Mean spherical model-structure of liquid argon

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Abstract. A new formulation for $S(k)$, the structure factor, has been obtained, treating the square-well potential as a perturbation on the hard-core in the mean spherical model approximation. The potential parameters have been varied not only to get a satisfactory peak height at the fitted temperature but also over a wide range of temperatures and densities. The agreement between the computed and experimental structure factor values shows that the representation of the attractive tail by a square-well potential yields a satisfactory method in understanding the structure of liquid argon.

Keywords. Liquid argon; lipid structure.

1. Introduction

A detailed knowledge of the structure factor is essential for a quantitative under-standing not only of the structure of liquids but also numerous other properties (Greenfield et al 1971; Ziman 1961, 1964). In this paper we propose to study the structure of liquid argon using mean spherical model (MSM) approximation with a square-well (SW) potential. Tago (1973) recently made extensive investigations on the experimental pressure of argon by theoretical calculations with $\epsilon/k_B = 124\cdot6°\,K$ and $\sigma = 3\cdot27\,Å$. He found that these parameters give a good fit between theoretical and experimental results. He therefore suggested that SW potential represents argon satisfactorily. Hence it is felt worthwhile to make extensive investigations of this fluid with a SW potential especially when a large amount of structure factor data (Eisenstein and Gingrich 1942; Gingrich and Tompson 1962; Micolaj and Pings 1967; Schmidt and Tompson 1968) is available at various temperatures and densities even up to critical point.

2. Theory

The MSM can be regarded as a perturbation version of the Percus-Yevick (PY) theory. In as much as perturbation theory has been found to be a successful theory of fluids (Barker and Henderson 1967; Smith et al 1970, 1971) it is hoped that MSM might also be useful as a theory of condensed fluids.

The MSM assumes that

$$c(r) = [e(r) - 1]\,y(r), \quad r < \sigma \tag{1}$$

$$c(r) = -u(r)/k_B T, \quad r > \sigma \tag{2}$$

where $y(r) = g(r)/e(r)$ and $e(r) = \exp[-u(r)/k_B T]$, $c(r)$ are the direct correlation function (DCF) and $g(r)$ the radial distribution function (rdf).

From the theory of Fourier transforms we have the well known result

$$\tilde{c}(k) = \frac{4\pi}{k} \int_0^\infty c(r)\, r \sin kr\, dr \tag{3}$$

We choose to write $c(r)$ as

$$c(r) = c_{hs}(r) + c_{sw}(r) \tag{4}$$

where $c_{hs}(r)$ is the hard sphere part while $c_{sw}(r)$ is the SW part of the DCF. Hence we write

$$c(r) = c(r)_{\text{wertheim}}, \qquad 0 < r < \sigma \tag{5}$$

$$c(r) = c_{sw}(r), \qquad \sigma < r < \lambda\sigma \tag{6}$$

$$c(r) = 0, \qquad r > \lambda\sigma. \tag{7}$$

Wertheim (1963) expression for the DCF can be most conveniently written as

$$c_{hs}(r) = -\frac{1}{(1-\eta)^4}\left[(1+2\eta)^2 - 6\eta\left(1+\frac{\eta}{2}\right)^2\right.$$
$$\left.\left(\frac{r}{\sigma}\right) + \frac{\eta}{2}(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right] \tag{8}$$

and

$$c_{sw}(r) = \epsilon/k_B T, \qquad \sigma < r < \lambda\sigma \tag{9}$$

Here

$$\eta = \frac{\pi\rho\sigma^3}{6} \quad \text{and} \quad \rho = \frac{N}{V}$$

while ϵ is the SW potential depth and λ its breadth. Substituting eqs (8) and (9) in eq. (3) and carrying out the straightforward integration we get

$$\tilde{c}_{\text{total}}(k) = -\frac{4\pi}{K(1-\eta)^4}\left\{(1+2\eta)^2\left[\frac{1}{k^2}\sin k\sigma - \frac{\sigma}{k}\cos k\sigma\right)\right.$$

