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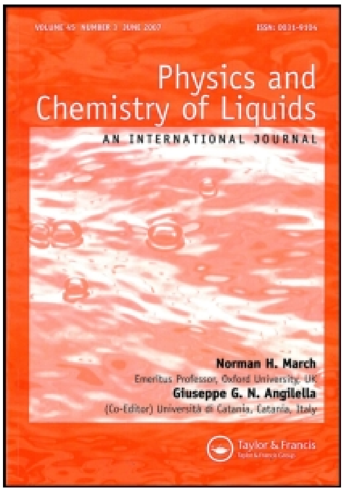

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EFFECT OF SOFT FORCES AND COMPUTATION OF THERMAL PROPERTIES OF LIQUID METALS

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Effect of the soft force component to the entropy of the system is discussed in the light of thermodynamic perturbation theory and an explicit expression is obtained as a function of the ingredients of the hardcore reference system. Same basic ingredients can thus produce the structural and thermal properties reasonably not only near the melting point but also at thermodynamic states considerably away from the melting point.

KEY WORDS: Gibbs–Bogoliubov inequality, entropy.

1 INTRODUCTION

Studies of the thermal properties of liquid metals and their temperature variation are important from various metallurgical point of view. Both the experimental results[1] and theoretical calculations[2–4] for most of the metallic systems are available, but the calculations were mostly based on the hard sphere description of the reference system. The effect of soft forces on the calculation of entropy of liquid metals and thermodynamics in general was demonstrated clearly by Young[2], Kumaravadivel and Evans[5] but these still lack sufficient quantitative analytic discussion. On the variational thermodynamic calculations through the Gibbs–Bogoliubov (GB) inequality[3] the soft force contribution is surely taken into account but the resulting hardcore ingredients depend on the nature of the pseudopotential and dielectric screening function and fails to produce a good reference structure factor. We consider in the present study the soft force contribution to the entropy in the vander Waals' picture with a hard sphere as reference system. The inclusion of the soft force contribution not only yields a good quantitative estimate of the properties at the melting point but also generates a good variation of the properties over a wide range of temperature.

Our consideration is two fold. Firstly, in the thermodynamic perturbation method we write the entropy expression of the system including the appropriate term arising from the soft forces. The effective entropy is thus assumed to be the sum of the hard sphere (hs), soft force (sf) and electronic (el) contributions. The hard sphere contribution comprising the bulk of the thermal properties is calculated by the Carnahan and Starling formula[6] (CS) characterised by a packing density, η. The soft

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force contribution is obtained from the free energy of the system in an analytic form (Appendix). Again the variation of density at higher temperature brings about notable changes in the free electron Fermi diameter and thus the inclusion of the electronic part in the temperature dependence of thermal properties is essential[2]. Our second consideration is that we must determine properly[7] the basic ingredients of the reference system, namely, the effective hard core diameter and take appropriately its temperature dependence (Section 2B). Careful comparison of the computed properties with hard sphere results shows that there is considerable improvement over the hard sphere values by the inclusion of soft forces. We have also done the calculations for three typical nonmetallic liquids to show the validity of the present approach in those cases as well.

2 THEORETICAL BACKGROUND

We briefly describe the formulations employed in the calculations.

A Expressions of Thermal Properties

Entropy The entropy of the liquid metal system at temperature T, with number density n and ionic mass m is given by

$$S = S^{hs} + S^{sf} + S^{el} \tag{1}$$

where, S^{hs} is the entropy relevant to the hard sphere description of the system and this is obtained from the Helmholtz free energy due to Carnahan and Starling[6]

$$\frac{S^{hs}}{Nk_B} = \frac{S^{id}}{Nk_B} - \frac{\eta(4-3\eta)}{(1-\eta)^2} \quad \text{with} \quad \frac{S^{id}}{Nk_B} = \tfrac{5}{2} + \ln\left\{1/n\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right\} \tag{1a}$$

where, $\eta = \pi n\sigma^3/6$, σ being the effective hard core diameter. Within vander Waals picture the contribution arising from the soft force is given by (please see Appendix)

$$\frac{S^{sf}}{Nk_B} = CnT^{1/2}\sigma^2 g_0(\sigma) \quad \text{with} \quad C = \frac{\pi f(\sigma_0 - \sigma_m)}{T_m^{1/2}} \tag{1b}$$

