PHYSICAL REVIEW A VOLUME 29, NUMBER 3 MARCH 1984

Core polarization and the structure factor of liquid alkali metals

H. B. Singh and A. Holz
Fachrichtung Theoretische Physik, Universität des Saarlandes, D-6600 Saarbrücken, Federal Republic of Germany

(Received 11 July 1983)

The static structure factor of liquid alkali metals is calculated using a classical one-component plasma as the reference system. The effect of electron-electron screening and the fluctuating dipole-dipole interaction (due to polarization of ion cores) is taken into account using low-order perturbation theory. The effect of the latter interaction is appreciable near the first two peaks and amounts to reducing the height of these peaks. The results obtained are in very good agreement with the experimental data for all the alkali metals.

I. INTRODUCTION

The system of neutral hard spheres has played a central role[1–3] as a reference system for liquid metals in understanding their structure and thermodynamics. However, the simple Ashcroft-Lekner[1] model is not sufficient in understanding the structure of liquid alkali metals, and a solution of the Percus-Yevick equation with realistic potential is required[3] to obtain reasonably good results for the structure factor of these metals.

Recently, it has been realized[4] that the classical one-component plasma (OCP) serves as a better reference system for liquid alkali metals because it yields lower free energy compared with the case where the reference system is taken to be a system of neutral hard spheres. Using the OCP as reference, the structure factors of liquid alkali metals have been calculated[5–7] to be in good agreement with the experimental results. Here, as in Refs. 6–8, the one-component plasma is approximated by a system of charged hard spheres (CHS) in a neutralizing background of electrons. For this system Palmer and Weeks[9] have obtained an exact solution for the direct correlation function in a mean spherical approximation. In an earlier paper[7] (hereafter referred to as I), we used this result to calculate the structure factor of liquid alkali metals. The only free parameter involved was the charged-hard-sphere diameter σ, which we determined by means of a one-point fit with the experimental data of the structure factor at its first minimum. Presently, we shall remove this artifact and determine σ uniquely from a scaling property[10] of the direct correlation function so that there is no parameter to be fitted.

Another problem to be examined in this paper is the effect of core polarization on the structure of alkali metals. It is clear that the ions in the underlying OCP in liquid metals are not point particles since they are not fully ionized. Their charge distribution has finite extension in space which gives rise to induced dipole-dipole interaction between different ions, as the van der Waals interaction between different atoms in inert gases. However, presently this interaction shall be screened by the conduction electrons. In this context Mon, Ashcroft, and Chester[11] have recently done extensive Monte Carlo simulations for the structure factor of liquid Ga using model potentials containing the effect of such screened dipole-dipole interaction. In this way they could reproduce features in the structure factor similar to the one observed experimentally. We, therefore, thought it worthwhile to study the effect of such interaction on the structure factor of liquid alkali metals.

II. FORMULATION AND RESULTS

In a low-order perturbation theory, the structure factor of simple liquid metals can be written[12] as

$$S(q)=\frac{S_0(q)}{1+n\beta\phi(q)S_0(q)} , \tag{1}$$

where $S_0(q)$ is the structure factor of a reference system at the same ion number density n, and temperature T as the liquid metal under consideration. Furthermore, $\beta=(k_BT)^{-1}$, and $\phi(q)$ is the Fourier transform of the perturbation potential. This quantity can be written as

$$\phi(q)=\phi_{ps}(q)+\phi_{d-d}^{s}(q) , \tag{2}$$

where $\phi_{ps}(q)$ is the contribution of the perturbation arising from the coupling of the ions to the electron gas via the pseudopotential. The term $\phi_{d-d}^{s}(q)$ denotes the Fourier transform of the perturbation potential whose origin lies in the screened dipole-dipole interaction between different ions. The effect of this term on the structure factor of alkali metals has not been investigated so far.

