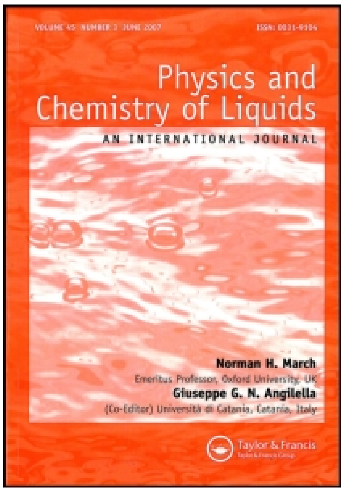

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PSEUDOPOTENTIAL METHOD FOR THE THERMODYNAMIC PROPERTIES OF LIQUID ALKALI METALS

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A pseudopotential method has been considered to study the enthalpy and compressibility of liquid alkali metals (Na, K, Rb and Cs) as a function of temperature. The diameters of the hard sphere reference system were determined by minimising the Helmholtz free energy to ensure thermodynamic stability. The enthalpy, which depends weakly on temperature, has been successfully explained. The investigation suggests that the structure dependent part of energy is sufficient to explain the compressibility of liquid alkali metals near and above the melting temperatures.

KEY WORDS: Enthalpy, compressibility, stability.

1 INTRODUCTION

In recent years considerable progress has been made[1–2] to describe the thermodynamics of liquid metals by blending the techniques of classical liquid state theory to that of pseudopotential method. First, this was successfully used by Stroud and Ashcroft[3] to describe the melting of Na. This has generated considerable interest among the workers to study the entropy and heat of mixing for liquid metals and alloys[4–8]. In most of the cases the earlier studies are confined near the melting temperature (*Tm*) and the properties like enthalpy and compressibility of liquid alkali metals have not been thoroughly investigated from pseudopotential method.

The major task in such studies concerns to choose an appropriate reference system among the various existing methods namely, (i) hard sphere and variational method[9] (ii) hard sphere and interionic pair potential[10] (iii) Weeks–Chandler–Andersen method[11] and (iv) one component plasma system[12]. Among the numerous existing methods, the use of hard sphere is largely justified because it provides analytical representation in terms of single parameter known as hard sphere diameter (σ). Further, it is very convenient to optimise σ in the variational method which ensures thermodynamic stability of the liquid metallic systems.

In the present work we therefore intend to apply this scheme to study the enthalpy and compressibility of liquid alkali metals (Na, K, Rb and Cs) as a function of temperature for $T \geq Tm$. Our investigation is likely to shed light on the behaviour of liquid alkali metals at elevated temperatures. It is well known that the hard sphere system serves a very good reference system for liquid metals near the melting points whose performance at higher temperatures is not fully understood. Our present investigation will also help us to examine the latter point more closely. Some necessary formalism in this regard shall be provided in Section 2. Results and discussion will follow in Section 3. Section 4 enlists a short conclusion.

2 FORMALISM

The advent of Gibbs–Bogoliubov variational method[13–14] synchronises the hard sphere results to the pseudopotential technique and provides a method for the thermodynamic investigation of liquid metals. This allows one to write an upper bound to the Helmholtz free energy, F, per ion at fixed temperature T and volume Ω:

$$F = F_{hs} + F_{ps} \tag{1}$$

where F_{hs} is the Helmholtz free energy of the hard sphere system and F_{ps} is the appropriate expectation value of the effective potential energy for the ion system. For a system of ions and electrons, F_{ps} can be expressed within the frame work of the second-order pseudopotential perturbation theory as,

$$F_{ps} = F_{eg} + F_f + F_s + F_M \tag{2}$$

where F_{eg} arises due to free electron–gas, F_f and F_s are due to electron–ion interaction defined via first and second order pseudopotential perturbation theory respectively, and F_M takes into account for the ion–ion interaction. The expressions for these contributions for a metal have been worked out in detail by Harrison[15],

$$F_{eg} = NZ\left(\tfrac{3}{10}K_F^2 - \frac{3}{4\pi}K_F - 0.0474 - 0.0155 \ln K_F\right) \tag{3}$$