where, σ_0 is the location of the minimum in the pair potential, σ_m refers to the melting point, T_m, $g_0(\sigma)$ is the hard sphere radial distribution function at the core and is given by CS formula

$$g_0(\sigma) = \frac{1-\eta/2}{(1-\eta)^3} \tag{1c}$$

f is a parameter related to the soft force part of the potential. Finally, the electronic contribution S^{el} arising from the near degeneracy of the electron gas[2] is obtained assuming that the relevant Fermi distribution function is safely replaced by a step function. This approximation allows us to consider the zeroth order Sommerfeld parameter and to neglect the corrections that could arise from the exchange and correlation. Thus, for temperatures much below the Fermi temperature, T_f, we have

$$\frac{S^{el}}{Nk_B} = zT/2\left(\frac{\pi^2 k_B}{k_f^2}\right) \tag{1d}$$

The excess entropy, S^{ex} is given by

$$S^{ex} = S - S^{id} \tag{2}$$

Specific heats In the spirit of the preceeding paragraphs we can express the specific heat capacity at constant volume as

$$C_v = C_v^{hs} + C_v^{sf} + C_v^{el} \tag{3}$$

where, C_v^{hs} is given by

$$\frac{C_v^{hs}}{Nk_B} = \tfrac{3}{2} - \frac{2\eta(2-\eta)}{(1-\eta)^3}\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_V \tag{3a}$$

The contribution arising from the soft part of the pair potential is

$$\frac{C_v^{sf}}{Nk_B} = \frac{S^{sf}}{2Nk_B}\left[1 + \frac{2}{3}\frac{4 + 9\eta - 4\eta^2}{(1-\eta)(2-\eta)}\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_V\right] \tag{3b}$$

The corresponding expression for the electron contribution is

$$\frac{C_v^{el}}{Nk_B} = \frac{S^{el}}{Nk_B} \tag{3c}$$

In the same way the specific heat capacity at constant pressure can be written as

$$C_p = C_p^{hs} + C_p^{sf} + C_p^{el} \tag{4}$$

where the various contributions are respectively given by

$$\frac{C_p^{hs}}{Nk_B} = \frac{3}{2} + T\alpha_p - \frac{2\eta(2-\eta)}{(1-\eta)^3}\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p \tag{4a}$$

$$\frac{C_p^{sf}}{Nk_B} = \frac{S^{sf}}{2Nk_B}\left\{1 - 2\alpha_p T + \frac{2\eta(5-2\eta)}{(1-\eta)(2-\eta)}\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p\right\} \tag{4b}$$

and

$$\frac{C_p^{el}}{Nk_B} = \frac{S^{el}}{Nk_B}(1 + \tfrac{2}{3}\alpha_p T) \tag{4c}$$

where, α_p is the expansivity of the metallic system.

Thermal pressure coefficient Using the thermodynamic relation $(\partial P/\partial T)_V = (\partial S/\partial V)_T$ we have

$$\gamma_v = \frac{1}{Nk_B}\left(\frac{\partial P}{\partial T}\right)_V = \gamma_v^{hs} + \gamma_v^{sf} + \gamma_v^{el} \tag{5}$$

where,

$$\gamma_v^{hs} = 1 - \frac{2\eta(2-\eta)}{(1-\eta)^3}\left(\frac{\partial \ln \eta}{\partial \ln V}\right)_T \tag{5a}$$

$$\gamma_v^{sf} = -\frac{S^{sf}}{3Nk_B}\left[1 - \frac{4+9\eta-4\eta^2}{(1-\eta)(2-\eta)}\left(\frac{\partial \ln \eta}{\partial \ln V}\right)_T\right] \tag{5b}$$

and

$$\gamma_v^{el} = \frac{z}{3}\frac{\pi^2 k_B T}{k_f^2} \tag{5c}$$

Heat of vaporization at B.P. We consider the entropy cycle consisting of four isothermal steps carried out at the boiling point, T_B. The liquid is vaporized to gas at one atmosphere pressure and the entropy change in this step is $\Delta H^0/T_B = \Delta S_1$. The real gas is then discharged at constant volume to the model soft force gas. The real intermolecular potential is modified to one we have in our model case and the entropy change in this step is very small $(-\Delta S_2(g))$. The soft force gas is then compressed from volume V_g at one atmosphere pressure to the volume V_1 at one atmosphere which the real liquid occupies and the entropy change in this step is

