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Structure factor of liquid alkali metals

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Liquid alkali metals are treated as a system of charged hard spheres (CHS) in the background of interacting electrons. Such a system of CHS in a uniform background of electrons has been solved exactly by Palmer and Weeks in a mean spherical approximation. With the use of this model as a reference, the effect of responding electrons is taken into account in a linear-response approximation. The resulting expression for the structure factor involves the CHS diameter as the only free parameter and is very simple to compute. It reduces to the familiar Ashcroft-Lekner model when the charge on the hard spheres is taken to be zero. The results obtained for the static structure factor of all the alkali metals at different temperatures are in excellent agreement with the experimental data.

I. INTRODUCTION

One of the important properties characterizing a liquid is its static structure factor $S(q)$, which is a measure of particle correlations in the reciprocal space. Apart from that an accurate knowledge of this quantity is crucial[1] for studying numerous thermodynamic and transport properties of the system.

All the earlier attempts[2-8] to calculate $S(q)$ of liquid alkali metals had the system of neutral hard spheres as their reference system. Such models are quite useful for studying inert-gas liquids or polyvalent metals but do not give satisfactory results[2-9] for alkali metals. Among these the simplest and most extensively used model is due to Ashcroft and Lekner.[2] In this model, the structure factor is obtained from the exact solution[10] of the Percus-Yevick equation for hard spheres. It involves only one independent parameter—the hard-sphere diameter which is obtained to get best fit of $S(q)$ with the experimental data. Although this model gives good results for other systems, no value of the hard-sphere diameter could fit[2,3] the alkali-metals data satisfactorily. In fact Greenfield *et al.*[3] have introduced one more parameter in this model and adjusted these two parameters independently to get a best fit to their experimental data for Na and K. The results, however, remained unsatisfactory as concluded by the authors.[3] The reason for general inadequacy of neutral hard-sphere models in the case of alkali metals seems to lie in the fact[9] that their repulsive cores are comparatively soft.

This implied the need for a better reference system for alkali metals and the system of classical one-component plasma (OCP) offered a natural choice since structurally they are quite similar.[11,12] According to this model the reference system consists of Coulombically interacting postively charged point charges in a uniform background of conduction electrons. The recent activity[11-17] in this field has shown that OCP is a better reference system than the neutral hard spheres for alkali metals. Chaturvedi *et al.*[16] have obtained an expression for the structure factor using this model and have applied it with good success to calculate $S(q)$ of some alkali metals near their melting temperatures. However it is not easy to use their result as it involves a large number of parameters, the determination of which requires the simultaneous solution of many complicated equations. Also they have used empirically scaled values of the plasma parameter Γ (e.g., 155 instead of the actual value 209 for sodium) the physical meaning of which is not clear.

The purpose of the present paper is to investigate the possibility of an accurate but simple model which could be applied with about the same ease to alkali metals as the Ashcroft-Lekner model to other systems. This is highly desirable for calculating other metallic properties.[1] The approach shall be similar to that of Chaturvedi *et al.*[16] While taking the classical OCP as the reference system, we keep in mind that in this model the positive ions are taken as point charges. This is not so in actual alkali metals whose ionic diameters are of the same order of magnitude as the Coulomb hole in the corresponding OCP. Therefore, we take a slightly different reference system—a system of charged hard spheres (CHS) in a uniform neutralizing background. Essentially this system is same as the usual OCP except that its particles (positive ions) have finite extension in space. This system has been solved exactly by Palmer and Weeks[18] within a mean spherical approximation. We use their result as such and account for the effect of electron screening using a linear screening approximation.[13,14] The static structure factor is then evaluated for all the alkali metals at different temperatures. The results obtained are in excellent agreement with the experimental[19–24] data.

II. THE MODEL

As already introduced, our model for liquid alkali metals is a system of charged hard spheres in the background of interacting electrons. To make the paper self-contained, we quote the exact result of Palmer and Weeks[18] for the direct correlation function of the system of CHS in a uniform background of electrons:

$$C_0(x)=\begin{cases} A+Bx+Cx^2+Dx^3+Ex^5 & \text{for } x<1 \\ -\gamma/x & \text{for } x>1 \end{cases} \tag{1}$$

where $x=r/\sigma$, σ being the effective hard-core diameter of the charged spheres. This diameter can be appreciably larger than the actual ion-sphere diameter in alkali metals due to strong Coulomb repulsion between the ion cores. The coefficients of $C_0(x)$ are conveniently written in terms of dimensionless variables,