$$F_f = \lim_{q \to 0} nz\left\{\mathcal{V}(q) + \frac{4\pi z}{q^2}\right\} \tag{4}$$

$$F_s = \frac{1}{16\pi^3}\int_0^\infty \mathcal{V}^2(q)a(q)\left\{\frac{1}{\varepsilon^*(q)} - 1\right\}q^4 dq. \tag{5}$$

$$F_m = \frac{z^2}{\pi}\int_0^\infty \{a(q) - 1\}dq. \tag{6}$$

where $K_F = (3\pi^2 Zn)^{1/3}$, n is the number density. $a(q)$ is the structure factor which can be obtained from Percus–Yevick approximation for hard sphere potential[16].

$$a(q) = \left[\begin{array}{l} 1 + \left[\dfrac{24\eta}{(1-\eta)^4\alpha^6}\right]\Big[(1+2\eta)^2\alpha^3(\sin\alpha - \alpha\cos\alpha) \\ \quad - 6\eta\left(1+\dfrac{\eta}{2}\right)^2\alpha^2\{2\alpha\sin\alpha - (\alpha^2 - 2)\cos\alpha - 2\} \\ \quad + \dfrac{\eta}{2}(1+2\eta)^2\{(4\alpha^3 - 24\alpha)\sin\alpha \\ \quad -(\alpha^4 - 12\alpha^2 + 24)\cos\alpha + 24\}\Big] \end{array}\right]^{-1} \tag{7}$$

where $\alpha = q\sigma$. σ is the hard sphere diameter which is related to the packing fraction, $\eta = (\pi\sigma^3 n/6)$. $\mathcal{V}(q)$ in Eqs (4) and (5) stands for unscreened form factor and are obtained using the Heine-Abarenkov[17] model potential

$$\mathcal{V}(q) = -\frac{4\pi zn}{q^2}\cos qr_m - \frac{4\pi An}{q^3}(\sin qr_m - qr_m \cos qr_m). \tag{8}$$

where A is the well depth and r_m is the model radius. These are obtained[18] quantum mechanically by matching the wave functions at $r = r_m \cdot \varepsilon^*(q)$ is the modified Hartree dielectric screening function,

$$\varepsilon^*(q) = 1 + \{\varepsilon(q) - 1\}\{1 - G(q)\} \tag{9}$$

$G(q)$ in Eq. (9) is the correction factor for the exchange and correlated motion of the conduction electrons. For the present work we use the modified Hubbard formula i.e.,

$$G(q) = \frac{q^2}{2(q^2 + \gamma K_F^2)} \tag{10}$$

The function γ has been introduced to satisfy the compressibility sum rule. By making use of the interpolation scheme of Nozieres and Pines[19], γ is given[20] by

$$\gamma = \frac{2\pi}{\pi K_F + 0.153} \tag{11}$$

If one considers the hard sphere potential as a reference system then under Percus–Yevick approximation[21] one writes.

$$F_{hS} = \tfrac{3}{2}K_B T - (TS) \tag{12}$$

where S is the entropy and can be expressed[8] as

$$S = \tfrac{5}{2}K_B + K_B \ln\left\{\Omega\left(\frac{mK_BT}{2\pi\hbar^2}\right)^{3/2}\right\} + K_B \ln(1-\eta)^{-1} + \tfrac{3}{2}K_B\{1 - (1-\eta)^{-2}\}. \tag{13}$$

The first two terms are structure independent and depend only on atomic mass m and atomic volume Ω. The last two terms depend on structure through the packing density η.