$$\int_{V_g}^{V_1} \frac{dQ}{T_B} = \Delta S_3$$

given by

$$\frac{\Delta S_3}{Nk_B} = \frac{S_1 - S_g}{Nk_B} = \ln(V_1/V_g) - \frac{\eta_l(4-3\eta_l)}{(1-\eta_l)^2} + \frac{\pi}{2} f \frac{(\sigma_o - \sigma_m)N\sigma^2}{V_1} \cdot \frac{(2-\eta_l)}{(1-\eta_l)^3}\left(\frac{T_B}{T_m}\right)^{1/2} \tag{6}$$

where, η_l refers to the liquid at B.P. and η_g that for gas is put equal to zero. The compressed model fluid is then changed at constant volume to the real fluid and the entropy change in this step is very small $(\Delta S_4(1))$. With reasonable assumption[8] of $\Delta S_2(g) = \Delta S_4(1)$ we have

$$\Delta H^\circ = Nk_B T_B\left[\ln(V_g/V_1) + \frac{\eta_l(4-3\eta_l)}{(1-\eta_l)^2} - \frac{\pi}{2} f \frac{(\sigma_0 - \sigma_m)N\sigma^2}{V_1}\frac{(2-\eta_l)}{(1-\eta_l)^3}\left(\frac{T_B}{T_m}\right)^{1/2}\right] \tag{7}$$

The entropy of vaporization is given by

$$\Delta S_v^0 = \Delta H^0/T_B \tag{8}$$

Isothermal compressibility Once the values of C_p and C_v are obtained the isothermal compressibility χ_T is given by

$$\chi_T = \frac{TV\alpha_p^2}{C_p - C_v} \tag{9}$$

B Choice of Hard Sphere Ingredients

There are various schemes for choosing the hardsphere ingredients. We use two distinct but accurate methods for doing this. One method that avoids the effective pair potential and uses the structure factor peak is quite successful[9,7]. As there is slight scatter in the values of η at m.p. from system to system[7] we have chosen η to be 0.46 at m.p. for all metallic systems. The temperature variation of η is given by

$$\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p = -\frac{(1 + aT)(1 + 2\eta)(1 - \eta)}{4\eta(2 + \eta)} \tag{10}$$

where 'a' is a constant as given by Joarder and Rao[9]. This method is fairly in agreement with variational method. Again, in accordance with the work of Protopapas *et al.*[10] (please see Appendix) we obtain $(\partial \ln \eta/\partial \ln T)_v$. Since $\eta = \eta\ (V, T)$ we have thermodynamically

$$\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p = \left(\frac{\partial \ln \eta}{\partial \ln T}\right)_V + \alpha_p T\left(\frac{\partial \ln \eta}{\partial \ln V}\right)_T \tag{11}$$

and so $(\partial \ln \eta/\partial \ln V)_T$ is obtainable.

Another method for hardcore ingredients intuitively appealing and easy to apply is due to Ashcroft and Langreth[11] (AL) and these ingredients also reasonably agree with those from variational calculation at or near the m.p.[12,13]. Thus, if the effective pair potential $\phi(r, n)$ is known then the effective hard core diameter σ for the liquid state ionic collisions can be estimated from

$$\phi(\sigma, n) = \tfrac{3}{2}k_B T + \phi_{\min}(r, n) \tag{12}$$

where, $\phi_{\min}(r, n)$ is the first minimum in $\phi(r, n)$ at $r = \sigma_0$. The method however disagrees with the variational method at higher temperatures[13]. The effective pair potentials are constructed[14] by using Asheroft empty core pseudopotential[15] with dielectric screening given by Vashishta and Singwi[16].

In nonmetallic liquid cases the LJ potential has been used for the hardcore ingredients.

