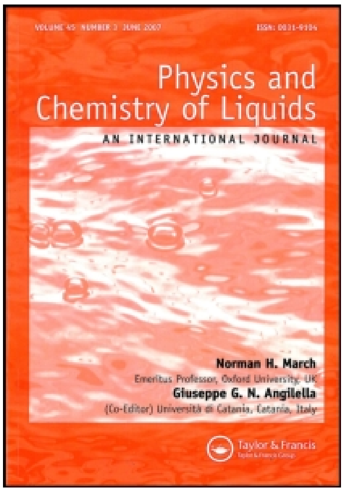

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THERMODYNAMIC PROPERTIES OF LIQUID ALKALI METALS

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Modified form of the pressure equation appropriate to liquid alkali metals is applied to the calculations of the thermal pressure coefficient and the thermal expansion coefficient. Comparison is made with the hard sphere reference system to understand the role of softness in the pair potential on the thermodynamic properties of alkali metals.

KEY WORDS: Direct correlation function. Soft core potential.

Softness in the pair potential plays a significant role in the determination of the structure factor of the liquid alkali metals[1]. The fact that the one component plasma (OCP)[2] works better than Hard Sphere reference system for the liquid alkali metals suggests that the softness in the pair potential is an essential factor for the soft alkali metals. Another soft reference system is the hard-sphere Yukawa (HSY) reference system proposed by Waisman[3]. The HSY reference system was first applied by Hayter *et al.*[4] to fit the structure factors of the liquid alkali metals. The main advantage of the HSY over the HS reference system fluid is to account not only the effective size of atoms, but for the softness of the interatomic interaction at close contact. This reference system has recently been applied for the determination of the structure factors of the liquid alkali and transition metals[5]. The disadvantage of the HS system i.e. Percus–Yevick solution is that it is not precisely correct towards high density. Recently this has been corrected by Colot *et al.*[6] who have presented a semiempirical expression for the direct correlation function (dcf) for the HS model with a Yukawa tail. We[7] have calculated the structure factors of alkali metals using this dcf combined with the Cummings potential in RPA, now referred as PYT, at different temperatures and shown that the softness in the pair potential is an important factor for the density dependence of the structure factors of liquid alkali metals, in particular that of the low q behaviour of $S(q)$.

The purpose of the present note is to calculate thermal pressure coefficient γ_v and the thermal expansion coefficient of liquid alkali metals and thereby comment on the affect of softness in the pair potential in describing thermodynamic properties of liquid alkali metals. Several authors[8,9] have found that the hard sphere model gives rather good description of γ_v for polyvalent and transition metals but not for alkali metals. Hasegawa and Watabe[10] pointed out that γ_v is a very sensitive quantity and appropriate pressure equation and suitable structure factors as well as their density—

derivatives are highly needed to reproduce γ_v of the alkali metals. The thermal pressure coefficient is defined by $\gamma_v = (\partial P/\partial T)_v$ which can be calculated as noted below.

The Fourier transformed dcf obtained by mixing the Percus–Yevick dcf with the dcf of the Yukawa tail can be written as[6]

$$C_{PYT}(q) = aC_{PY}(q) + [24\eta b/(q^2 + d^2)]\left[\cos q + \frac{d}{q}\sin q\right] \tag{1}$$

The parameters $a(\eta)$, $b(\eta)$ and $d(\eta)$ are given by Colot *et al.*[6] Using RPA approximation, the long wavelength limit can be written as[1]

$$[S(0)]^{-1} = \beta\left[\frac{\partial P}{\partial \rho}\right] = 1 - aC_{PY} - \frac{24\eta b(1+d)}{d^2} - \frac{24\eta(x_1a_1 + x_2a_2)}{(a_2^2 + a_1^2)} \tag{2}$$

where x_1, x_2, a_1, a_2 are the potential parameters defined in the earlier work[1]. By integrating Eq. (2), we get the equation of state as

$$\frac{P}{\rho K_B T} = 1 - a + \frac{a(1+\eta+\eta^2)}{(1-\eta)^3} - \frac{12b(1+d)\eta}{d^2} - \frac{12\eta(x_1a_1 + x_2a_2)}{(a_1^2 + a_2^2)} \tag{3}$$

Here $a(\eta)$, $b(\eta)$ and $d(\eta)$ are treated as constants at a particular temperature. Substituting $a = 1$ and $b = 0$, we get equation of state for the HS system. We can now derive γ_v as

$$\gamma_v = \left(\frac{\partial P}{\partial T}\right)_v = \frac{P}{T} + \rho K_B T\left[a\frac{(\eta+2)^2}{(1-\eta)^4} - \frac{12b(1+d)}{d^2} - \frac{12(x_1a_1 + x_2a_2)}{(a_1^2 + a_2^2)}\right]\left(\frac{d\eta}{dT}\right)_v \tag{4}$$