3 RESULTS AND DISCUSSION

3.1 Optimized values of hard sphere diameters for the reference system

It is well known that hard sphere potential serves as an effective reference system for liquid metals. The only parameter is the hard sphere diameter (σ). It is usually determined from the observed entropy, or by minimizing the interionic pair potential or by fitting the first peak of the observed static structure factor. These methods yield diversified results and therefore can not be used uniquely[22] to determine the parameter for the reference system. Therefore, in the present work, we consider a more rigorous approach to determine σ by minimizing the Helmholtz free energy.

$$\left(\frac{\partial F}{\partial \sigma}\right)_{\Omega, T} = 0 \tag{14}$$

where F is expressed in Eq. (1). σ has been determined for Na, K, Rb and Cs over a wide range of temperatures above the melting point. The densities of the liquid metals at different temperatures required in the calculations are determined from the relation provided in the work of Huijben[23]. The computed values of σ and η are tabulated in Table 1. The packing fraction η decreases as the temperature increases above the melting point. Since the derivative of η with respect to temperature is required for many thermodynamic calculations, the results of Table 1 have been represented by higher order polynomials i.e.,

$$\eta_{\mathrm{Na}} = 0.643 - 6.831 \times 10^{-4}T + 6.327 \times 10^{-7}T^2 - 3.286 \times 10^{-10}T^3 + 5.158 \times 10^{-14}T^4. \tag{15}$$

$$\eta_K = 0.634 - 8.067 \times 10^{-4}T + 9.240 \times 10^{-7}T^2 - 6.633 \times 10^{-10}T^3 + 19.481 \times 10^{-14}T^4. \tag{16}$$

$$\eta_{\mathrm{Rb}} = 0.678 - 12.939 \times 10^{-4}T + 23.433 \times 10^{-7}T^2 - 25.478 \times 10^{-10}T^3 + 112.187 \times 10^{-14}T^4. \tag{17}$$

$$\eta_{\mathrm{Cs}} = 0.674 - 12.653 \times 10^{-4}T + 23.217 \times 10^{-7}T^2 - 25.876 \times 10^{-10}T^3 + 116.477 \times 10^{-14}T^4. \tag{18}$$

$d\eta/dT$ computed from Eqs (15) to (18) are also tabulated in Table 1. In past also considerable effort has been made[24] to determine $d\eta/dT$ from the knowledge of Percus–Yevick phonon theory at the melting temperature. Ashcroft and Langreth[10], on the other hand, attempted to estimate $d\eta/dT$ from the knowledge of pair potentials. These are also tabulated in Table 1 for the sake of comparison.

3.2 Enthalpy

In the frame work of formalism of Section 2, the enthalpy (H) of liquid metals can be expressed as

$$H = \tfrac{3}{2}K_B T + F_{eg} + F_f + F_s + F_M \tag{19}$$

The various terms occurring in Eq. (19) are already defined in Section 2. Once the parameter (σ) of the reference system is known, the evaluation of the various terms is straight forward. Our results reveal that the maximum contribution to the enthalpy comes from the Madelung term F_M. The band structure term F_s, has negligibly small contribution. The magnitude of first order contribution, F_f, is significantly greater than F_s. The computed values of various terms for Na are shown in Figure 1 as a function of temperature. The figure indicates that the magnitudes of F_f and F_M decrease with the rise of temperature, whereas the magnitude of F_{eg} and F_s increases. A similar trend has also been observed for other alkali metals.

Table 1

Metal	*T°K*	*Density* *gm/cm*^{3}	σ *au*	η	$\left(\frac{d\eta}{dT}\right)$ *in °K 10*$^{-4}$		
					Present	*Yokoyama et al.*[24]	*Ashcroft & Langreth*[10]
Na	371	0.9265	6.2579	0.4612	−3.388	−3.13	−3.05
	473	0.9014	6.1659	0.4296	−2.833	—	—
	573	0.8754	6.0922	0.4034	−2.429	—	—
	673	0.8494	6.0293	0.3806	−2.151	—	—
	773	0.8234	5.9741	0.3600	−1.987	—	—
K	336.4	0.8270	7.6632	0.4441	−3.805	−3.32	—
	423	0.8067	7.5449	0.4138	−3.220	—	—
	523	0.7832	7.4313	0.3842	−2.729	—	—
	623	0.7597	7.3349	0.3587	−2.392	—	—
	723	0.7362	7.2623	0.3360	−2.162	—	—
Rb	312.6	1.4881	8.2179	0.4355	−4.386	−3.87	—
	373	1.4600	8.1174	0.4110	−3.763	—	—
	473	1.4139	7.9788	0.3769	−3.122	—	—
	573	1.3678	7.8625	0.3477	−2.737	—	—
	673	1.3217	7.7623	0.3224	−2.338	—	—
Cs	301.6	1.8328	8.7922	0.4425	−4.431	−5.78	—
	373	1.7936	8.6678	0.4136	−3.715	—	—
	473	1.7386	8.5191	0.3797	−3.126	—	—
	573	1.6836	8.3973	0.3503	−2.768	—	—
	673	1.6286	8.2914	0.3245	−2.360	—	—