3 RESULTS AND DISCUSSION

The results of our calculations are shown in Table 1 and 2 for various liquids. The temperature variations of some of the properties are depicted in Figures 1–3 while in Figure 4 we show the variation of basic ingredient and the soft force component of entropy. The required densities at various temperatures are obtained from standard literature[17]. There is good agreement with the observed quantities. The variation of the hard core volume with volume finds its expression in the pressure coefficient while that with temperature in the heat capacity. Correct evaluation of these thermal properties surely means that the temperature variation of η accounts well the softness of the pseudoatom. The softness parameters agree fairly well with those of other workers[18,7]. It is to be mentioned that the effects of the soft forces and electronic term

Table 1 Basic ingredients and thermal properties of liquid metals.

		Na		*K*		*Rb*		*Cs*	
		A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Basic ingredients									
$T(K)$		371		337		313		303	
η		0.46	0.459	0.46	0.466	0.46	0.46	0.46	0.452
$-\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p$	Present	0.259	0.259	0.252	0.247	0.264	0.264	0.263	0.260
	Ref. 7	0.21		0.194		0.16		0.162	
$-\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_V$	Present	0.203	0.204	0.20	0.204	0.20	0.204	0.20	0.206
	Ref. 18	0.21,0.275		0.19,0.262		0.18,0.28		0.17,0.406	
$-\left(\frac{\partial \ln \eta}{\partial \ln V}\right)_T$	Present	0.53	0.537	0.50	0.44	0.57	0.558	0.535	0.48
	Ref. 18	0.407		0.462		0.512		0.539	
Thermal properties									
$-S^{ex}/Nk_B$	Present	3.44	3.40	3.417	3.35	3.413	3.38	3.404	3.43
	Expt.	3.45		3.46		3.63		3.56	
C_v/Nk_B	Present	3.323	3.311	3.345	3.425	3.349	3.344	3.358	3.292
	Expt.	3.42		3.48		3.29		3.2	
C_p/Nk_B	Present	3.868	3.859	3.842	3.891	3.941	3.949	3.945	3.813
	Expt.	3.83		3.86		3.78		3.84	
$\gamma(=C_p/C_V)$	Present	1.164	1.166	1.148	1.136	1.177	1.181	1.175	1.158
	Expt.	1.12		1.11		1.15		1.20	
$\frac{1}{nk_B}\left(\frac{\partial P}{\partial T}\right)_V$	Present	4.607	4.622	4.412	4.13	4.922	5.208	4.659	4.126
	Expt.	3.89		4.43		4.87		4.99	
$\chi_T \times 10^{12}$	Present	14.48	15.9	31.3	35.6	43.8	42.6	69.22	69.20
(cm^{2}dyne)	Expt.	18.6		38.2		49.3		68.8	
ΔS^0 at B.P.	Present	19.51	19.65	20.04	20.08	19.38	19.38	18.68	18.62
(Cal/deg Mole)	Expt.	17.84		17.95		19.02		16.95	

are very important. The magnitude of the soft force contribution to entropy at m.p. compares favourably with those of the WCA calculation of Ref. 5. It decreases gradually with temperature (Figure 4) and this has the correct trend^2. This contribution is entirely given in terms of the hard sphere ingredients and this is remarkable. In consistency with PY results at m.p. we have fixed the value of the soft force parameter 'f' to be 0.35 for all systems at all temperatures though in practice it decreases very slowly with temperature. The calculations of the temperature dependent properties show that this choice is quite reasonable. It is to be mentioned that a small decrease of 'f' at higher temperatures will improve the results e.g. C_p/Nk_B in particular. The approximation is however very good at or near the m.p. The evaluation of the electronic term in Sommerfeld model is approximate particularly at very high temperature. The discrepancies in the computed properties at high temperature need a