The reference system is taken to be the classical OCP which is characterized by the coupling parameter

$$\Gamma=\beta(Ze)^2/a_0 , \tag{3}$$

where Ze denotes the ionic charge and a_0 is the average ion sphere radius. Once the OCP is approximated by a system of charged hard spheres in a neutralizing background, its direct correlation function $c(r)$ is known[9] in a mean spherical approximation. It is then easy to Fourier transform this expression and obtain a simple analytic expression for $S_0(q)$ as can be seen in I. Clearly, the results for $S_0(q)$ depend on the CHS diameter σ as well as on Γ. Recently one of us used[10] the CHS model to study the structure and thermodynamics of the classical OCP. There it was noted that, to a good approximation, $c(r)/\Gamma$ is a scaled quantity at strong couplings. Especially, the computer simulation values of $c(r=0,\ \sigma)$ at different values of Γ seem to satisfy the scaling relation

$$\frac{c(r=0,\sigma)}{\Gamma}=\frac{4}{3} \tag{4}$$

very well, which was thus used to determine σ. In fact, the results obtained[10] for different quantities for the OCP are almost in quantitative agreement[13] with the computer simulation data. Therefore, presently also we shall use Eq. (4) to determine the values of the charged-hard-sphere diameter in a unique way.

A. Results for the structure factor without core polarization

When the polarizability of alkali-metal ions is taken to be zero, then the situation is the same as in I. The only perturbation correction[12] is due to electron screening of the ionic motion and is given by

$$\phi(q)=\phi_{ps}(q)=\frac{v_{ps}^2(q)}{\phi_c(q)}\left[\frac{1}{\epsilon(q)}-1\right] . \qquad (5)$$

Here $v_{ps}(q)$ and $\phi_c(q)$ denote, respectively, the Fourier transform of the electron-ion pseudopotential and the bare electron-electron interaction, and $\epsilon(q)$ is the wave-vector-dependent dielectric function of interacting electrons. As in I, we use for $\epsilon(q)$ an expression due to Vashishta and Singwi,[14] and the pseudopotential is approximated by the Ashcroft empty-core model,[1]

$$v_{ps}(q)=-Z\phi_c(q)\cos qR_c .$$

This pseudopotential is truncated[6,7,15] beyond its first node and the Ashcroft core radius R_c is determined to obtain correct long-wavelength behavior of Eq. (1); this gives[7]

$$R_c=\left[q_D^{-2}\left[\xi-1+\frac{1}{S(0)}\right]-q_e^{-2}\right]^{1/2} . \qquad (6)$$

Here q_D is the Debye-Hückel inverse screening length, $(\xi-1)$ and q_e^{-2} determine[7] the compressibility of the OCP and the interacting electrons, respectively. $S(0)$ is the value of $S(q)$ in the long-wavelength limit (for which an experimental value is used) and is related to the compressibility of the liquid metal.

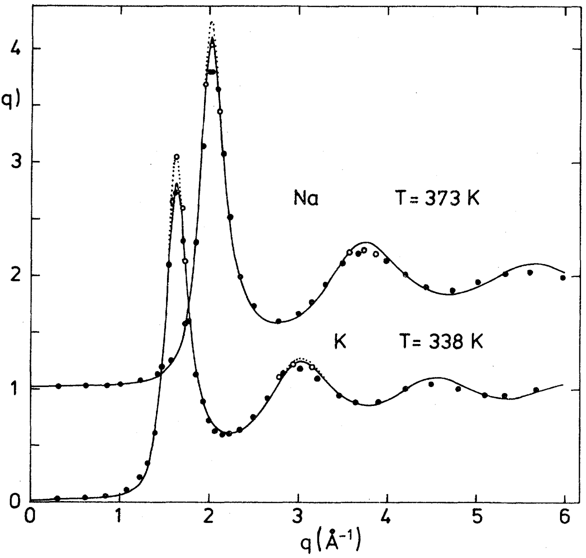

FIG. 1. Structure factor $S(q)$ of liquid sodium and potassium vs wave number q, compared with the experimental data (filled circles) of Greenfield, Wellendorf, and Wiser (Ref. 16). Open circles near the first two peaks represent the data of Huijben and van der Lugt (Ref. 17). In other q regions, these two sets of data are indistinguishable on the scale of the present graph. In all the graphs of this paper, the dotted curve is obtained when the effect of screened dipole-dipole interaction is not taken into account; the full curve represents the results obtained in the presence of such dipole-dipole interaction, using the values of α_0 and u_0 as listed in Table I.