$$-\frac{6\eta}{\sigma}(1+\eta/2)^2\left[-\frac{\sigma^2}{k}\cos k\sigma + \frac{2\sigma}{k^2}\sin k\sigma + \frac{2}{k^3}\cos k\sigma - \frac{2}{k^3}\right]$$

$$+\frac{\eta}{2\sigma^3}(1+2\eta)^2\left[-\frac{\sigma^4}{k}\cos k\sigma + \frac{4\sigma^3}{k^2}\sin k\sigma + \frac{12\sigma^2}{k^3}\cos k\sigma\right.$$

$$-\frac{24\sigma}{k^4}\sin k\sigma - \frac{24}{k^5}\cos k\sigma + \frac{24}{k^5}\right]\left.\right\} + \frac{4\pi\epsilon}{k_B T}\left[\frac{1}{k^3}\sin \lambda k\sigma\right.$$

$$\left.-\frac{\lambda\sigma}{k^2}\cos \lambda k\sigma + \frac{\sigma}{k^2}\cos k\sigma - \frac{1}{k^3}\sin k\sigma)\right] \tag{10}$$

Equation (10) is very important since the structure factor can be calculated analytically through the equation given by

$$S(k) = \frac{1}{1 - \rho\tilde{c}(k)} \tag{11}$$

The value of λ for all calculations has been taken as $1\cdot5$ and has been so chosen since the value as determined from second virial coefficient data is nearly equal to this value. Further both in the case of Monte Carlo (MC) and molecular dynamics (MD) the value of λ has been chosen as $1\cdot5$. At this juncture it may be pointed out that Woodhead *et al* (1968) in their so-called random phase approximation also write their $c(r)$ as a sum of $c_{hc}(r)$ and $c_{lr}(r)$ and use Wertheim's hard sphere expression for $c_{hc}(r)$ while they used Lennard-Jones (LJ) 6–12 potential for $c_{lr}(r)$. The subscripts ' *hc* ' and ' *lr* ' denote hard core and long range respectively.

In the present work the value of the parameters are adjusted at $T = 148°$ K and $\rho = 1\cdot479 \times 10^{-2}/\text{Å}^3$ so as to get the satisfactory peak height of $S_{max}(k)$. Throughout our computations we have not altered these parameters. In table 1 we give the various temperatures and densities with potential parameters. In this connection it may be noted that Ashcroft and Lekner (1966) in their theoretical evaluation of structure factor obtained their parameter $\eta (= \pi\rho\sigma^3/6)$ by fitting $S(k)$ to give a correct peak height $S_{max}(k)$. One can also fit the parameter σ with the known compressibility value at $k = 0$ from the well-known thermodynamic relation

$$S(0) = \rho k_B T \chi_T \tag{12}$$

where χ_T is the isothermal compressibility. However we found it convenient to use the peak value to obtain the parameters.

3. Results and discussion

The set of parameters $\sigma = 3\cdot0$ Å, $\epsilon/k_B = 124\cdot6°$ K and $\lambda = 1\cdot5$ are so adjusted to get not only a satisfactory peak height at the fitted temperature but also over a wide range of temperatures (even above critical temperature) and densities.

The calculated first peak maxima lie above the experiment at all densities and temperatures except at $153°$ K and $163°$ K at a density of $1\cdot175 \times 10^{-2}$ atom/Å³. In this connection it may be pointed out that Khan (1964) calculated $g(r)$ using LJ 6–12 and Guggenheim-McGlashan (GM) potentials and from these calculated radial distribution functions he obtained the coherent scattering curves by simple Fourier transformation. His computed curves also lie above the experimental