Zn		*Hg*		*Pb*		*Al*		*Cu*	
A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
723		293		613		943		1423	
0.46	0.441	0.46	0.424	0.46	0.444	0.46	0.453	0.46	0.456
0.312	0.305	0.254	0.277	0.282	0.292	0.228	0.312	0.346	0.348
0.182		0.12		0.318		0.324		0.283	
0.20	0.206	0.20	0.205	0.20	0.205	0.20	0.205	0.20	0.204
0.12		0.064		0.076,0.178		0.129,0.206		0.093,0.159	
1.01	0.983	0.975	1.37	1.10	1.22	0.851	0.88	1.05	1.066
—		—		0.792		0.749		0.897	
3.417	3.19	3.455	3.23	3.376	3.20	3.20	3.377	3.398	3.13
3.89		4.54		4.10		3.52		3.44	
3.346	3.138	3.308	2.968	3.386	3.149	3.385	3.31	3.364	3.284
3.02		2.42		3.07		3.04		3.08	
4.302	3.928	3.803	3.467	4.095	3.85	4.310	4.23	4.586	4.486
3.78		2.72		3.68		3.80		3.9	
1.285	1.251	1.15	1.168	1.21	1.223	1.273	1.278	1.363	1.366
1.25		1.13		1.20		1.25		1.27	
8.035	7.047	7.755	8.5	8.706	8.73	7.075	6.85	8.373	8.24
6.70		8.47		7.74		6.56		7.47	
2.12	2.15	2.29	2.28	2.07	2.08	2.36	2.37	1.027	1.02
2.50		3.75		3.49		2.42		1.49	
15.10	15.09	18.9	18.74	19.8	19.6	21.01	21.01	15.14	16.99
22.2		21.3		21.3		20.04		25.4	

A: From structure factor; B: From AL prescription using liquid metal potential.

better treatment of electronic term. The electronic term is very small at or near the m.p. compared to other terms and almost negligible. It is, however, comparable with soft force term at high temperature. In case of specific heats at high temperature there is a cancellation of soft force and electronic terms and so the general trend of variation is almost decided by the hard sphere term. A more accurate calculation of electronic term taking into account the effects from exchange and correlation will change the situation only slightly in the total property. It is also to be noted that the basic ingredients in the two distinct methods adopted agree very well and so also the calculated properties. Since the second method is less applicable at high temperature[13] we have not used this method in the computation of properties in that region.

Table 2 Basic ingredients and thermal properties of non-metallic liquids.

		Ar		*Ne*		CCl_4	
		A	*B*	*A*	*B*	*A*	*B*
Basic ingredients							
T(K)		83.8		25		293	
η		0.448	0.446	0.420	0.418	0.459	0.456
$-\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_v$	Calc.	0.22	0.221	0.256	0.26	0.205	0.209
$-\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_P$	Calc.	0.633	0.64	0.462	0.472	0.522	0.584
$-\left(\frac{\partial \ln \eta}{\partial \ln V}\right)_T$	Calc.	1.038	1.109	1.648	1.704	0.876	1.034
Thermal properties							
$-S^{ex}/Nk_B$	Present	3.263	3.23	2.62	2.778	3.468	3.230
	Expt.	3.62		—		3.44	
C_v/Nk_B	Present	3.247	3.239	3.149	3.141	3.367	3.359
	Expt.	2.47		3.458†		10.8	
C_p/Nk_B	Present	6.332	6.317	4.467	4.480	5.964	6.346
	Expt.	5.16		4.32†		15.4	
$\gamma(=C_p/C_v)$	Present	1.95	1.95	1.42	1.426	1.73	1.89
	Expt.	2.09		1.25		1.415	
$\frac{1}{\eta k_B}\left(\frac{\partial P}{\partial T}\right)_V$	Present	7.894	7.869	9.449	9.586	7.036	7.988
	Expt.	7.137		—		6.53	
$\chi_T \times 10^{12}$	Present	184.1	184.7	93.17	93.1	169.8	170.3
(cm^2/dyne)	Expt.	212.0		—		106.0	
ΔS^0 at B.P.	Present	11.38	11.35	11.57	11.54	11.24	11.18
(cal/deg. Mole)	Expt.	17.85		15.29		20.49	

A: Using *LJ* core diameter from 2nd virial coeff. and viscosity data

B: From *AL* prescription using *LJ* potential as in *A*.