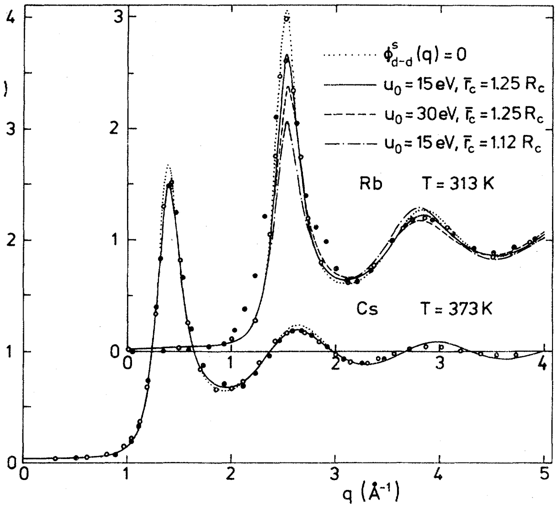

FIG. 2. Structure factor of liquid rubidium and cesium is compared with the x-ray data (filled circles) of Zei (Ref. 19). Open circles on the graph for Rb indicate the molecular-dynamics results of Rahman (Ref. 20). The x-ray data of Huijben and van der Lugt (Ref. 17) for Cs is also represented by open circles.

It is now straightforward to calculate the structure factors of different liquid alkali metals, and the results obtained are presented in Figs. 1 and 2. The results for lithium are not shown here as they are of the same quality as the one obtained for sodium. It is encouraging to note that these results are practically the same as obtained in I and the agreement with experimental data[16–20] is very good. The first peak height for Li and Na, however, seems to be a bit overestimated, although it should be mentioned that there exists a large discrepancy (see Fig. 4 of Ref. 16) in the magnitude of this quantity among different experimental measurements.

B. Results for the structure factor with finite core polarization

The perturbation correction to the pairwise potential between polarizable ions in simple metals, due to the screened fluctuating dipole interactions, has been calculated before.[11,21] Following Mon and co-workers,[11,22] it is given by

$$\phi^s_{d\text{-}d}(r)=-\int_0^\infty\frac{du}{2\pi}\frac{\hbar}{e^4}\alpha^2(iu)\times\left[\left[\frac{\partial^2\phi(r,iu)}{\partial r^2}\right]^2+\frac{2}{r^2}\left[\frac{\partial\phi(r,iu)}{\partial r}\right]^2\right] , \qquad (7)$$

where $\alpha(iu)$ is the frequency-dependent ionic polarizability and $\phi(r,iu)$ is the Fourier transform of the screened dynamic interaction

$$\phi(k,iu)=\phi_c(k)\left[1+\cos^2[kr_c(u)]\left[\frac{1}{\epsilon(k,iu)}-1\right]\right] . \qquad (8)$$

TABLE I. Inputs used in the calculation of the present results for different alkali metals. The approximate melting temperatures are underlined.

Metal	T (K)	n (g/cm^3)	Γ	$\frac{R_c}{a_0}$	$\frac{\sigma}{a_0}$	α_0 (Å^3)	u_0 (eV)
Li	573	0.498	165.0	0.414	1.532	0.03	50
Na	$\underline{373}$	0.928	209.2	0.433	1.557	0.2	30
K	$\underline{338}$	0.827	186.2	0.463	0.545	0.9	20
Rb	$\underline{313}$	1.475	187.8	0.462	1.546	1.7	15
Cs	$\underline{303}$	1.840	180.3	0.476	1.541	2.5	10
Cs	373	1.770	144.6	0.469	1.518	2.5	10

Here $\epsilon(k,iu)$ is the frequency and wave-vector-dependent dielectric function of the conduction electrons for which we use an expression due to Vashishta and Singwi.[14] Further, following Mon *et al.*, r_c $(u\neq 0)$ is approximated by a constant $\bar{r}_c$ whose value we choose to be equal to $1.25R_c$ (unless otherwise stated) for all the liquid alkali metals. The only other unknown quantity in Eq. (7) is the ionic polarizability which is approximated[11] in the form

$$\alpha(iu)=\frac{\alpha_0}{1+(u/u_0)^2}\ , \tag{9}$$

where α_0 is the static polarizability for which experimental values[23] are available. The parameter u_0 is a measure of the binding of the electrons in the ion whose typical values can be inferred from ionization potential data.

It is now possible to calculate $S(q)$ from Eq. (1) including the effect of $\phi^s_{d-d}(q)$ which is just the Fourier transform of Eq. (7). The parameter σ [and hence $S_0(q)$] remains the same as in the earlier case since it refers to the reference system. Furthermore, since the fluctuating dipole-dipole interaction has a short range, $\phi^s_{d-d}(q)$ is expected to be very small compared with $\phi_{ps}(q)$ in the $q\rightarrow 0$ limit. This means that the Ashcroft core radius R_c may again be safely determined from Eq. (6). R_c and σ along with other relevant parameters are listed in Table I for different alkali metals.

