

I. PHYSICS

Chemical Physics

STRUCTURE AND ISOTHERMAL COMPRESSIBILITY OF LIQUIDS WITH STICKY HARD SPHERE POTENTIAL

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Using Baxter's solution (Baxter, 1971) for the direct correlation function in the Percus-Yevick equation for a sticky hard sphere potential, the structure functions of Ar, Li, Na, Mg, Ba, Cu, Ag, Fe and Co have been evaluated. Isothermal compressibilities of these liquids have also been calculated from the structure function in the long wave limit. The results are in good agreement with experiment, showing that the sticky hard sphere potential is capable of explaining liquid state properties very well.

Keywords : Sticky Hard Sphere Potential; Structure Function; Direct Correlation Function; Percus-Yevick Equation; Fourier Transform; Attractive Perturbation Potential; Isothermal Compressibility.

INTRODUCTION

USING the Wertheim-Thiele solution (Wertheim, 1963; and Thiele, 1963) for the direct correlation function (DCF) in the Percus-Yevick (PY) equation for a hard sphere (HS) potential, liquid state properties have been extensively studied (Ashcroft & Leckner, 1966; and Halder & Jena, 1972). Though the hard sphere potential explains the structure of liquids fairly well, which is determined primarily by the repulsive forces between molecules, it lacks the essential requirement of a realistic potential in the sense that it rules out any attraction between molecules and thus fails to explain the first order transition. Thus comes the need of the introduction of some attractive part into the hard sphere potential through some perturbation over it.

The sticky hard sphere (SHS) potential which is a perturbation version of the HS potential with an attractive well removes this deficiency of the HS potential. The PY equation has been solved for this potential by Baxter (1968, 1971) taking the limit that the attraction is over an infinitely small range. In this limit, the potential consists of a hard core together with an infinitely deep and narrow attractive well. Such a potential can be regarded as applicable to hard spheres of diameter ' R ' with surface adhesion. This potential incorporates the significant features of a real potential. It has an advantage over the HS potential in that it contains a temperature dependent parameter ' τ '. It also explains the first order transition as well.

We find that not much work has been done in evaluating liquid state properties with the use of the SHS potential. With these points in mind, we extend the application of the SHS potential in the evaluation of structure and isothermal compressibility of several metallic and non-metallic liquids.

THEORY

The sticky hard sphere potential is defined by

$$\left. \begin{aligned} \beta u(r) &= + \infty && r < \sigma \\ &= - \ln [R/12\tau(R - \sigma)] && \sigma < r < R \\ &= 0 && r > R \end{aligned} \right\} \dots(1)$$

where $\beta = \frac{1}{k_B T}$ and σ is the hard sphere diameter. $R - \sigma$ is infinitesimally small.

The parameter ‘ τ ’ is a dimensionless measure of the temperature, and the relation between τ and T is arbitrary.

The DCF in the PY approximation for such a potential has been solved by Baxter (1971) and is given by

$$\begin{aligned} C(r) &= -a - \frac{bR}{r} + \frac{\lambda R^2}{12r} \delta(r - R_-) + 2\pi\rho \left[-\frac{a^2}{24}r^3 + \left(\frac{a^2}{2} + ab \right. \right. \\ &\quad \left. \left. + \frac{b^2}{2} - \frac{a\lambda}{12}\right)R^2r + \left(-\frac{a^2}{3} - \frac{ab}{2} + \frac{a\lambda}{12}\right)R^3 + \left(-\frac{a^2}{8} - \frac{ab}{2} \right. \right. \\ &\quad \left. \left. - \frac{b^2}{2} + \frac{a\lambda}{24} + \frac{b\lambda}{12} - \frac{\lambda^2}{144}\right)\frac{R^4}{r} \right] && r < R \\ &= 0 && r > R \end{aligned} \dots(2)$$

Here R_- is used to denote the fact that the delta function lies just to the left of R and

$$a = (1 + 2\eta - \mu)/(1 - \eta)^2 \dots(3)$$

$$b = \frac{1}{2}(-3\eta + \mu)/(1 - \eta)^2 \dots(4)$$

$$\mu = \lambda\eta(1 - \eta) \dots(5)$$

The parameter λ depends on τ and is given by

$$\lambda = \frac{6}{\eta} [\alpha - (\alpha^2 - \gamma)^{1/2}] \dots(6)$$

where

$$\alpha = \tau + \eta/(1 - \eta) \dots(7)$$

$$\gamma = \frac{\eta(1 + \eta/2)}{3(1 - \eta)^2} \dots(8)$$

$$\eta = \pi\rho R^3/6 \dots(9)$$

ρ being the number density $\left(\rho = \frac{N}{V} \right)$

From equation (2), we get the Fourier transform of $C(r)$ and this can be written as