$$\eta=\frac{\pi}{6}n\sigma^3,\quad \gamma=\beta\frac{(Ze)^2}{\epsilon_0\sigma},\quad \kappa=(24\eta\gamma)^{1/2} \tag{2}$$

which determine the packing fraction, ion-ion coupling strength, and the Debye-Hückel inverse screening length, respectively, for the system at a given density n and temperature T. Further, $\beta=(k_BT)^{-1}$, Ze is the ionic charge, and ϵ_0 is the static dielectric constant of the system. Since the electron background is uniform, its dielectric constant is unity. However, the ion cores have finite dimensions and thus their polarization should in principle give rise to ϵ_0 which should be slightly greater than unity. For the present we shall take $\epsilon_0=1$ to keep the matter simple. The familiar plasma parameter Γ is related to γ as $\Gamma=(\sigma/a_0)\gamma$ where a_0 is determined from the average volume available to an ion, i.e., $a_0=(3/4\pi n)^{1/3}$. The coefficients in Eq. (1) are given[18] by

$$A=-\frac{(1+2\eta)^2}{(1-\eta)^4}+\frac{Q^2}{4(1-\eta)^2}-\frac{(1+\eta)Q\kappa}{12\eta}-\frac{(5+\eta^2)\kappa^2}{60\eta}, \tag{3a}$$

$$B=6\eta M^2,\quad C=\kappa^2/6, \tag{3b}$$

$$D=\frac{\eta}{2}(A+\kappa^2 U), \tag{3c}$$

and

$$E=\eta\kappa^2/60. \tag{3d}$$

Here

$$Q=\frac{1+2\eta}{1-\eta}\left[1-\left[1+\frac{2(1-\eta)^3\kappa}{(1+2\eta)^2}\right]^{1/2}\right], \tag{4a}$$

$$M=Q^2/24\eta-(1+\tfrac{1}{2}\eta)/(1-\eta)^2, \tag{4b}$$

and

$$U=-(1+\eta-\eta^2/5)/(12\eta)-(1-\eta)Q/(12\eta\kappa). \tag{4c}$$

The static structure factor $S_0(q)$ of the reference system is related to its direct correlation function by the familiar relation

$$S_0(q)=\frac{1}{1-nC_0(q)}. \tag{5}$$

It is straightforward but lengthy to Fourier transform Eq. (1). The result is given by

$$\begin{aligned} nC_0(q)=\frac{24\eta}{q^6}\{&Aq^3(\sin q-q\cos q)+Bq^2[2q\sin q-(q^2-2)\cos q-2]+cq[(3q^2-6)\sin q-(q^2-6)q\cos q]\\ &+D[(4q^2-24)q\sin q-(q^4-12q^2+24)\cos q+24]\\ &+E[6(q^4-20q^2+120)q\sin q-(q^6-30q^4+360q^2-720)\cos q-720]/q^2-\gamma q^4\cos q\}, \end{aligned} \tag{6}$$

where only in this equation q is expressed in units of σ^{-1}. For a given temperature and density, the only parameter involved in Eq. (5) is the diameter σ of a CHS, which makes the application of this approximation very simple. A reasonably good estimate of σ is obtained by requiring that the CHS pair correlation should be continuous at the hard-sphere boundary.[25] This criterion can be seen to imply the equation $M=0$, whose solution determines σ uniquely. We shall refer to this value of the CHS diameter as σ_0.

In the long-wavelength limit, Eq. (5) reduces to

$$\lim_{q\to 0} S_0(q)=\frac{q^2\sigma^2}{24\eta\gamma}\left[1+\frac{\alpha-1}{24\eta\gamma}q^2\sigma^2\right], \tag{7}$$

where

$$\alpha=24\eta\left[\frac{A}{3}+\frac{B}{4}+\frac{C}{5}+\frac{D}{6}+\frac{E}{8}+\frac{\gamma}{2}\right]. \tag{8}$$

Equation (7) represents the typical plasma-mode behavior and is thus in contrast to the sound-wave mode actually found in metals in this limit. It is known,[14] however, that the bare OCP plasma mode transforms into the required acoustic mode in metals if the effect of electron screening is taken into account. Evidently the electrons in metals do not form a stiff background as assumed in the reference system, rather they are quite mobile and move about to screen out any charge imbalances.

