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The long-wavelength-limit structure factor of liquid alkali metals with the classical plasma reference system

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Abstract. The long-wavelength-limit structure factor of liquid alkali metals is investigated using the mean-density approximation. The one-component classical plasma model is used as the unperturbed reference system. It is shown that a consistent description of the long-wavelength-limit structure factor and the overall structure factor as well as the thermodynamics can be achieved to some degree using the reduced plasma parameter.

The one-component classical plasma (OCP) is a system of point particles, each carrying a charge $Z_r e$ and moving in a uniform neutralising background. The system is characterised by the plasma parameter $\Gamma_r = (Z_r e)^2/ak_BT$, where $a = (3/4\pi n)^{1/3}$ is the ion sphere radius with density n and T is the temperature. The use of the Gibbs–Bogoliubov variational method with the OCP reference system in the thermodynamic calculation of liquid alkali metals tells us that the magnitude of the plasma parameter Γ_r of the reference system is significantly smaller than that ($\Gamma = (Ze)^2/ak_BT$) fixed by the real charge Z carried by the ion core [1–3]. Although the free energy minimum is so shallow that we cannot determine the optimum value of the plasma parameter accurately [2, 3], the magnitude of the apparent charge Z_r of the OCP reference system is definitely smaller than that of the bare ionic charge Z. Furthermore the analysis of the structure factor of liquid alkali metals reveals the same tendency [4, 5]. The overall form of the structure factor is well approximated by the OCP, with the reduced plasma parameter, in the thermodynamic calculation. In contrast, the compressibility and the long-wavelength-limit structure factor $S(0)$, within the random-phase approximation (RPA), are well explained by the plasma parameter Γ corresponding to the real charge Z [5, 6]. Thus the consistent description of the various properties of liquid alkali metals using the single plasma parameter Γ_r is not possible.

In order to resolve this problem, Yokoyama [7] has proposed an improvement on the RPA. By decreasing the number of valence electrons artificially so as to compensate for the deficit of the apparent core charge $Z - Z_r$, Yokoyama was able to reproduce well the long-wavelength-limit structure factor from the RPA formula. Although his theory, which we call the modified RPA (MRPA) hereafter, reproduced the experimental compressibility rather well, the physical meaning of the artificial reduction of the valence electron number is unclear. Instead of this artificial trick, we show in this paper that by using the mean-density approximation (MDA), which is considered to be exact in the long-wavelength limit [8], as well as the recently proposed dielectric screening function [9], we can obtain a physically appealing result.

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Using the standard lowest-order pseudopotential perturbation theory, the inter-atomic pair potential is written as the sum of the repulsive core–core Coulomb potential and the electron-mediated screening potential:

$$\varphi(r) = (Ze)^2/r + \varphi_{sc}(r). \tag{1}$$

When applying the mean-density-approximation (MDA) theory of the structure factor of liquid we start by dividing the given inter-atomic potential (1) into the unperturbed (reference) potential $\varphi_0(r)$ and the perturbation $\varphi_1(r)$. The separation is not specified within the theory [8, 10]. When we use the hard-sphere (HS) potential as the reference potential, we normally employ the so-called WCA prescription [11]. When we consider a 'soft' potential, such as the Coulomb potential of the OCP, as the reference potential, we find that no prescription is available as yet. Use of the RPA—that is, a simplified version of the MDA—involves using the separation given by equation (1).

Instead of this, we follow the idea of the Gibbs–Bogoliubov variational calculation [12–14], and we put

$$\varphi_0(r) = (Z_r e)^2/r \tag{2a}$$

$$\varphi_1(r) = \varphi_{sc}(r) + [(Ze)^2 - (Z_r e)^2]/r. \tag{2b}$$

The thermodynamic variational calculation starts from this separation and the free energy is minimised with respect to the reference plasma parameter $\Gamma_r = (Z_r e)^2/ak_BT$ corresponding to the apparent charge Z_r of the reference OCP system.

We use the above separation in our analysis of the structure factor [13, 14]. Within the MDA the low-angle structure factor $S_{MDA}(q)$ reads

$$\frac{1}{S_{MDA}(\boldsymbol{q})} = \frac{1}{S_{OCP}(\boldsymbol{q})} + \beta n\varphi_1(\boldsymbol{q}) + \int \frac{d\boldsymbol{k}}{(2\pi)^3}\beta n\varphi_1(\boldsymbol{k})\left(\frac{\partial}{\partial n} + \frac{1}{2}n\frac{\partial^2}{\partial n^2}\right) S_{OCP}(|\boldsymbol{q}-\boldsymbol{k}|) \tag{3}$$

where $S_{OCP}(\boldsymbol{q})$ is the structure factor of the OCP reference system described by the pair potential (2*a*) with the apparent charge Z_r. $\varphi_1(q)$ is the Fourier transform of the perturbation potential (2*b*), and β is the inverse of the temperature. It should be noted that the perturbation potential consists of two parts.