$$\begin{aligned} \bar{c}(k) = \frac{4\pi}{k^6} & \left[-ak^3(\sin kR - kR \cos kR) - bk^4R(1 - \cos kR) \right. \\ & + \frac{\lambda k^5 R^2}{12} \sin kR + 2\pi\rho \left\{ -\frac{a^2}{24}(-24 \cos kR - 24 kR \sin kR \right. \\ & + 12k^2 R^2 \cos kR + 4k^3 R^3 \sin kR - k^4 R^4 \cos kR + 24) \\ & + k^2 R^2 \left(\frac{a^2}{2} + ab + \frac{b^2}{2} - \frac{a\lambda}{12} \right) (2 \cos kR + 2 kR \sin kR \\ & - k^2 R^2 \cos kR - 2) + k^3 R^3 \left(-\frac{a^2}{3} - \frac{ab}{2} + \frac{a\lambda}{12} \right) (\sin kR \\ & - kR \cos kR) + k^4 R^4 \left(-\frac{a^2}{8} - \frac{ab}{2} - \frac{b^2}{2} + \frac{a\lambda}{24} + \frac{b\lambda}{12} - \frac{\lambda^2}{144} \right) \\ & \left. \left. (1 - \cos kR) \right\} \right] \quad \dots(10) \end{aligned}$$

Now the structure function, $S(k)$, is given by the well-known relation

$$S(k) = [1 - \rho \bar{c}(k)]^{-1} \quad \dots(11)$$

From eqns. (2) and (11), we obtain in the long wave limit

$$\begin{aligned} \bar{c}(0) = 4\pi & \left[-R^3 \left(\frac{a}{3} + \frac{b}{2} - \frac{\lambda}{12} \right) + 2\pi\rho R^6 \left\{ -\frac{a^2}{144} + \frac{1}{4} \left(\frac{a^2}{2} + ab \right. \right. \right. \\ & + \frac{b^2}{2} - \frac{a\lambda}{12} \left. \left. \right) + \frac{1}{3} \left(-\frac{a^2}{3} - \frac{ab}{2} + \frac{a\lambda}{12} \right) + \frac{1}{2} \left(-\frac{a^2}{8} - \frac{ab}{2} \right. \right. \\ & \left. \left. - \frac{b^2}{2} + \frac{a\lambda}{24} + \frac{b\lambda}{12} - \frac{\lambda^2}{144} \right) \right\} \right] \quad \dots(12) \end{aligned}$$

and

$$S(0) = [1 - \rho \bar{c}(0)]^{-1} \quad \dots(13)$$

But $S(0)$ is related to isothermal compressibility χ_T by the well-known expression

$$S(0) = \rho k_B T \chi_T \quad \dots(14)$$

from which χ_T can be calculated.

RESULTS AND DISCUSSION

As is the usual practice (Rao & Joarder, 1978; and Rao & Murty, 1974) the two independent parameters σ and τ involved in the calculation were chosen so as to get the best possible fitting at the principal peak of the experimental structure function curve. Thus the structure function for nine different simple metallic and non-metallic liquids, namely, argon, lithium, sodium, magnesium, barium, copper, silver, iron and cobalt, were calculated and compared with experimental results of

Gingrich & Heaton (1961), Greenfield *et al.* (1971), Waseda (1975) and of Henshaw (1957), which are show in Figures 1-5.

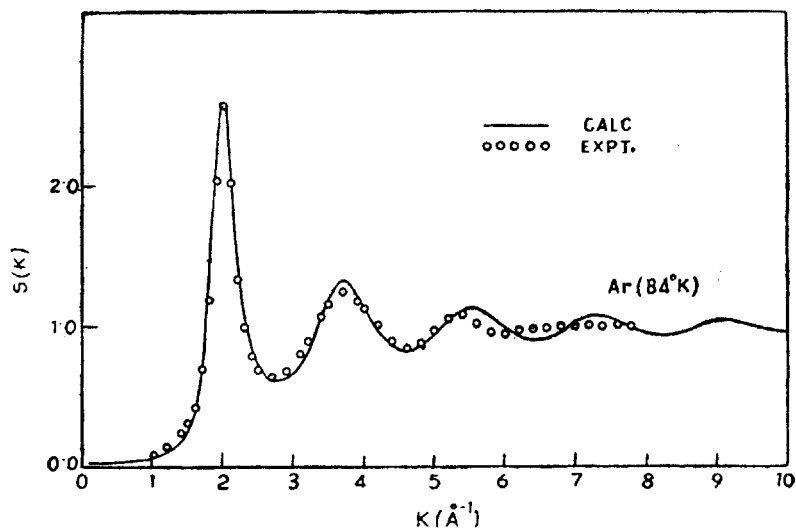


FIG. 1. Comparison of calculated and experimental $S(k)$ vs. k curves for liquid Ar (84°K).

