Structure Factors of Liquid Sodium and Potassium

R. V. Gopala Rao and A. K. Murthy

Physical Chemistry Section, Jadavpur University, Calcutta

(Z. Naturforsch. **30 a**, 383–384 [1975]; received December 31, 1974)

The liquid structure factors of sodium and potassium have been calculated by taking a Lennard-Jones 6:12 potential as a perturbation of the hard sphere potential in the mean spherical model approximation. Typical results are in good agreement with the experimental ones.

Recent advances in statistical mechanics of simple fluids employing perturbation theory methods [1, 2] suggest that a similar approach may be useful for liquid metals [3]. A perturbation version of the Percus-Yevick (PY) hard sphere model [4] is the mean spherical model (MSM) approximation [5]. Presently we propose to take a Lennard-Jones 6:12 potential as a perturbation of the hard sphere potential.

In MSM, the direct correlation function, $C(r)$, can be written as,

$$C(r) = C_{\mathrm{WT}}(r)\,, \quad 0 < r \leqq \sigma \tag{1}$$

$$C(r) = -\frac{U(r)}{k_{\mathrm{BT}}}\,, \quad r \geqq \sigma \tag{2}$$

where $C_{\mathrm{WT}}(r)$ is the Wertheim-Thiele solution of the PY equation for hard sphere systems [4] and $U(r)$ is the pair potential, being presently represented by a Lennard-Jones 6:12 potential.

$C_{\mathrm{WT}}(r)$ can conveniently be written as [4]

$$C_{\mathrm{WT}}(r) = -\frac{1}{(1-\eta)^4}\left\{(1+2\eta)^2 - 6\eta(1+\eta/2)^2 \cdot\left(\frac{r}{\sigma}\right) + \eta/2(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right\} \tag{3}$$

and

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Here the packing fraction, η is related to the hard sphere diameter σ by $\eta = \pi\varrho\sigma^3/6$, ϱ being the average number density.

Hence, $\tilde{C}(k)$, the Fourier transform of $C(r)$ [6] is written as,

$$\varrho\tilde{C}(k) = \left[\frac{-24\eta(1+2\eta)^2}{(1-\eta)^4}\right]\left[\frac{\sin k\sigma - k\sigma\cos k\sigma}{(k\sigma)^3}\right] + \left[\frac{144\eta^2(1+\eta/2)^2}{(1-\eta)^4}\right][(2k\sigma\sin k\sigma + (2-k^2\sigma^2) \times\cos k\sigma - 2)/(k\sigma)^4] + \left[\frac{-12\eta^2(1+2\eta)^2}{(1-\eta)^4}\right]\{[(4k^3\sigma^3 - 24k\sigma)\sin k\sigma - (k^4\sigma^4 - 12k^2\sigma^2 + 24) \times\cos k\sigma + 24]/(k\sigma)^6\} - \frac{4\pi\varrho}{k}\int_{\sigma}^{\infty} r\cdot\frac{U(r)}{k_{\mathrm{BT}}}\cdot\sin kr\,\mathrm{d}r \tag{4}$$

and is related to the liquid structure factor, $S(k)$ by

$$S(k) = [1 - \varrho\tilde{C}(k)]^{-1}\,. \tag{5}$$

The integral part of Eq. (4) has been solved numerically. The potential parameters σ and $\varepsilon/k_{\mathrm{B}}$ have been fitted with the experimental value to give the correct first peak height. $S(k)$ for liquid sodium and potassium (near the melting temperatures) has been calculated from Eqs. (4) and (5) and the results are shown in Fig. 1 along with the experimental results [7]. The potential parameters used in the

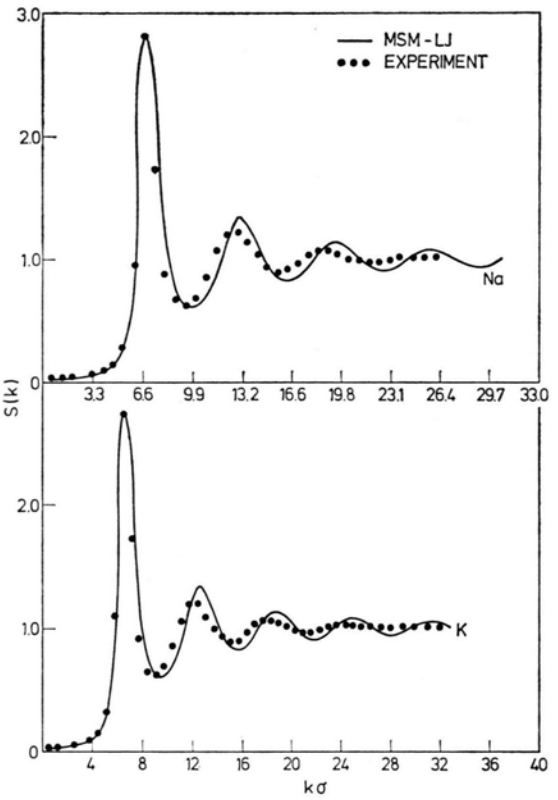

Fig. 1. Structure factor of liquid sodium (373 K) and potassium (338 K).

Reprint requests to Prof. R. V. Gopala Rao, Physical Chemistry Section, Jadavpur University, *Calcutta 700032, India.*

calculations are:

$$\text{for Na:}\quad \sigma = 3.30\,\text{Å} \quad \text{and} \quad \varepsilon/k_B = 68.29\,\text{K},$$
$$\text{for K:}\quad \sigma = 4.10\,\text{Å} \quad \text{and} \quad \varepsilon/k_B = 54.36\,\text{K}.$$

The agreement obtained between the theory and experiment, especially upto the first peak region, which incidentally determines the electronic transport properties of liquid metals [8], is quite encouraging and suggests that the concept of pairwise interactions is a useful one even in the theory of liquid metals.

AKM is grateful to the University Grants Commission, New Delhi, for partial financial support and also to Dr. R. K. Datta for his help in computer programming.

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