Table 1. Temperatures, densities and potential parameters for liquid argon

Sl. No.	Substance	Temperature °K	Density atom/Å³	σ, Å	(ϵ/k_B) °K	λ
1.	Argon	163	$1\cdot175 \times 10^{-2}$	$3\cdot0$	$124\cdot6$	$1\cdot5$
2.		153	$1\cdot371 \times 10^{-2}$	,,	,,	,,
3.		153	$1\cdot175 \times 10^{-2}$	,,	,,	,,
4.		148	$1\cdot479 \times 10^{-2}$	,,	,,	,,
5.		148	$1\cdot371 \times 10^{-2}$	,,	,,	,,
6.		148	$1\cdot175 \times 10^{-2}$	,,	,,	,,
7.		143	$1\cdot479 \times 10^{-2}$	,,	,,	,,
8.		143	$1\cdot371 \times 10^{-2}$	,,	,,	,,

points especially at temperatures $T = 144 \cdot 1^\circ$ K and $149 \cdot 3^\circ$ K and densities $1 \cdot 312 \times 10^{-2}$ atom/Å^3 and $1 \cdot 11 \times 10^{-2}$ atom/Å^3 respectively. We find in our present computations that the agreement at a given density gets better as the temperature increases except at the low density of $1 \cdot 175 \times 10^{-2}$ atom/Å^3. In general, as in Khan's case, the agreement is better at high temperatures than at low temperatures. Further it may be noticed that in the $S(k)$ curves there is a slight shift of the experimental points towards the left of the computed values. Such a shift in the structure factor curves was also observed in the case of liquid alkali metal Rb (Ashcroft and Lekner 1966). It is also observed that the computed peak maxima of the structure factor increase as the temperature is decreased. But contrary to this it is seen that the peak heights of the experimental structure factor curves decrease with decrease of temperature. This may be due to different pressures employed at different temperatures. It may be pointed out that with
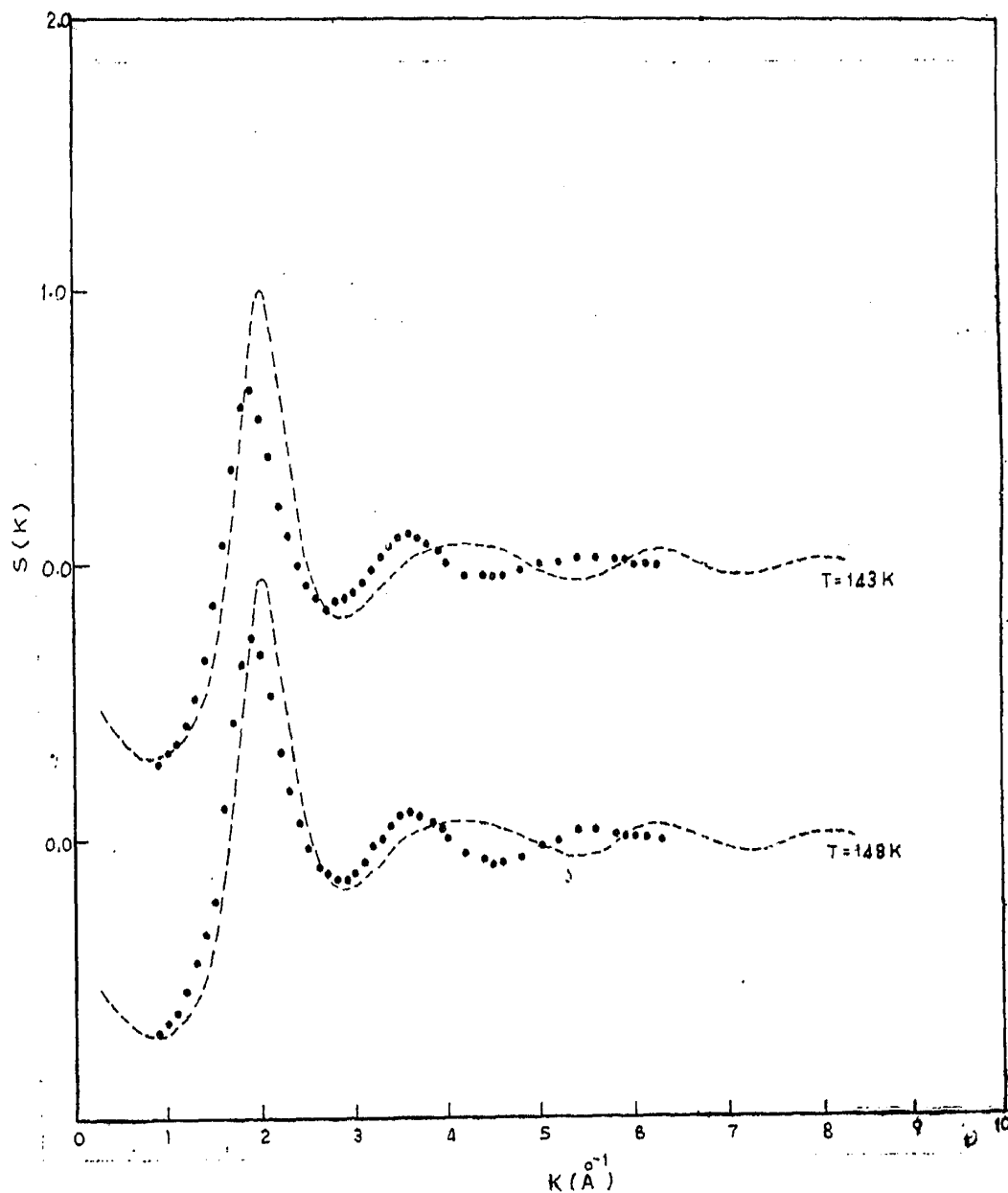