The RPA truncates the last term involving the density derivative (MDA term) in (3). The long-wavelength limit of the OCP structure factor $S_{OCP}(q)$ is known analytically [6]. The perturbation $\varphi_1(q)$, equation (2*b*), may be calculated and the long-wavelength limit may be taken if we know the pseudopotential and the screening function. We use the simple Ashcroft pseudopotential with core radius [6], and the Ichimaru–Utumi (IU) screening function [9]. In the limit $q \to 0$, the divergent terms cancel out, and we get [5]

$$1/S_{RPA}(0) = 1 - \Gamma_r x_0^2/6 + k_D^2 r_c^2 + k_D^2/k_e^2 \tag{4}$$

where

$$k_D^2 = 4\pi n(Ze)^2/k_BT$$

is the Debye–Hückel inverse screening length, k_e is the inverse screening length of the electron gas [9] and r_c is the core radius of the Ashcroft pseudopotential [6]. x_0^2 is obtained from the compressibility of the OCP derived from the expression for the free energy [5, 6]

$$x_0^2 = -\tfrac{8}{3}a - \tfrac{13}{6}b\Gamma_r^{-3/4} - \tfrac{11}{6}c\Gamma_r^{-5/4} - 2d\Gamma_r^{-1} \tag{5}$$

where $a = -0.897744$, $b = 0.95043$, $c = 0.18956$, and $d = -0.81487$ [16]. The

expression for $S_{RPA}(0)$, equation (4), depends sensitively on the choice of the core radius r_c and the screening function through k_e.

It should be noted that in equation (4) the first two terms are derived from the reference system and are therefore calculated using the reduced ionic charge Z_r, whilst the last two terms are from the screening potential $\varphi_{sc}(r)$ and should be calculated with the original real valence Z.

In the traditional RPA [5, 6] we set $Z_r = Z$. In the MRPA [7], we use the reduced Z_r, corresponding to $\Gamma_r = 155$, which fits the experimental structure factor near melting quite well, and we further reduce the real valence Z artificially to Z_r in the last two terms in (4), thus modifying k_D and k_e.

The results of straightforward application of equation (4) are not encouraging if we use the reduced Z_r, which is consistent with the thermodynamic variational calculation or the structure analysis, as shown in table 1, where we set $\Gamma_r = 155$ arbitrarily as in [7]. Therefore we should inevitably take into account the MDA term

$$\frac{1}{S_{MDA}(0)} = \frac{1}{S_{RPA}(0)} + \int \frac{d\boldsymbol{k}}{(2\pi)^3} \beta n \varphi_1(k) \left(\frac{\partial}{\partial n} + \frac{1}{2} n \frac{\partial^2}{\partial n^2} \right) S_{OCP}(ka, \Gamma_r). \tag{6}$$

We have used the fact that in the OCP structure factor $S_{OCP}(ka, \Gamma_r)$ the momentum transfer is scaled as ka. Since the perturbation potential $\varphi_1(k)$ consists of two terms, equation (2*b*)—one from the screening potential $\varphi_{sc}(r)$ and the other from the residual Coulomb potential—the MDA term is divided into two terms $I_1(0)$ and $I_2(0)$. Therefore we have

$$1/S_{MDA}(0) = 1/S_{RPA}(0) + I_1(0) + I_2(0). \tag{7}$$

Since the screening potential $\varphi_{sc}(q)$ can be expressed in terms of the energy–wavenumber characteristics $G_n(q)$ [3, 13], $I_1(0)$ is written as

$$I_1(0) = -\frac{2\beta(Ze)^2}{\pi} \left(n \frac{\partial}{\partial n} + \frac{1}{2} n^2 \frac{\partial^2}{\partial n^2} \right) \int_0^\infty dk\, G_n(k) [S_{OCP}(ka, \Gamma_r) - 1] \tag{8}$$

where it is understood that the energy–wavenumber characteristics $G_n(q)$ are kept constant as the density is varied to allow us to calculate the derivative numerically [11]. In order to improve the convergence of the numerical integration, we have added a constant term as in [11]. $I_2(0)$ is written as

$$I_2(0) = \frac{2\beta(Z^2 - Z_r^2)\, e^2}{\pi a} \int_0^\infty d(ka) \left(n \frac{\partial}{\partial n} + \frac{1}{2} n^2 \frac{\partial^2}{\partial n^2} \right) (S_{OCP}(ka, \Gamma_r) - 1).$$

