

Structure Factors of Liquid Sodium and Potassium

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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 metals³. A perturbation version of the Percus-Yevick (PY) hard sphere model⁴ is the mean spherical model (MSM) approximation⁵. 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,

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

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

where $C_{WT}(r)$ is the Wertheim-Thiele solution of the PY equation for hard sphere systems⁴ and $U(r)$ is the pair potential, being presently represented by a Lennard-Jones 6:12 potential.

$C_{WT}(r)$ can conveniently be written as⁴

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

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

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

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

$$\begin{aligned} \rho \tilde{C}(k) = & \left[\frac{-24\eta(1+2\eta)^2}{(1-\eta)^4} \right] \left[\frac{\sin k\sigma - k\sigma \cos k\sigma}{(k\sigma)^3} \right] + \left[\frac{144\eta^2(1+\eta/2)^2}{(1-\eta)^4} \right] [(2k\sigma \sin k\sigma + (2-k^2\sigma^2) \\ & \times \cos k\sigma - 2)/(k\sigma)^4] + \left[\frac{-12\eta^2(1+2\eta)^2}{(1-\eta)^4} \right] \{ [(4k^3\sigma^3 - 24k\sigma) \sin k\sigma - (k^4\sigma^4 - 12k^2\sigma^2 + 24) \\ & \times \cos k\sigma + 24]/(k\sigma)^6 \} - \frac{4\pi\rho}{k} \int_{\sigma}^{\infty} r \cdot \frac{U(r)}{k_{BT}} \cdot \sin kr \, dr \end{aligned} \quad (4)$$

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

$$S(k) = [1 - \rho \tilde{C}(k)]^{-1}. \quad (5)$$

The integral part of Eq. (4) has been solved numerically. The potential parameters σ and ϵ/k_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 results⁷. The potential parameters used in the

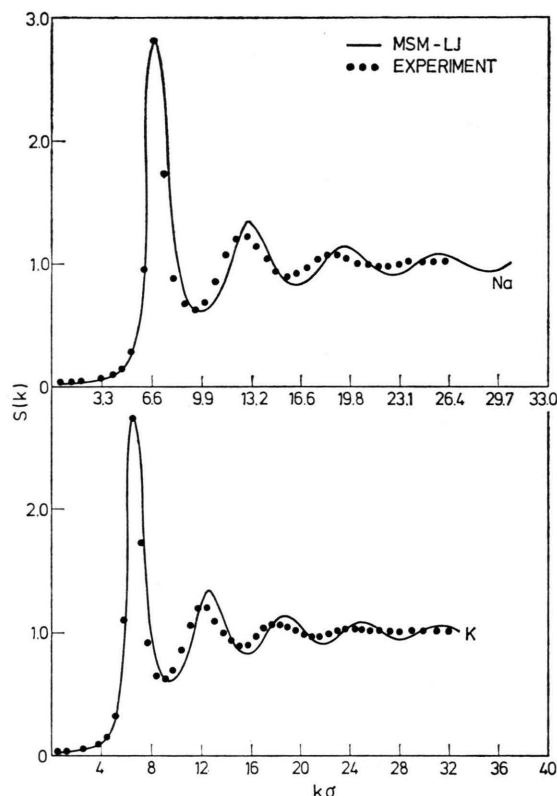


Fig. 1. Structure factor of liquid sodium (373 K) and potassium (338 K).



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calculations are:

for Na: $\sigma = 3.30 \text{ \AA}$ and $\varepsilon/k_B = 68.29 \text{ K}$,

for K: $\sigma = 4.10 \text{ \AA}$ and $\varepsilon/k_B = 54.36 \text{ K}$.

The agreement obtained between the theory and experiment, especially upto the first peak region, which incidentally determines the electronic transport properties of liquid metals⁸, is quite encour-

aging and suggests that the concept of pairwise interactions is a useful one even in the theory of liquid metals.

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¹ J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 2856 & 4714 [1971].

² J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 [1971]; Phys. Rev. A **4**, 1597 [1971]; D. Chandler and J. D. Weeks, Phys. Rev. Letts. **25**, 149 [1970].

³ R. V. G. Rao and A. K. K. Murthy, Phys. Stat. Solid (b) **66**, 703 [1974].

⁴ M. S. Wertheim, Phys. Rev. Letters **10**, 321 [1963]; E. Thiele, J. Chem. Phys. **39**, 474 [1963].

⁵ J. L. Lebowitz and J. K. Percus, Phys. Rev. **144**, 251 [1966].

⁶ eg. R. J. Baxter, in Physical Chemistry, An Advanced Treatise, Vol. 8 A, ed. by. D. Henderson, Academic Press, New York, 1971, p. 302.

⁷ A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A **4**, 1607 [1971].

⁸ A. J. Greenfield and N. Wiser, Phys. Letts. **34 A**, 123 [1971].