma^{1/2} + c_7) \tag{14a}$$

$$\lambda = (\Gamma - \Gamma_0)^{1/2}(d_1\Gamma + d_2\Gamma^{1/2} + d_3)/(\Gamma + d_4\Gamma^{1/2} + d_5). \tag{14b}$$

Here $\Gamma_0 = 19.55$, c_1-c_7 are respectively 0.614944, -3.31353 , 3.51334, -2.49714 , -5.17022 , 6.84416 and -36.7746 , and d_1-d_5 are respectively -3.45004 , 103.689, 68.1194, 29.1990 and 403.246. We have not found any reasonable solution below $\Gamma = \Gamma_0$. The accuracy of our approximation (14) is about 10^{-5} in the region $60 < \Gamma < 180$ and slightly lower outside this interval.

The other coefficients can be found from the following sequence of relations

$$\begin{aligned} A &= -(\gamma/6\eta)^{1/2} & p_3 &= \kappa/6 & \kappa &= (24\eta\gamma)^{1/2} \\ p_1 &= x_1 + by_1 & p_2 &= x_2 + by_2 \\ w &= (p_1 + 2p_2 + 3p_3) \exp \lambda/\lambda & p_0 &= -[p_1 + p_2 + p_3 + w \exp(-\lambda)] \\ b &= (\frac{1}{2}A - I - x_1z_1 - x_2z_2 - p_3z_3)/(y_1z_1 + y_2z_2 + z_4) \end{aligned} \tag{15}$$

$$12\eta\gamma I = a_s\Gamma + b_s\Gamma^{1/4} + c_s\Gamma^{-1/4} + d_s$$

where x_i , y_i and z_i ($i = 1, \dots, 4$) can be found from the following relations

$$\begin{aligned} f_1 &= [2 - (2 + 2\lambda + \lambda^2) \exp(-\lambda)]/2\lambda^2 & f_2 &= f_1 \exp \lambda/\lambda \\ h_1 &= [1 - (1 + \lambda) \exp(-\lambda)]/\lambda & h_2 &= h_1 \exp \lambda/\lambda \\ u_1 &= 2/\lambda^3 - (\frac{1}{3} + 1/\lambda + 2/\lambda^2 + 2/\lambda^3) \exp(-\lambda) \\ u_2 &= [1 - 12\eta \exp \lambda (Ih_1 + \frac{1}{2}u_1)]/\lambda \\ v_1 &= 1 + 2\eta - 12\eta f_2 & v_2 &= 3\eta(1 - 8f_2) \\ v_3 &= 6\eta(1 - 2h_2) & v_4 &= -2 + 8\eta(1 - 3h_2) \\ v_5 &= v_1v_4 - v_2v_3 \\ r_1 &= -6\eta\kappa(\frac{1}{10} - f_2) + \kappa I & r_2 &= -1 - 6\eta\kappa(\frac{1}{4} - h_2), \\ r_3 &= 12\eta/\lambda^2 & r_4 &= 12\eta/\lambda \\ x_1 &= (v_4r_1 - v_2/r_2)/v_5 & x_2 &= (v_1r_2 - v_3r_1)/v_5 \\ y_1 &= (v_4r_3 - v_2r_4)/v_5 & y_2 &= (v_1r_4 - v_3r_3)/v_5 \\ z_1 &= 1 + 6\eta(\frac{1}{12} + I) + u_2 & z_2 &= 1 + 4\eta(\frac{1}{8} + 2I) + 2u_2 \\ z_3 &= 1 + 3\eta(\frac{1}{3} + 3I) + 2u_2 & z_4 &= -12\eta(1/\lambda^2 + I)/\lambda. \end{aligned}$$

From (3)–(6) we can obtain the following expression for the structure factor

$$S_k = (k^2/\kappa^2)/(T_k^2 + k^2R_k^2/\kappa^2)$$

where

$$\begin{aligned} T_k &= 1 - 12\eta[kU_k + bk^2/(k^2 + \lambda^2)]/\kappa & R_k &= 1 - 12\eta[V_k + b\lambda/(k^2 + \lambda^2)], \\ U_k &= p_0s_0 + p_1s_1 + p_2s_2 + p_3s_3 + w[k - \exp(-\lambda)(k \cos k + \lambda \sin k)]/(k^2 + \lambda^2) \\ V_k &= p_0c_0 + p_1c_1 + p_2c_2 + p_3c_3 + w[\lambda + \exp(-\lambda)(k \sin k - \lambda \cos k)]/(k^2 + \lambda^2) \\ s_n &= \int_0^1 dx x^n \sin(kx) & c_n &= \int_0^1 dx x^n \cos(kx). \end{aligned}$$

3. Discussion

The structure factor calculated in the present model is shown in figures 1 and 2 for the coupling constant values $\Gamma = 20, 40, 70, 100, 160$ and 178 compared with the results of Monte Carlo simulation in [14]. The agreement with the Monte Carlo results is very good and the relative accuracy of the present analytical S_k is about 1 per cent in the range $\Gamma > 100$. It should be noted that the height of the first peak in the vicinity of the OCP freezing point ($\Gamma_m = 178$) is 3.04 in correspondence with some simple criteria of freezing.