The coefficient of thermal expansion (α_P) can be written in terms of isothermal compressibility X_T and thermal pressure coefficient γ_v.

$$\alpha_P = X_T\gamma_v \tag{5}$$

and the long wavelength limit of the structure factor $S(0)$ can be written as

$$S(0) = \rho K_B T X_T \tag{6}$$

Thus we can derive an expression for α_P as

$$\alpha_P = \frac{S(0)}{T}\left[\left\{1 - a + \frac{a(1+\eta+\eta^2)}{(1-\eta)^3} - \frac{12b(1+d)\eta}{d^2} - \frac{12\eta(x_1a_1 + x_2a_2)}{(a_1^2 + a_2^2)}\right\}\right.$$
$$\left. + T\left\{\frac{a(\eta+2)^2}{(1-\eta)^4} - \frac{12b(1+d)}{d^2} - \frac{12(x_1a_1 + x_2a_2)}{(a_1^2 + a_2^2)}\right\}\left(\frac{d\eta}{dT}\right)_v\right] \tag{7}$$

with $S(0)$ defined by Eq. (2).

Firstly, we have calculated the full structure factors of liquid alkali metals at different temperatures using the dcf of Colot *et al.* combined with Cummings potential in RPA[7]. The value of η is obtained by fitting the first peak of the structure factor at different temperatures. At higher temperatures, we have established the uniqueness of the potential parameters and setting the hard sphere diameters as density dependent. The parameters used in the calculations are tabulated elsewhere.[7,11] Knowing the data from the structural analysis, we are now interested to visualize the effect of softness on the thermodynamic properties of the alkali metals. We have calculated γ_v and α_P of the liquid alkali metals for soft reference system (PYT). In the calculations of Eqs (4) and (7), the value of $(\partial\eta/\partial T)_v$ is taken from the work of Hasegawa and Watabe[10] as the various empirical relations present in the literature for its calculations, are not reliable. We have also calculated γ_v for hard sphere system by setting $a = 1$ and $b = 0$ in the Eqs (3) and (4) and using the parameters as those obtained by Bretonnet[12]. The calculated values of γ_v for PYT and HS systems are shown in Table 1 at different temperatures along with the experimental results. A clear trend is that the softness improves the γ_v values over HS system at the melting temperature. At higher temperatures the γ_v values decrease with increasing temperature and the effect of softness decreases. We have assumed that the temperature derivative of the packing fraction $(\partial\eta/\partial T)_v$ is independent of η as also assumed by others[9].

The thermal expansion coefficient α_P is calculated using Eq. (7) and the results are presented in Table 2. Comparison is made with the experimental values[13] and with the calculated values obtained by using hard sphere model. The parameters including $S(0)$ values for HS system are obtained from the work of Bretonnet[12]. We find that there is a little effect of the softness on the values of the coefficient of thermal expansion. It may be due to the fact that the increase in the γ_v value due to the hardness in the pair potential is compensated by the decrease in the value of $S(0)$ due to hardness.

Table 1 Calculations of thermal pressure coefficient (bar K^{-1}) of liquid alkali metals.

Element	*Temp.* (K)	η (PYT)	$-\left(\frac{d\eta}{dT}\right)_v$ $(10^{-4}\,K^{-1})$	γ_v (PYT)	γ_v $(Expt)$	γ_v (HS)
Li	463	0.493	1.87	26.5	27.3*	31.9 (470 K)
	725	0.441	1.87	5.07	—	5.5 (725 K)
Na	378	0.465	2.11	14.4	13.0	18.9 (373 K)
	473	0.4395	2.11	9.1	—	13.6 (423 K)
	573	0.427	2.11	7.3	—	—
K	343	0.451	2.07	7.8	7.6	10.5 (338 K)
	378	0.432	2.07	6.3	—	8.9 (373 K)
	473	0.431	2.07	4.6	—	7.0 (423 K)
Rb	313	0.470	1.89	7.9	6.9	—
	373	0.448	1.89	6.1	—	—

* Theoretical value from Ref. [10].

Table 2 Calculations of thermal expansion coefficient (10^{-4} K^{-1}).

Element	*Temp* (*K*)	η (*PYT*)	α_P (*PYT*)	α_P (*HS*)	α_P (*Expt*)
Li	463	0.493	1.7	1.8	1.6
Na	378	0.465	2.8	2.9	2.75, 2.42
K	343	0.451	3.7	3.8	2.90
Rb	313	0.470	4.1	—	3.4

We can now conclude that the softness in the pair potential of the alkali metals significantly affects the thermodynamic properties such as specific heat[11] (Cp) and thermal pressure coefficient while a few properties such as thermal expansion coefficient remain almost unaffected.

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