Figure 1. Structure factor curves at $\rho = 1 \cdot 479 \times 10^{-2}$ atom/Å^3. Dashed (- - - - - -) curves represent present work, dotted (........) curves represent the x-ray diffraction points.

increase of pressure the peak height is supposed to increase while the effect of increased temperature is to lower the peak maxima. Hence the decrease in experimental peak height with decrease of temperature may be due to the combined effect of temperature and pressure. Mikolaj and Pings (1967) attributed this to the usage of the same potential parameters corresponding to different temperatures and densities (figures 1–3). In all these cases both the experimental and theoretical value tend to unity from $k \simeq 6 \cdot 5 \text{Å}^{-1}$ onwards. The maximum deviation between the experimental and theoretical values is not more than 10 to 15%. The general shift in the second and third peak maxima at all these temperatures might be due to the fact that a single set of parameters has been used to cover a wide range of temperatures and densities. In this connection, it may be pointed out that Greenfield et al (1972) while discussing about alkali metals suggested that in the evaluation of a structure factor at a given temperature and density one may treat σ and η as
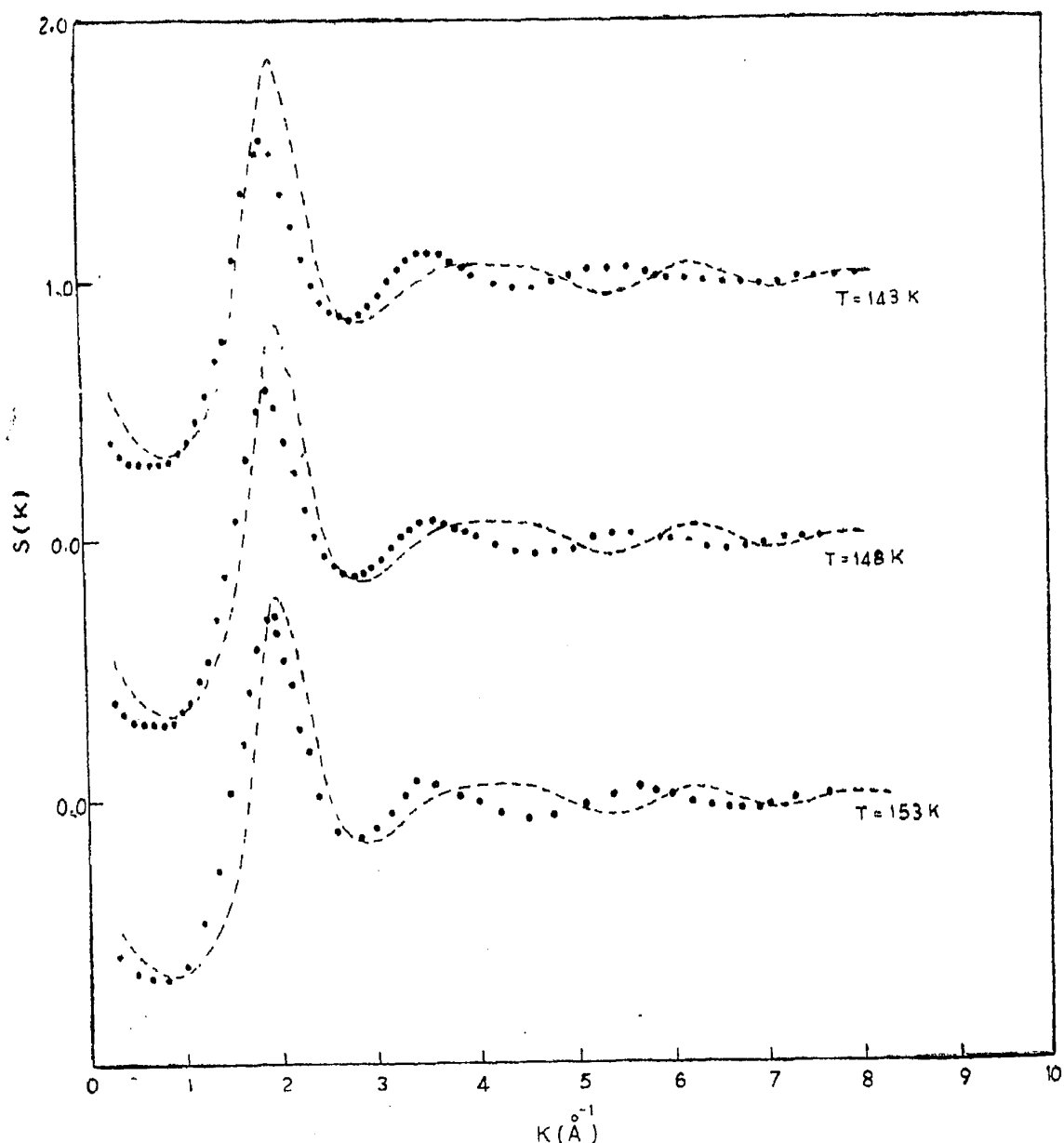