The effect of responding electrons on the ionic motion is taken into account by assuming weak electron-ion coupling which is also the basis of standard pseudopotential approach.[1] Within a linear screening approximation,[13,14,16] the static structure factor of a liquid metal is given by

$$S(q)=\frac{S_0(q)}{1+n\beta\tilde{v}(q)S_0(q)}, \tag{9}$$

where

$$\tilde{v}(q)=\frac{v^2(q)}{\phi(q)}\left[\frac{1}{\epsilon(q)}-1\right] \tag{10}$$

is the attractive screening correction to the direct ion-ion potential. In Eq. (10), $v(q)$ is the electron-ion pseudopotential, $\phi(q)=4\pi e^2/q^2$ is the Fourier transform of bare Coulombic interaction between two electrons, and $\epsilon(q)$ is the wave-vector-dependent dielectric function of interacting electrons. For $\epsilon(q)$ an expression due to Vashishta and Singwi[26] is used since it is known to give accurate descriptions of electron correlations in metals. The pseudopotential is approximated by the simplest function available, which is obtained within the Ashcroft empty-core model[27] in the form

$$v(q)=-\frac{4\pi Ze^2}{q^2}\cos qR_c, \tag{11}$$

where Ashcroft core radius R_c is expected to be close to the actual ionic radius. In the literature,[28] R_c is determined from Fermi-surface or phonon-dispersion data of crystalline metals, or from the resistivity of liquid metals, and so on. We shall determine it[16] from the compressibility sum rule which relates the isothermal compressibility of the system to the long-wavelength limit $S(0)$ of its structure factor $S(q)$. Taking the $q\to 0$ limit in Eq. (9), we get

$$R_c=\left[\frac{\sigma^2}{24\eta\gamma}\left[\alpha-1+\frac{1}{S(0)}\right]-q_e^{-2}\right]^{1/2}, \tag{12}$$

where q_e^2 is the coefficient of q^{-2} in the long-wavelength expansion[26] of $\epsilon(q)$ and determines the compressibility of interacting electrons. It is trivial to see that if $Z=0$ (as is the case for neutral hard spheres), then Eq. (9) reduces to the Ashcroft-Lekner[1,2] model.

We now proceed to the calculation of the structure factor using Eq. (9). The value of the unknown CHS diameter σ is taken to be equal to σ_0. Like Chaturvedi *et al.*,[16] we also get unphysical (negative) values for $S(q)$ near its principal peak region. To overcome this difficulty, we truncate[16] $v(q)$ after its first node which in alkali metals occurs roughly around $q \lesssim 2q_F$, q_F being the electron Fermi wave vector. Similar truncation of pseudopotentials is desirable[28] to appropriately take into account the nonlocal effects and the optimization of the pseudopotentials in the sense of getting smoothest pseudo wave functions. Recently Senatore and Tosi[29] have convincingly argued the need for such a truncation within the spirit of a standard optimized random phase approximation[30] for $S(q)$.

III. RESULTS AND DISCUSSION

We present our results for the static structure factor of Na at 473 and 373 K in Fig. 1 and compare them with the experimental data.[19–20] Results obtained with $\sigma=\sigma_0$ are in reasonably good agreement

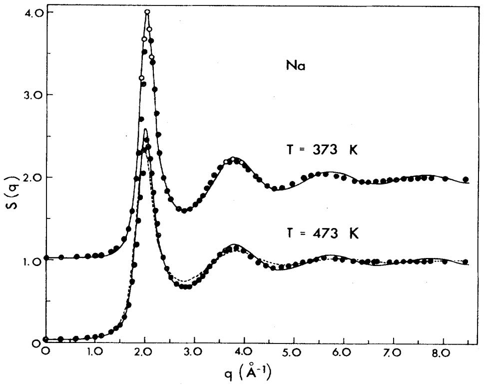

FIG. 1. The structure factor $S(q)$ of liquid sodium at 473 and 373 K versus wave number q, compared with the experimental data (filled circles) of Greenfield *et al.* (Ref. 19). Dashed curve is obtained for $\sigma=\sigma_0$ and full-curve results when the charged-hard-sphere diameter is taken instead as an adjustable parameter σ_P. Open circles near the first two peaks at lower temperature represent the experimental data of Huijben and van der Lugt (Ref. 20). In other q regions these two sets of data are indistinguishable on the scale of the present graph.