Direct numerical integration of this term is difficult because of the long-ranged nature of the integrand. This can be bypassed in the following way: firstly, noting that a is related to the density, we interchange the order of taking the integral performing the partial differentiation, then integration is performed and is expressed in terms of the excess internal energy of the OCP. Finally we express the partial differentiations with respect to the density in terms of those with respect to the plasma parameter:

$$I_2(0) = \tfrac{1}{6}(\Gamma - \Gamma_r)[(4\Gamma_r\, \partial/\partial\Gamma_r + \Gamma_r^2\, \partial^2/\partial\Gamma_r^2)\beta U(\Gamma_r)/\Gamma_r + 2\beta U(\Gamma_r)/\Gamma_r].$$

$U(\Gamma_r)$ is the excess internal energy of the OCP with the plasma parameter Γ_r. Using the

analytic expression for the internal energy fitted to the Monte Carlo simulation [16], we have

$$I_2(0) = \tfrac{1}{9}(\Gamma - \Gamma_r)(2a + \tfrac{5}{16}b\Gamma_r^{-3/4} - \tfrac{3}{16}c\Gamma_r^{-5/4}). \tag{9}$$

The constants a, b and c are the same as in equation (5).

The results from the calculation using these MDA terms are given in table 1. Again we set $\Gamma_r = 155$ in order to allow comparison with the RPA and the MRPA calculations. This value is known to give an OCP structure factor and an entropy that are close to the experimental values [4, 5, 14]. Therefore the choice is in qualitative accord with the variational theory which should give a realistic structure factor and thermodynamic quantities [1].

In order to calculate the integral in (8), we approximate the OCP structure factor using the analytic expression for the structure factor of the charged hard spheres (CHS) obtained using the mean-sphere approximation [17, 18]. The hard-sphere diameter of the CHS is fixed by the prescription of Singh [18], which seems most appropriate and simplest since it is directly fitted to the direct correlation function of the OCP structure factor obtained from the simulation.

From table 1 we see that the MDA term is not as important as suggested by Young [13], and is of the same magnitude as that calculated by Ono and Yokoyama [2] using a different approximation to the structure factor of the OCP and to the screening function [19]. Although the MDA term $I_1(0) + I_2(0)$ is small compared with $1/S_{\mathrm{RPA}}(0)$, the final result for the $S_{\mathrm{MDA}}(0)$ is reasonable and the degree of the agreement with experiment is almost the same as that achieved using the existing RPA [5, 6] or MRPA [7] calculation.

We now comment on the RPA [5, 6] and the MRPA [7] calculations. Firstly, using the RPA and setting $\Gamma_r = \Gamma$ is not appropriate since the inclusion of the higher-order MDA term worsens the final result, $S_{\mathrm{MDA}}(0)$, as shown in table 2. A small difference in the $S_{\mathrm{RPA}}(0)$ from those reported in [5] (table 1) and [6] is due to the use of a different screening function [20] and a different core radius r_c. It should be noted, however, that from the definition of the perturbation potential, equation (2*b*), $I_2(0)$ is identically zero and the MDA term is less important than $S_{\mathrm{RPA}}(0)$ when $\Gamma_r = \Gamma$. The RPA term $S_{\mathrm{RPA}}(0)$ and the MDA term are complementary and a delicate balance of these two terms determines $S_{\mathrm{MDA}}(0)$. The physical meaning of the assumption used in the MRPA is unclear and seems not to be soundly based. The good final result obtained from using the MRPA seems to be not only due to the artificial assumption but also to a happy combination of the choice of the r_c and the screening function [21].

The value of the plasma parameter Γ_r of the reference OCP system should be calculated by a variational calculation. However, the previous analysis did not show $\Gamma_r \simeq 155$; instead smaller values were predicted [2, 3] even though the authors had used either a different core radius r_c or a different screening function. We did the thermodynamic variational calculation again using the core radius r_c used here [6] and the Ichimaru–Utumi screening function [9]. The band structure energy was calculated approximately using the CHS structure factor as used here [18]. The values of the optimum Γ_r are 90, 115, 126, 125, 137 for Li to Cs respectively. They are on the whole smaller than the value of 155 used here. However, since the minimum is shallow and accurate determination of Γ_r is difficult, our approximation $\Gamma_r = 155$ is not unreasonable.

In order to check further on the importance of the MDA term, we have calculated $S(0)$ for the expanded fluid rubidium (Rb). In table 3 we show the calculated values of $S_{\mathrm{MDA}}(0)$ together with the experimental values compiled by Evans and Sluckin [6]

Table 1. The long-wavelength-limit structure factor $S_{MDA}(0)$ calculated from the mean-density approximation (MDA) by setting $\Gamma_r = 155$. The input data for the temperature and the density are those cited in table 1 of [7]. The Ashcroft core radius is taken from [6]. For the sake of comparison we have also listed the experimental values of $S_{exp}(0)$ as well as the results from the theoretical modified RPA (MRPA) calculation, $S_{MRPA}(0)$ [7], and the RPA calculation, $S_{RPA}(0)$, with $\Gamma_r = \Gamma$ [6].