The present S_k is accurate in long wavelength limit where k tends to zero as follows from equations (9) and (12b). Consequently, this behaviour provides a high accuracy of thermodynamic calculations within the variational method because the long wavelength region and the first peak of the structure factor contributes the major part of the

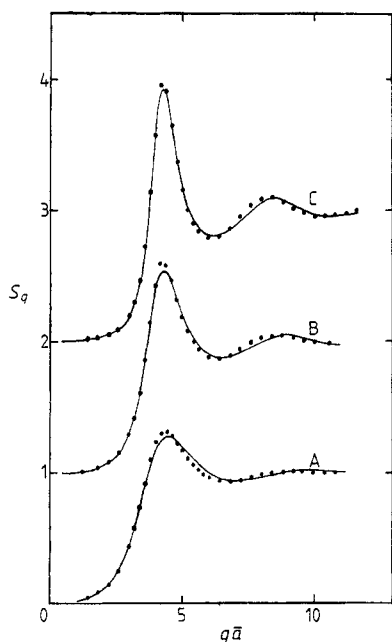


Figure 1. The OCP structure-factor S_q versus momentum $q\bar{a}$ for various values of the coupling constant Γ . Curve A, $\Gamma = 20$; curve B, $\Gamma = 40$; curve C, $\Gamma = 70$. Data points: Monte Carlo simulation of [14].

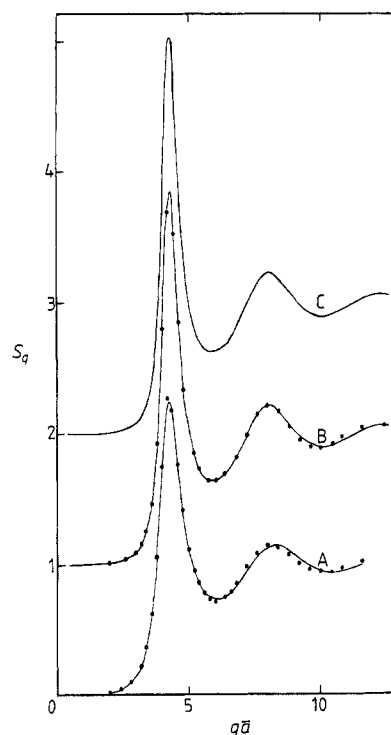


Figure 2. The OCP structure factor S_q versus momentum $q\bar{a}$ for various other values of the coupling constant Γ . Curve A, $\Gamma = 100$; curve B, $\Gamma = 160$; curve C, $\Gamma = 178$. Data points: Monte Carlo simulation of [14].

Table 1. The computed thermodynamic properties for liquid sodium near its melting point.

Method	Internal thermal energy U^* (K)	Pressure p (kbar)	Bulk modulus B_T (kbar)	Entropy S (k_B)	Heat capacity (k_B)		Thermal expansion coefficient α_p (10^{-4} K^{-1})
					c_v	c_p	
HSV ^a	1521	1.94	51.5	7.25	3.74	4.39	3.38
WCA ^a	1361	0.16	54.8	7.72	3.48	3.94	2.75
OCPV	1381	-0.36	51.3	7.47	3.47	3.86	2.62
Experiment ^b	1345	0	52.6	7.78	3.47	3.83	2.51

^a The experimental values and the results of HSV and WCA methods in the table are taken from [6].

free energy of liquid phase [6]. This is illustrated in table 1 where the results of such calculations with the OCP reference system (the OCPV method) are compared with other methods and experiments for liquid sodium near the melting point. The methods used are the variational one with the hard-sphere reference (HSV) and the thermodynamic perturbation theory of Weeks, Chandler and Andersen (WCA) [6]. The results presented in table 1 confirm the high accuracy of the OCPV method. There is only a minor difference

between the OCPV and WCA methods in calculation of the equation of state and entropy in the liquid phase. The underestimation of entropy S in comparison with experiment can be related to some inaccuracy in predicting the 'softness' of the inter-ionic potential in the system [6]. The accuracy of the 'soft sphere' approximation appears to be slightly less than in the OCPV method in the low pressure region [15, 16]. In contrast to the WCA method, the accuracy of the variational method is as a rule less sensitive to the external parameters such as temperature and pressure [6, 15]. Hence the OCPV method is perspective for the computations in the high pressure region with accurate pseudopotentials. For instance, it enables one to calculate the melting characteristics of alkali metals up to very high pressures [15, 17] and to investigate the universality of the OCPV in this region.

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