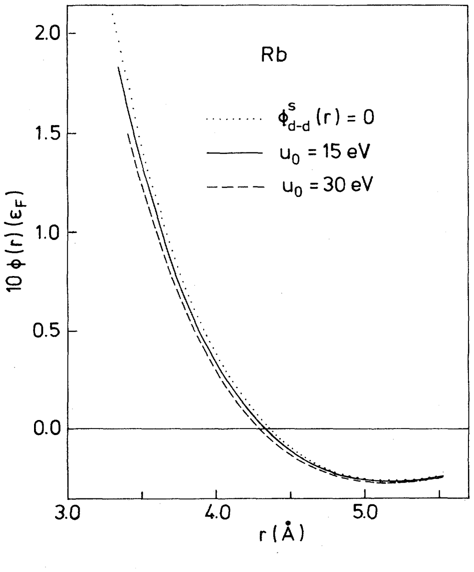

FIG. 3. Effective ion-ion potential in liquid Rb is plotted with and without the screened dipole-dipole interaction.

The numerical computations required for the evaluation of $\phi^s_{d-d}(q)$ involves a three-dimensional integral; in comparison with that the numerical work needed to determine $\phi_{ps}(q)$ is trivial. The results obtained for the structure factor with the full perturbation potential $\phi(q)$ are plotted in Figs. 1 and 2 for different alkali metals. For Li and Na, the effect of the fluctuating dipole-dipole interaction is very small and amounts only to a weak reduction of the first peak height. This is reasonable as the polarizability (see Table I) for these metals is very small. For heavier alkali metals the effect of $\phi^s_{d-d}(q)$ on $S(q)$ is comparatively large and is noticeable at the second peak also. Note that the value of parameter u_0 is taken in descending order when going from Li to Cs since the binding energies are expected to decrease with increase in core size. As can be seen from Fig. 2 for rubidium, the results for $S(q)$ are reasonably sensitive to the values of u_0 and $\bar{r}_c$. In Fig. 3, we have plotted the ion-ion potential with and without the screened dipole-dipole interaction. It follows from this figure that the dipole-dipole interaction only softens the interionic potential slightly.

III. CONCLUDING REMARKS

The effect of core polarization on the structure factor of alkali metals turns out to be small. This is in contrast to liquid gallium,[11] for instance, where this effect seems to give rise to a highly asymmetric first peak. As a matter of fact, the latest x-ray data[19] on $S(q)$ of liquid Rb (see Fig. 2) and Cs show a slightly asymmetric first peak. We, therefore, expected that it might be possible to explain this effect by including core polarization, which, however, is not the case—at least within the present model. The origin of this may lie in the fact that the interionic potential for Ga, as used by Mon *et al.*[11] in their Monte Carlo simulations, contained a secondary minimum, whereas the interionic potential for alkali metals exhibits no such feature.

There has also been some discussion[6,7] about the value of the parameter Γ to be used for liquid alkali metals. For example, in order to have a better agreement of the first peak height in $S(q)$ with experimental data, Chaturvedi, Rovere, Senatore, and Tosi[6] have scaled down the values of Γ by requiring that its value Γ_f^{alk} at a temperature and density at which an alkali metal freezes should be equal to Γ_f^{OCP}, the value of Γ at which an ideal classical one-component plasma freezes. These authors used $\Gamma_f^{\mathrm{OCP}} = 155$. The present calculation seems to indicate that such a scaling is not necessary if one takes into account the effect of the screened dipole-dipole interaction, because the main effect of this interaction on $S(q)$ is to reduce its first peak height. Since this effect is small and its evaluation is quite involved, it may be reasonable to neglect this effect altogether and calculate $S(q)$ using Eq. (5) and the above-mentioned scaling. In that connection it may be noted that the latest estimate[24] of Γ_f^{OCP} based on a more careful location of the liquid-solid transition in an OCP gives $\Gamma_f^{\mathrm{OCP}} = 178$. For heavier alkali metals, this latter value is quite close to Γ_f^{alk} as calculated (see Table I) from Eq. (3). Thus the above-mentioned scaling does not practically affect the results for Cs, Rb, and K, except for reducing the first peak height by about 1–3%. However, for Li and Na, the difference between Γ_f^{OCP} and Γ_f^{alk} as calculated from Eq. (3) is large, and using such a scaling would reduce the first peak height of $S(q)$ by about 8%—thus further improving the agreement with the experimental data.