† at 27.7 K

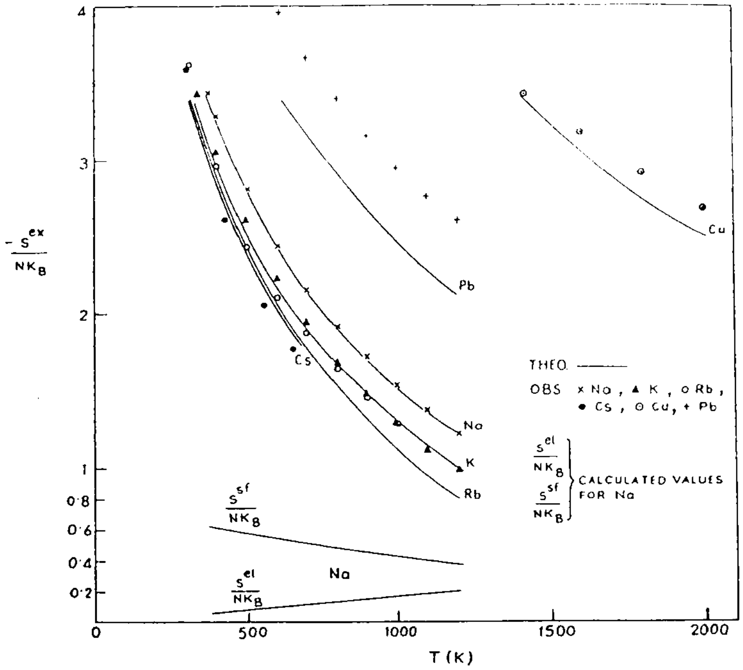

Figure 1

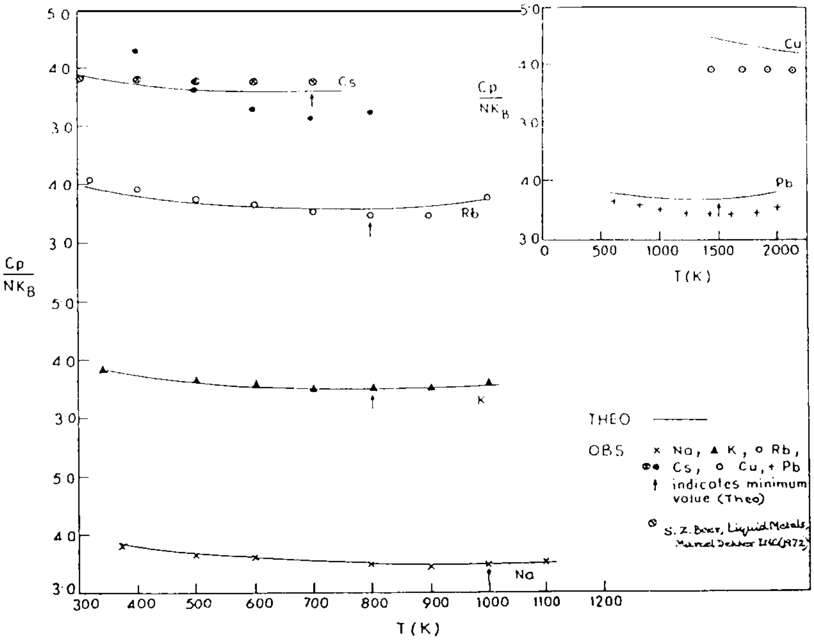

Figure 2

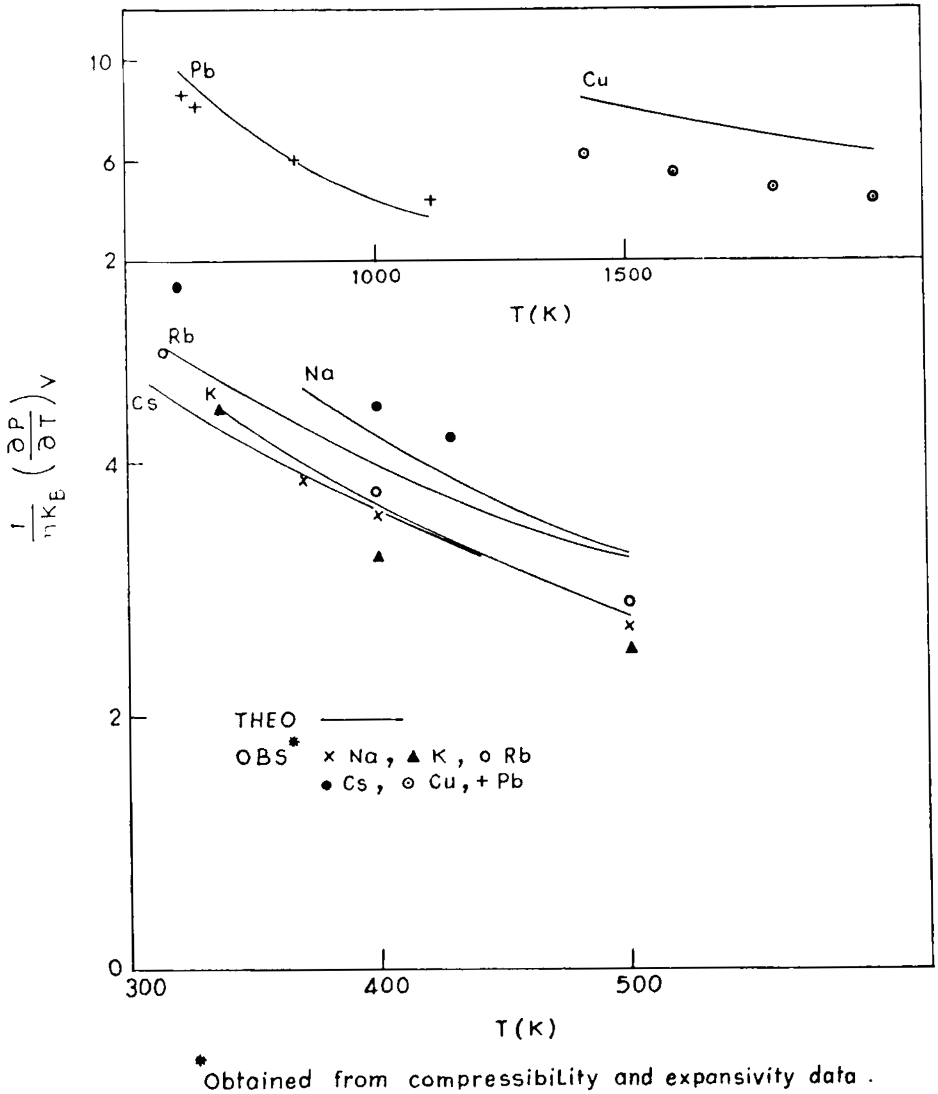

Figure 3

In the calculation for nonmetallic liquids the basic hard core ingredients are taken to be equal to the L-J core diameter σ obtained from second virial coefficient and viscosity data[19]. Where more than one value is available lowest value is taken to approximate the effective hardcore diameter. In the second set of calculations A-L prescription[11] is used to obtain the effective core diameter through LJ potential defined in Ref. 19. There is good agreement again between the two methods. The computed properties are in good agreement with observed quantities.

Thus, the present method is simple but distinctively advantageous in the sense that