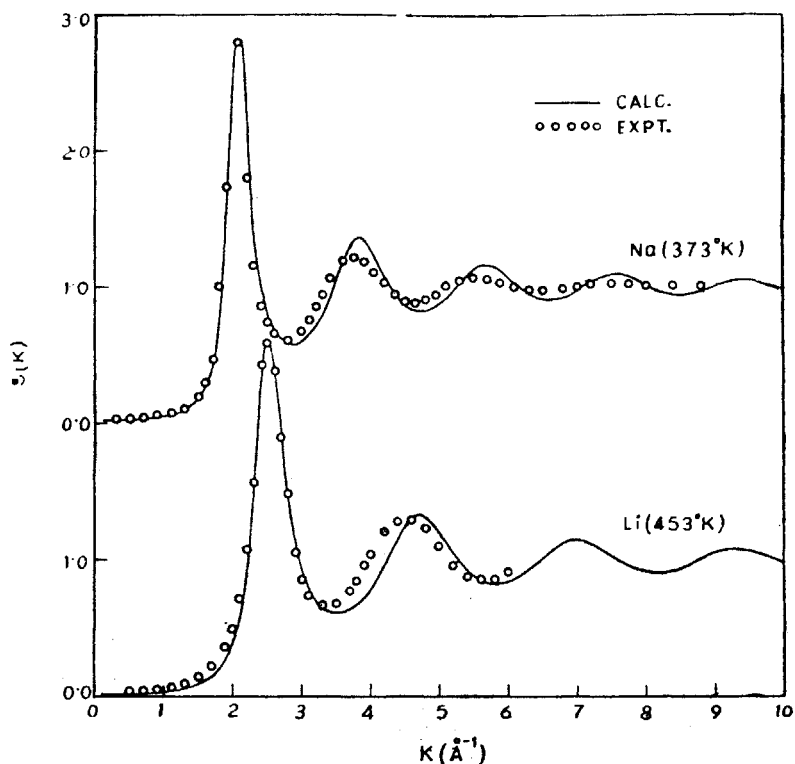


FIG. 2. Comparison of calculated and experimental $S(k)$ vs. k curves for liquid Li (453°K) and Na (373°K) metals.

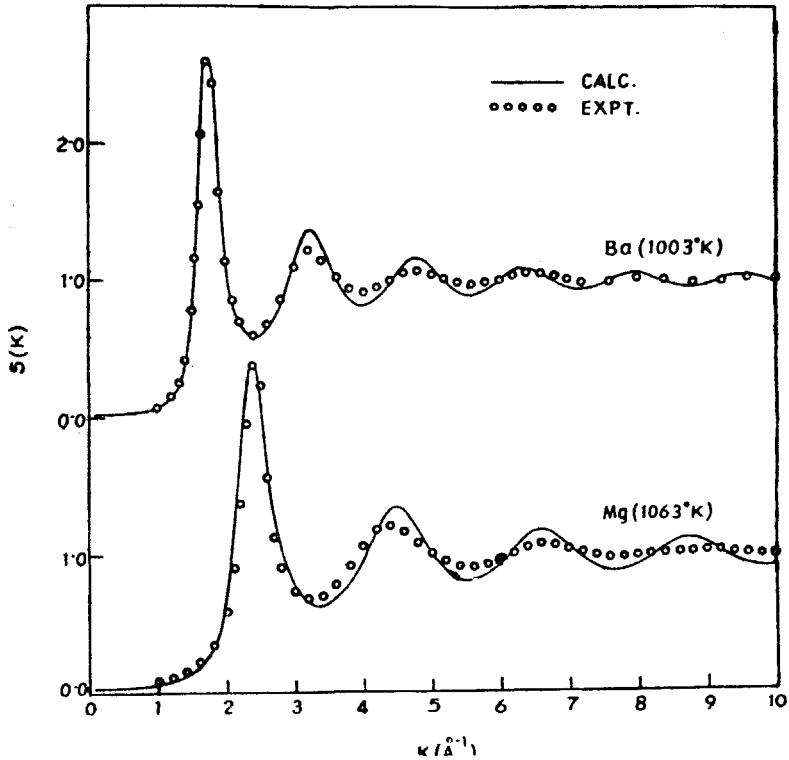


FIG. 3. Comparison of calculated and experimental $S(k)$ vs. k curves for liquid Mg (1063 °K) and Ba (1003 °K) metals.