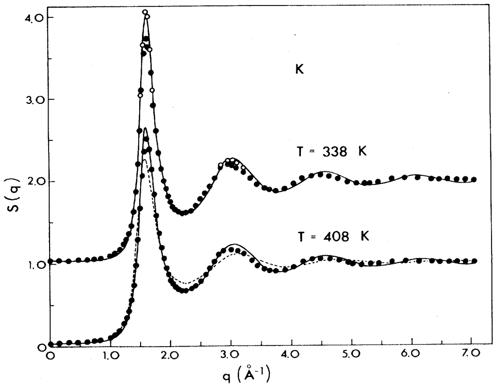

FIG. 2. $S(q)$ of liquid potassium at 408 and 338 K versus q. The curves and experimental data are labeled as in Fig. 1.

with the experimental data[19] of Greenfield, Wellendorf, and Wiser (GWW), as is shown by the dashed curve. This is encouraging in view of the simplicity of the model and the fact that there is no adjustable parameter. These results are of better quality than most of the results obtained[2–8] using neutral hard spheres as the reference system and with a few free parameters therein. We find, however, that if σ is taken as a free parameter, then there is a marked improvement in our results and the agreement with experiments becomes quantitative (as shown by the continuous curves) in all respects. We do not determine σ by a least-squares fit to the experimental data. Rather, its value is increased beyond σ_0 in small steps until the first minimum of $S(q)$ is well reproduced. So in this sense σ is determined through a one-point fit to the experimental data. We refer to this value of σ as σ_P, and hereafter the present results refer to this value of σ. It is interesting to note that the value of σ_P for all the alkali metals at different temperatures is about 10% higher than the corresponding value of σ_0.

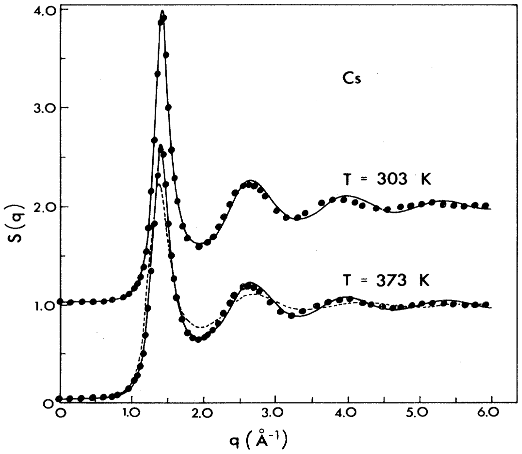

FIG. 3. The structure factor of liquid cesium at 373 and 303 K versus q. The curves are labeled as in Fig. 1, and the experimental data (filled circles) used for comparison are due to Huijben and van der Lugt (Ref. 20).

We have chosen to determine σ from the first minimum of $S(q)$ in contrast to the usual practice of fitting the first maximum (the so called principal maximum). We are prompted to do so because there is a lot of discrepancy between different experiments in the value of the height of the first maximum. It is not so for the value of the depth of the first minimum. For example, the first peak height as measured in earlier[19] experiments deviates about 40% from the accurate measurements of GWW.[19] However, such a deviation in the depth of the first minimum is only about 4%. Another accurate measurement for $S(q)$ of Na, K, and Cs has been reported[20] recently by Huijben and van der Lugt (HL) using the x-ray diffraction method in transmission geometry like GWW. On the scale of the present graphs their data for Na and K are indistinguishable from those of GWW except that the amplitude of their[20] first maximum for Na and K is about 10% higher than that of GWW. Huijben and van der Lugt have attributed this discrepancy mainly to the fact that their[20] detection system had a better resolution. This difference is not noticeable after the second peak. In contrast, there is no discrepancy between these two experiments for either Na or K as far as the depth of the first minimum is concerned.

As seen in Fig. 1, the agreement of the present results with the data of GWW (Ref. 19) is good except that the calculated first peak height is slightly higher. However, as shown (by open circles) for $T=373$ K, this peak height is in good agreement with the data of HL.[20] Such a comparison could not be shown at higher temperatures in Figs. 1 and 2 since for these temperatures HL have no data. In the q region where the data of HL are not shown, they are indistinguishable from those of GWW. Again for the sake of clarity, the theoretical results obtained with $\sigma=\sigma_0$ are not shown at lower temperatures in Figs. 1—3. Their trends relative to experimental data are similar to those at higher temperatures. In Fig. 2, we present our results for $S(q)$ of K at 408 and 338 K. The first peak height is again slightly higher than that of GWW and is in good agreement with the data of HL as shown for $T=338$ K. Our results for Cs at 373 and 303 K are plotted in Fig. 3 and are compared with the experimental data of HL. The agreement, as in the case of sodium and potassium, is excellent. It may be noted that all the experimental data plotted in Figs. 1—3 are read from tables.