It follows from the present study that in any practical calculation of $S(q)$ for alkali metals, one can safely neglect the contribution arising from the core-polarization effect which is, in fact, computationally much involved. Then the expression for $S(q)$ becomes the same as used in I and the computational work involved is insignificant. However, in contrast to I, the charged-hard-sphere diameter σ is not anymore an adjustable parameter but is determined from Eq. (4). Results obtained for the structure factor of all the alkali metals are once again in very good agreement with the experimental data. This can be taken as a further support for the validity of Eq. (4).

ACKNOWLEDGMENTS

This work has been supported by Deutsche Forschungsgemeinschaft within Sonderforschungsbereich 130.

---

[1] N. W. Ashcroft and J. Lekner, Phys. Rev. 165, 83 (1966); A. J. Greenfeld, N. Wiser, M. R. Leenstra, and W. van der Lugt, Physica 59, 571 (1972).

[2] R. E. Jacobs and H. C. Anderson, Chem. Phys. 10, 73 (1975); R. Kumaravadivel and R. Evans, J. Phys. C 9, 3877 (1976); I. L. McLaughlin and W. H. Young, J. Phys. F 12, 245 (1982).

[3] A. M. Bratkovsky, V. G. Vaks, and A. V. Trefilov, J. Phys. F 12, 611 (1982), and references therein.

[4] M. Ross, H. E. DeWitt, and W. B. Hubbard, Phys. Rev. A 24, 1016 (1981); K. K. Mon, R. Gann, and D. Stroud, *ibid.* 24, 2145 (1981).

[5] H. Minoo, C. Deutsch, and J. P. Hansen, J. Phys. (Paris) Lett. 38, L191 (1977); R. Evans and T. J. Sluckin, J. Phys. C 14, 3137 (1981).

[6] D. K. Chaturvedi, M. Rovere, G. Senatore, and M. P. Tosi, Physica B 111, 11 (1981); Nuovo Cimento 62B, 375 (1981); M. Iwamatsu, R. A. Moore, and S. Wang, Phys. Lett. 92A, 283 (1982).

[7] H. B. Singh and A. Holz, Phys. Rev. A 28, 1108 (1983).

[8] M. J. Gillian, J. Phys. C 1, L1 (1974).

[9] R. G. Palmer and J. D. Weeks, J. Chem. Phys. 58, 4171 (1973).

[10] H. B. Singh, J. Stat. Phys. 33, 371 (1983).

[11] K. K. Mon, N. W. Ashcroft, and G. V. Chester, Phys. Rev. B 19, 5103 (1979).

[12] S. Galam and J. P. Hansen, Phys. Rev. A 14, 816 (1976); F. Postogna and M. P. Tosi, Nuovo Cimento 55B, 399 (1980).

[13] Except that the direct space correlation functions exhibit a small discontinuity at the hard-sphere boundary. Its origin lies in the hard-sphere nature of the approximation and the fact that σ is not constrained to make this inherent discontinuity zero as, e.g., in Refs. 6 and 8.

[14] P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).

[15] G. Senatore and M. P. Tosi, Phys. Chem. Liq. 11, 365 (1982).

[16] A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A 4, 1607 (1971).

[17] M. J. Huijben and van der Lugt, Acta Crystallogr. Sect. A 35, 431 (1979).

[18] H. Ruppersberg and H. Egger, J. Chem. Phys. 63, 4095 (1975).

[19] M. S. Zei, Phys. Rev. B 24, 4509 (1981).

[20] A. Rahman, Phys. Rev. A 9, 1667 (1974); J. R. D. Copely and J. M. Rowe, *ibid.* 9, 1656 (1974).

[21] J. J. Rehr, E. Zaremba, and W. Kohn, Phys. Rev. B 12, 2062 (1975).

[22] Following Mon *et al.* (Ref. 11), we shall also not modify our pair potentials by a small background dielectric constant resulting from the ions regarded as a dielectric continuum.

[23] A. Dalgarno, Adv. Phys. 11, 281 (1962).

[24] W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. A 26, 2255 (1982).