The potential parameters thus obtained for all the liquids studied are presented in Table I. Using these parameters the isothermal compressibilities have been calculated at the corresponding temperatures and are also shown in Table I, along

TABLE I
Potential parameters and isothermal compressibilities of the liquids

Liquid	Temp. (°K)	ρ (atom Å ⁻³)	σ (Å)	τ	χ_T ($\times 10^{-12}$ cm ² /dyne)	
					Present calc.	Exptl.
Ar	84	0.02130	3.500	5.000	96.54	170
Li	453	0.04373	2.750	5.600	8.70	11
Na	373	0.02430	3.360	25.000	15.52	19
Mg	1063	0.03550	3.000	1.125	6.18	4
Ba	1003	0.01460	4.025	4.000	10.26	—
Cu	1573	0.07450	2.275	9.250	1.60	1.5
Ag	1573	0.05010	2.550	13.000	2.88	2.1
Fe	1833	0.07560	2.250	10.000	1.45	1.27*
Co	1823	0.07860	2.225	11.750	1.35	1.55*

*Computed results of Rao and Sen (1976)

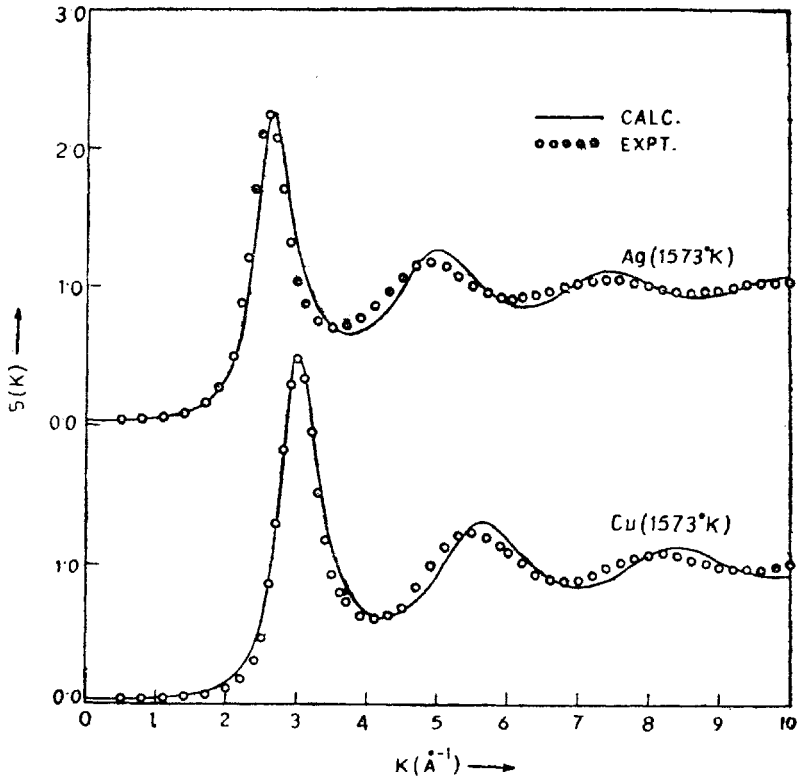


FIG. 4. Comparison of calculated and experimental $S(k)$ vs. k curves for liquid Cu (1573 °K) and Ag (1573 °K) metals.

TABLE II

Shift in the position and percentage variation of heights of second peak of the $S(k)$ versus k curves of the liquids

Liquid	Shift in second peak position (\AA^{-1})	Height variation of second peak (%)
Ar	0	7.09
Li	0.1	3.75
Na	0.1	13.77
Mg	0.1	10.63
Ba	0	12.11
Cu	0.1	6.20
Ag	0.1	7.76
Fe	0.3	2.79
Co	0.2	8.91