The experimental situation for the accurate determination of $S(q)$ of Rb and Li does not seem to be

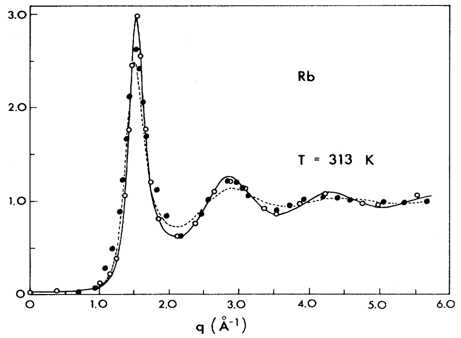

FIG. 4. $S(q)$ of liquid rubidium versus q at $T=313$ K. The curves are labeled as in Fig. 1. Filled circles represent the x-ray data of Zei (Ref. 21) and the open circles are the molecular-dynamics results of Rahman (Ref. 23).

so good as for Na, K, and Cs. An x-ray diffraction experiment on Rb has been carried out only recently by Zei.[21] There is an appreciable difference[21,22] in the first peak height as measured by different neutron diffraction experiments.[22] There exists also a molecular-dynamics (MD) calculation[23] for $S(q)$ of Rb. The agreement of the MD data of Rahman[23] and the neutron-scattering data of Copely and Rowe[22] is good except that the first peak height in the latter is a bit higher. In Fig. 4, we present our results for Rb at 313 K and compare them with the data of Zei[21] and Rahman.[23] The agreement is very good—especially with the MD data of Rahman. To our knowledge, the only experimental data for Li is due to the x-ray scattering experiment of Ruppersberg and Egger[24] at 573 K. The MD calculation[23] of $S(q)$ is at a different temperature. Our results are shown in Fig. 5 at 573 K and are in good agreement with the experimental data.

In order to facilitate the further application of this model and to bring out the similarities among different alkali metals, we have tabulated the inputs used along with the packing fraction η in Table I.

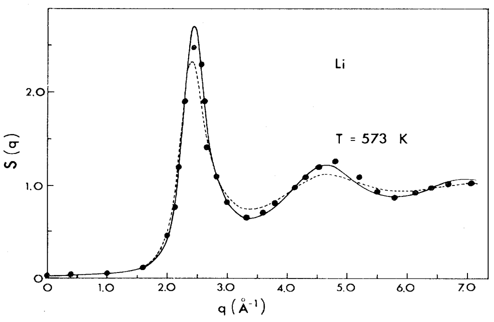

FIG. 5. The structure factor of liquid lithium versus wave number q at 573 K. Curves are again labeled as in Fig. 1 and the experimental results (filled circles) used for comparison are due to Ruppersberg and Egger (Ref. 24).

TABLE I. The inputs used in the calculation of present results for different alkali metals along with the packing fraction η. The approximate melting temperatures are underlined. $a_0=(3/4\pi n)^{1/3}$.

Metal	T (K)	n (g/cm^3)	$\frac{R_c}{a_0}$	$\frac{\sigma_P}{a_0}$	η
Li	573	0.498	0.43	1.51	0.430
Na	$\underline{373}$	0.928	0.45	1.52	0.449
Na	473	0.903	0.45	1.50	0.418
K	$\underline{338}$	0.827	0.47	1.54	0.457
K	408	0.811	0.47	1.51	0.430
Rb	$\underline{313}$	1.475	0.47	1.54	0.452
Cs	$\underline{303}$	1.840	0.48	1.54	0.457
Cs	373	1.770	0.47	1.51	0.430

For a given metal, T and n are naturally given and R_c was determined from Eq. (12) using the experimental value of the compressibility $S(0)$. The only free parameter σ_P was determined from the one-point fit of the experimental data at the first mimimum of $S(q)$. η was calculated from Eq. (2). It can be seen that there is a wide variation in the absolute value of R_c and σ_P from one metal to another. However, it is interesting to see from Table I that the values of R_c/a_0 and σ_P/a_0 are almost constant for all alkali metals near their melting temperatures. This indicates that different liquid alkali metals are scaled versions[2,16,20] of each other. Further it is remarkable to note that the packing fraction of all the alkali metals at their melting temperatures is equal (within 2%) to 0.45. Thus to calculate the structure factor of different alkali metals near their melting temperatures, σ can be simply determined from $\eta=0.45$ without affecting the present results in any way.

To conclude, we have given a simple but accurate model for calculating the structure factor of liquid alkali metals. Because of its simplicity it should be quite practical for calculating the thermodynamic properties and transport coefficients of these metals. We have proposed but not taken into account the effect of core polarization, which is expected to be small. However, it is desirable to take core polarization into acount since it may be one physical reason for the scaling[16] of plasma parameter Γ. We hope to investigate this problem in the near future.

ACKNOWLEDGMENT

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