Figure 2. Structure factor curves at $\rho = 1 \cdot 371 \times 10^{-2}$ atom/Å³. Dashed (- - - - -) curves represent present work, dotted (.........) curves represent the x-ray diffraction points.
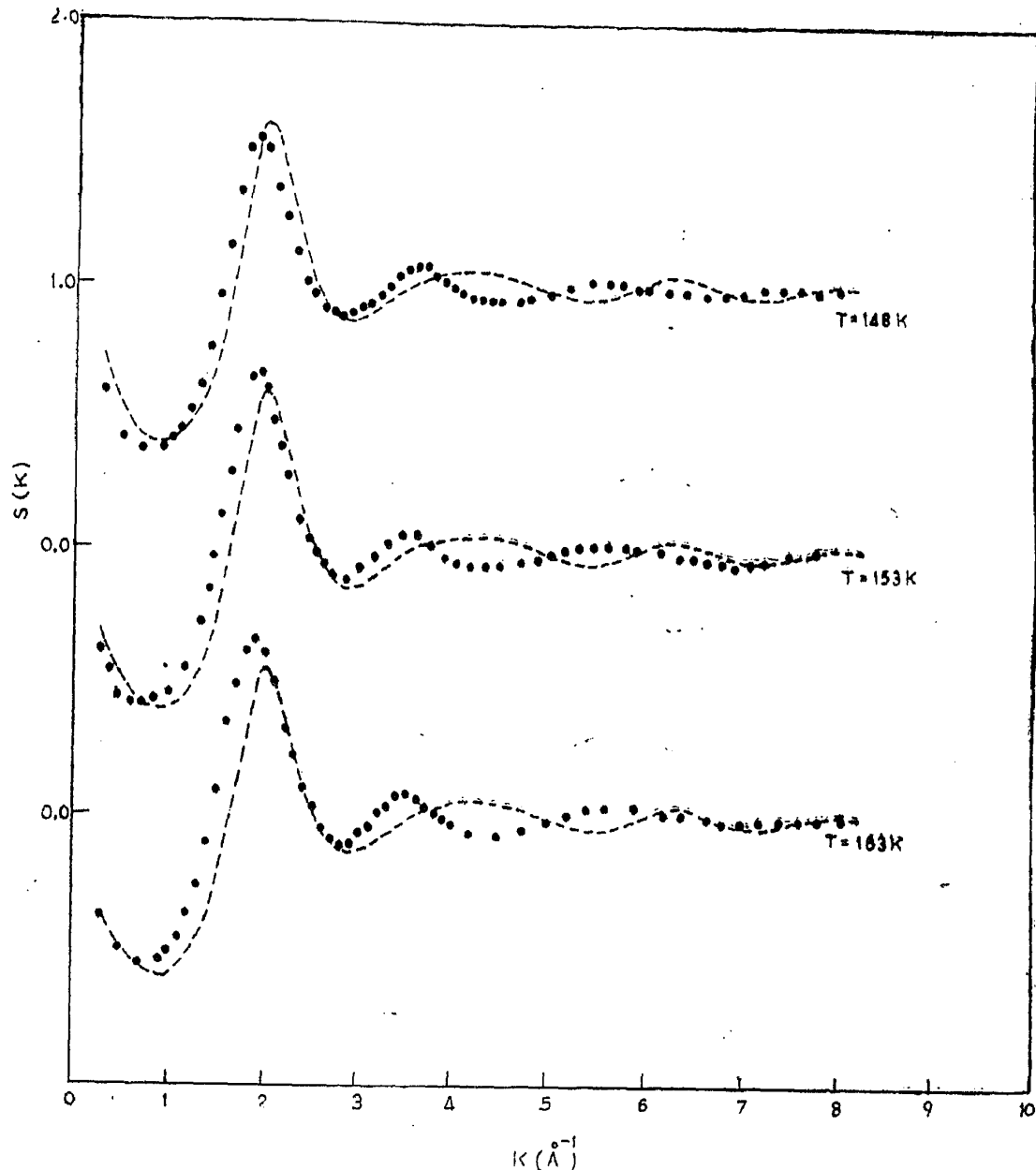
Figure 3. Structure factor curves at $\rho = 1\cdot175 \times 10^{-2}$ atom/Å^3. Dashed (------) curves in all figures represent present work, dotted (........) curves represent the x-ray diffraction points.

independent parameters. But this unfortunately amounts to abandoning the hard sphere potential and the Wertheim solution of the DCF obtained from Percus-Yevick (PY) equation. Therefore the present fit of structure factors $S(k)$ over a wide range of temperatures and densities with a maximum deviation of about 15% can be treated as very good especially considering the fact that the present treatment does not involve any iteration process, while Khan (1964) adopted Broyle's iteration technique. In general it is concluded that square-well potential satisfactorily represents argon.

Acknowledgement

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