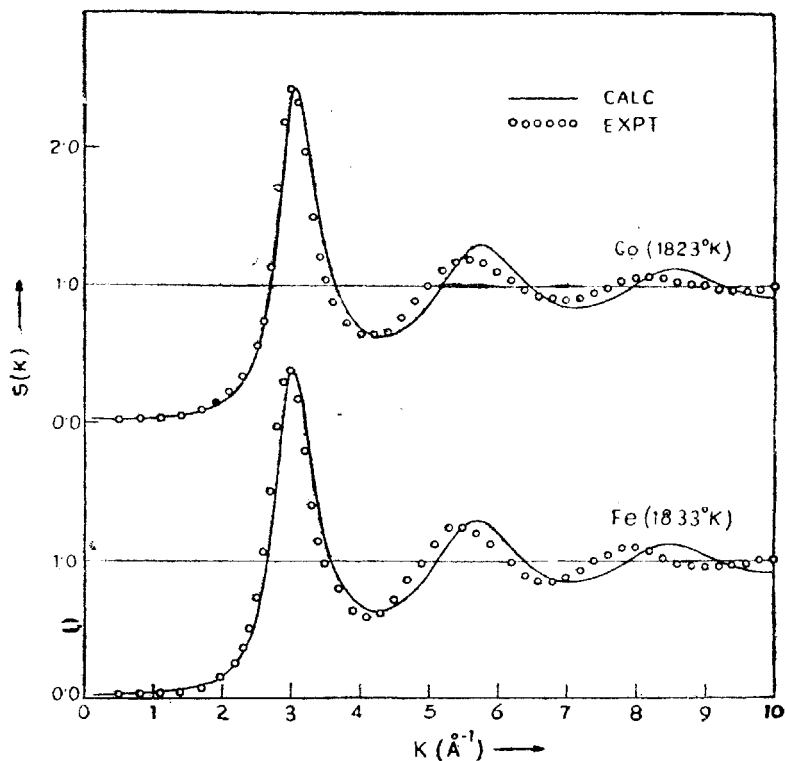


Fig. 5

FIG. 5. Comparison of calculated and experimental $S(k)$ vs. k curves for liquid Fe (1833 °K) and Co (1823 °K) metals.

with the experimental compressibility results at the melting temperatures given by Faber (1972) and the calculated values of Rao and Sen (1976) for Fe and Co.

In general, the results obtained by the present method agrees very well with experiment for all the liquids considered around the first peak region, excepting in the case of silver and cobalt, for which the first peak in the calculated $S(k)$ values shift to the right of the experimental peak by 0.1 \AA^{-1} . This, of course, has been done in the case of these two metals to obtain a fairly good agreement throughout the k -space. At the second peak the calculated values are only in fair agreement with experiment. It may be mentioned that, in the case of sodium, Ailawadi & Miller (1976) also obtained not only phase deviation of the structure function but also deviations in peak heights as well. They also presented the results based on WCA perturbation theory (Anderson *et al.*, 1972) and the calculated values from it are also not in good agreement with experiment. Thus, the present calculations even with only two parameters give reasonably good values throughout the k -region, while giving good agreement around the entire first peak region.

We present in Table II, the shift and the variation of height of the second peak.

Further, we observe that beyond the first peak, the oscillations in computed $S(k)$ goes out of phase from the experimental oscillations, throughout the k -space, for most of the liquids. The same type of behaviour has been observed by Rao and Murty (1975) while calculating $S(k)$ with the square-well potential in the random phase approximation. However, it is important to remember that the first peak results are the most important, primarily determining the transport properties.

This may be due to, as pointed out by Waseda and Suzuki (1973) that in the case of hard sphere model, the pair correlation function has a sharp edge at the position corresponding to the hard sphere diameter. On Fourier transformation, this sharp edge gives the structure function values which oscillate even in the large k -region. However, in reality, liquid metals have a soft repulsive core and thus it is expected that the oscillations in the experimental $S(k)$ values would damp more rapidly in large k -region and move out of phase with the values calculated using a potential with a steep repulsive core. Although the SHS potential incorporates certain significant features of a real potential, it still contains a steep repulsive core. Hence the deviation of computed $S(k)$ values at large k -region. This also explains the observed fact that the calculated second peak height is always more than the experimental peak height.

Expression for the $S(k)$ value in the long wave limit has been obtained and is given by eqns. (12) and (13), from which the isothermal compressibilities have been computed and are given in Table I. The experimental values (Faber, 1972) compare favourably with the present computed values. However, for Fe and Co, no experimental result is available even at the melting temperatures and hence comparison is made with the computed results of Rao and Sen (1976) obtained through a different method.

In the case of Ar, it is not expected to get a good result for the compressibility with a SHS potential, which is essentially repulsive in nature, since the atoms of liquid Ar are governed by Van der Waal's forces and the free electron repulsive forces of metallic liquids are absent. Even though SHS potential has an ideal attractive adhesive surface, it is still highly repulsive in nature and hence in a liquid like Ar, the long range attractive forces are not accounted well. A long range attractive perturbation over this potential may yield good results in the case of Van der Waal's liquids.

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