The values of heat function (H) computed as a function of temperature is displayed in Figure 2 along with the experimental observation of Hultgren *et al*[25]. The best agreement is obtained for Cs followed by Na, K and Rb. It may be noted that the enthalpy of liquid alkali metals does not depend sensitively on temperature above the melting point. The rise of temperature experiences an increase in enthalpy function. Our results suggest that the decrease of the magnitude of enthalpy function due to F_f and F_M terms is compensated by virtue of the increasing values of $|F_s|$ and $|F_{eg}|$. The net effect is such that the enthalpy depends very little on temperature above the melting point.

3.3 Compressibility

The hard sphere reference system under Pencus–Yevick approximation has been very successful to explain the compressibility of liquid metals near the melting temperature. η for alkali metals is usually taken as 0.47. Our basic aim here is to use the optimized values of η (see, Table 1) to compute the compressibility as a function of temperature. The Percus–Yevick equation and the hard sphere potential in its simplest form yield

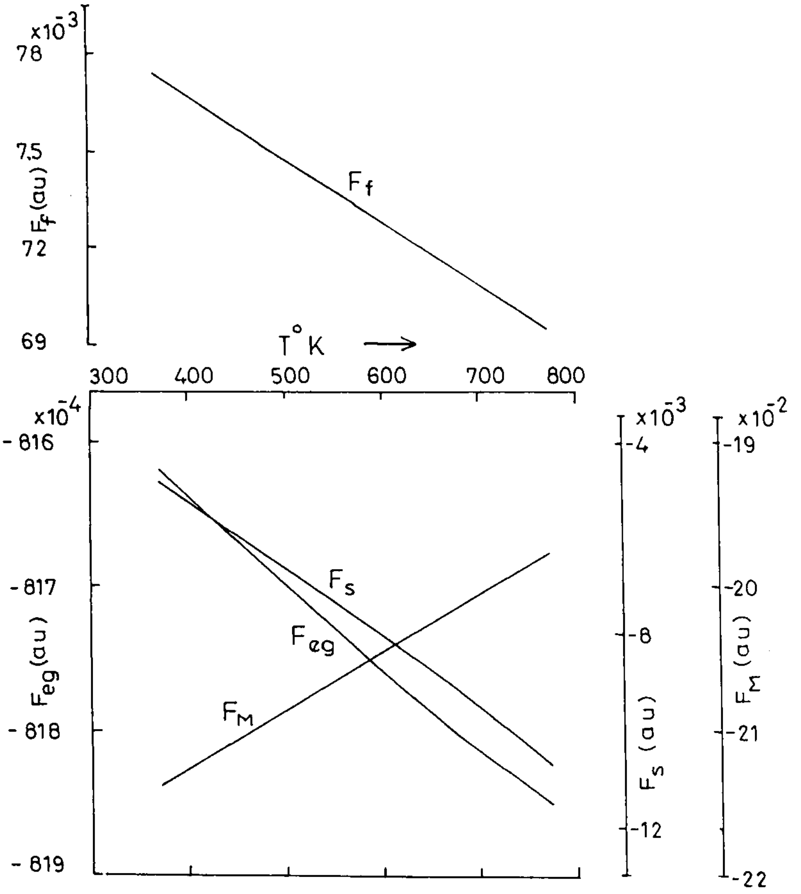

Figure 1 Various contributions of Helmholtz free energy to enthalpy for Na as a function of temperature: F_f—first order perturbation energy, F_s—band structure energy, F_M—Madelung energy and F_{eg} is the free electron gas term.

an expression for compressibility, as

$$\chi_T = \left\{ nK_B T \frac{(1+2\eta)^2}{(1-\eta)^4} \right\}^{-1} \tag{20}$$