	T† (K)	n† (g cm^{-3})	r_c‡ (au)	$S_{RPA}(0)$	$I_1(0)$	$I_2(0)$	$S_{MDA}(0)$	$S_{MRPA}(0)$†	$S_{RPA}(0)$‡	$S_{exp}(0)$§
Li	463	0.512	1.28	0.0160	−9.65	−10.13	0.0234	0.0175	0.025	(0.0260)
Na	371	0.928	1.70	0.0149	−8.21	−10.98	0.0209	0.0212	0.024	0.0240(0.0233)
K	337	0.826	2.25	0.0183	−4.52	−6.26	0.0228	0.0243	0.026	0.0247(0.0225)
Rb	312	1.416‖	2.45	0.0195	−4.51	−6.12	0.0246	0.0251	0.026	(0.0220)
Cs	302	1.838	2.67	0.0195	−2.32	−5.11	0.0228	0.0258	0.027	0.026(0.0237)

† From [7].
‡ From [6].
§ From [5, 6]. Values in parentheses are deduced from the compressibility. The other values are deduced from the diffraction data.
‖ The density of Rb in [7] seems to have the wrong third digit, from comparison with that in [15], and we take the data of the latter.

Table 2. The long-wavelength-limit structure factor $S_{MDA}(0)$ calculated from the mean-density approximation (MDA) by setting $\Gamma_r = \Gamma$. The input data are the same as in table 1. Note that $I_2(0)$ is identically zero. The experimental values of $S_{exp}(0)$ are the same as in table 1.

	$S_{RPA}(0)$	$I_1(0)$	$S_{MDA}(0)$	$S_{exp}(0)$
Li	0.0237	−9.80	0.0308	(0.026)
Na	0.0222	−8.21	0.0271	0.0240(0.0233)
K	0.0238	−4.36	0.0265	0.0247(0.0225)
Rb	0.0256	−4.33	0.0289	(0.0220)
Cs	0.0243	−2.21	0.0257	0.026(0.0237)

and using their RPA calculation, setting $\Gamma_r = \Gamma$. In our MDA calculation we reduce the magnitude of the plasma parameter as suggested in [5] by using the formula

$$\Gamma_r = \Gamma_s(T_s/T)(n/n_s)^{1/3}.$$

Subscript s indicates the standard state, which we choose to be the state of the first row of table 3, and we determine the standard plasma parameter Γ_s so as to fit $S_{MDA}(0)$ to the experimental value $S(0)$ for the standard state. We see that with use of the above scaling formula for the reference system, we can reproduce well the experimental $S(0)$. The MDA seems better than the RPA for a wider range of the temperature and the density.

We have shown in this paper that the proper inclusion of the perturbation potential for the MDA formula of the long-wavelength-limit structure factor $S(0)$ is important for the OCP reference systems. We show that a consistent description of the long-wavelength structure factor using the mean-density approximation and of the thermodynamics using the Gibbs–Bogoliubov variational theory is theoretically achievable. Unfortunately, a consistent value for the plasma parameter cannot be found, but this should be resolvable

Table 3. The long-wavelength-limit structure factor $S_{MDA}(0)$ of expanded Rb as calculated from the MDA. Experimental values of $S_{exp}(0)$ as well as from the RPA calculation $S_{RPA}(0)$ are taken from table 2 of [6].

n (10^3 Å^{-3})	T (K)	Γ_r	$S_{MDA}(0)$	Γ	$S_{RPA}(0)$	$S_{exp}(0)$
9.74	573	78.0	0.045	100.4	0.056	0.045
9.27	723	60.9	0.065	78.3	0.081	0.070
8.80	873	49.5	0.091	63.7	0.115	0.10
8.32	1023	41.5	0.126	53.3	0.164	0.13
7.81	1173	35.4	0.173	45.6	0.242	0.18
7.29	1323	30.7	0.242	39.5	0.389	0.24
6.73	1473	26.8	0.358	34.5	0.771	0.37
6.34	1573	24.6	0.486	31.7	1.81	0.51
6.12	1623	23.6	0.588	30.3	5.94	0.57
5.90	1673	22.6	0.725	29.1	—	0.67
5.66	1723	21.6	0.946	27.9	—	0.72
5.42	1773	20.7	1.29	26.7	—	0.79
5.14	1823	19.8	2.13	25.5	—	0.94

by using a more accurate approximation to the structure factor of the OCP and/or by using non-local pseudo-potentials [13]. Our formalism should also be useful for long wavelengths and finite wavenumber.

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