It may be noted that Eq. (20) arises only due to structure dependent part of energy. Therefore a simple correction is required for volume dependent part of the total energy which includes kinetic energy of a free electron gas, Coulomb, exchange-correlation and the energy of lowest state of valence electron. Ascarelli[26] approximated that the volume dependent energy consists of two terms, the kinetic energy of the electron gas and a negative energy term, $-B\Omega^{1/3}$. The latter includes the energy of interaction of valence electrons with ions and the energy of interaction among themselves. The constant B can be determined from the condition that the pressure

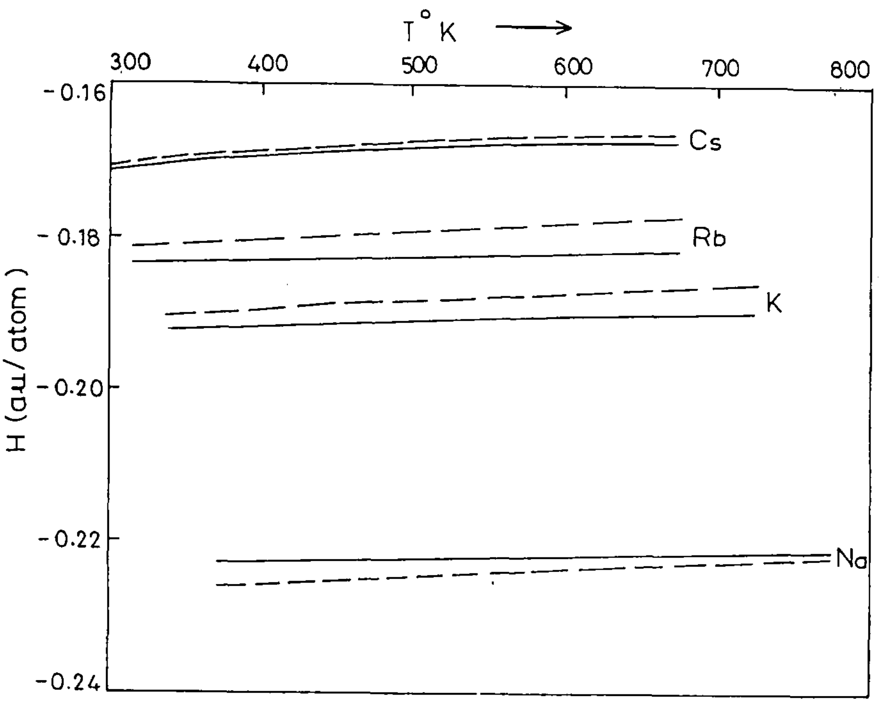

Figure 2 Enthalpy (H) of Na, K, Rb and Cs as a function of temperature ——— represents theory and ---- stands for experiment[25].

of the system is zero at the melting point. The resultant expression for the compressibility becomes

$$\chi_T = \left[nK_B T \left\{ \frac{(1 + 2\eta)^2}{(1 - \eta)^4} - \frac{4}{3} \frac{(1 + \eta + \eta^2)}{(1 - \eta)^3} + \frac{2ZE_F}{15K_B T} \right\} \right]^{-1} \tag{21}$$

where z is the valency and E_F is the Fermi energy. It may be mentioned that the compressibility can also be deduced from the knowledge of the various contributions of the Helmholtz free energy as in Section 2. By doing so we have observed that the condition P=O, is not achieved easily. In order to achieve it, one usually adjusts[27–28] the pressure due to first order band structure energy which comes out a large number. Therefore we have avoided it in our approach.

η as obtained in Section 3.1 has been used to compute the compressibility of Na, K, Rb and Cs from Eqs (20) and (21) at the melting temperature. These are tabulated in Table 2 and are compared with the experimental observation[29–30]. The best agreement has been obtained for Na and the values computed with Eqs (20) and (21), are almost the same. This shows that the contribution due to second and third terms of (21) for Na cancel each other. For K, Rb, and Cs the values due to Eq. (20) are better in agreement with experimental observation. The results of Table 2 also suggest that main contribution to the compressibility for liquid alkali metals arises

Table 2 Isothermal compressibility (in 10^{-12} cm^2/dyne) near the melting point.

Element	*Temp.* °*K*	*From Eq. (20)*	*From Eq. (21)*	*Hafner*[5]	*Hasegawa & Young*[31]	*Expt.*[29–30]
Na	371	18.366	18.996	26.31	22.93	18.599
K	336.4	45.327	50.077	55.55	53.76	38.199
Rb	312.6	64.176	71.089	66.666	70.42	49.30
Cs	301.6	78.699	90.768	90.91	90.91	68.80

from the structure dependent part of energy. The volume dependent part either has no contribution as in case of Na or it enhances the computed value of compressibility for K, Rb and Cs in comparison to experimental observation.

By judging the performance of Eq. (20) at the melting point, it has been used to compute χ_T at $T > Tm$ by making use of η as depicted in Eqs (15) to (18). The computed results of compressibility for Na, K, Rb and Cs are plotted in Figure 3 and are compared with the experimental observation[29–30]. The temperature gradients of compressibility due to theory and experiment are very much alike. The discrepancies between theory and experiment at higher temperatures are of the same order as that near the melting points. This indicates that Eq. (20) works reasonably well at temperatures above the melting point.

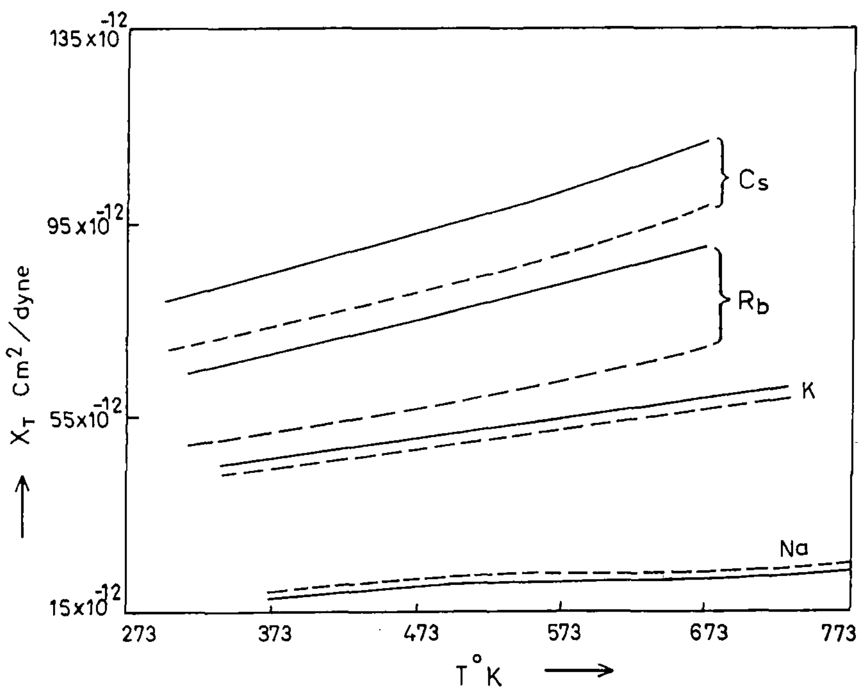

Figure 3 Compressibility (χ_T) of Na, K, Rb and Cs as a function of temperature ——— is due to theory and ---- represents experimental values.[29–30]

4 CONCLUSION

The enthalpy and compressibility of liquid alkali metals (Na, K, Rb and Cs) as a function of temperature can successfully be studied by blending the technique of pseudopotential method to the hard sphere result.

The enthalpy which depends weakly on temperature has been explained by considering various contributions to the Helmholtz free energy. The decrease of the magnitude of the enthalpy (H) due to first order energy (F_f) and Madelung energy (F_M) is compensated due to increasing values of free electron gas term, $|F_{eg}|$ and band structure energy, $|F_s|$ and as a result H only depends weakly on temperature.

The structure-dependent part of energy has been found sufficient to explain the compressibility of liquid alkali metals near and above the melting temperatures.

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