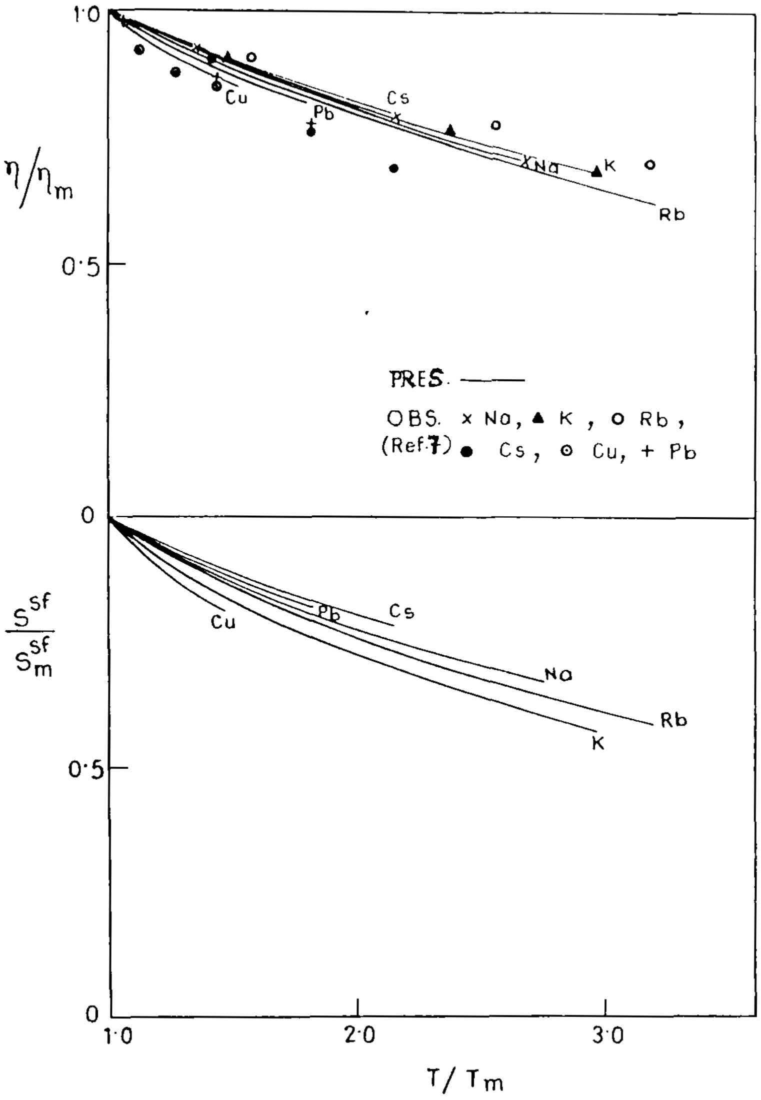

Figure 4

soft force effect is expressible analytically in terms of hard core ingredients and same ingredients can generate the structure and thermodynamic properties quite successfully even at high temperature. The ingredients in WCA method[20] too depend on the choice of the effective pair potential. In the light of present calculations we can conclude the following.

1) The soft force contributions to the thermal properties are important at all temperatures though the effect reduces gradually and vanishes in the limit of very high temperature.

2) The electronic contribution is also important particularly in the limit of high temperatures. We have used the sommerfeld approximation within a complete degeneracy of the electron gas ($T \ll T_f$) suitable for many cases[12].

3) The analytic approach adopted for the soft force contribution works for nonmetallic liquids as well.

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APPENDIX Softforce contribution to the entropy

We view the liquid metal as a collection of ions and electrons with potential energy per ion, $\psi(r_1, r_2, \ldots, r_N)$ described by a structure independent term $u_0(n)$ and a pairwise term $\phi(r, n)$

$$\psi(r_1, r_2, \ldots, r_N) = u_0(n) + \frac{1}{2N}\sum_{i \neq j}\phi(r_{ij}, n) \tag{A1}$$

both terms in principle depend on density. In thermodynamic perturbation method we separate the pairwise term into a hard sphere reference potential and a perturbation term $u(r, n)$. Now, in the framework of vander Waals theory with the choice of core diameter through an appropriate criterion the free energy of the metallic system is given by

$$\frac{F}{N} = \frac{F^{hs}}{N} + 2\pi n \int_{\sigma}^{\infty} u(r, n) g_0(r, n) r^2 dr + u_0(n) \tag{A2}$$

The entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial F}{\partial T}\right)_{V,\sigma} - \left(\frac{\partial F}{\partial \sigma}\right)_{V,T} \cdot \left(\frac{\partial \sigma}{\partial T}\right)_V \tag{A3}$$

From (A2) we have

$$-\frac{1}{N}\left(\frac{\partial F}{\partial T}\right)_{V,\sigma} = -\frac{1}{N}\left(\frac{\partial F^{hs}}{\partial T}\right)_{V,\sigma} - 2\pi n \int_{\sigma}^{\infty} u(r, n) \left(\frac{\partial g_0(r, n)}{\partial T}\right)_{V,\sigma} r^2 dr + \frac{S^{el}}{N}$$

where S^{el}/N is the electronic entropy which arises from the non-degeneracy of the election assembly. Since, $g_0(r, n)$ does not contain T explicity so the second term vanishes and so

$$-\left(\frac{\partial F}{\partial T}\right)_{V,\sigma} = -\left(\frac{\partial F^{hs}}{\partial T}\right)_{V,\sigma} + \frac{S^{el}}{N} = \frac{S^{hs}}{N} + \frac{S^{el}}{N} \tag{A4}$$

We have then

$$\begin{aligned} \frac{S}{N} = \frac{S^{hs}}{N} - \frac{1}{N}\left(\frac{\partial F}{\partial \sigma}\right)_{V,\sigma}\left(\frac{\partial \sigma}{\partial T}\right)_V &= \frac{S^{hs}}{N} - \left(\frac{\partial \sigma}{\partial T}\right)_V \left[\left(\frac{\partial F^{hs}}{\partial T}\right)_{V,T}\right. \\ &\left. + 2\pi n \left(\frac{\partial}{\partial \sigma}\right) \int_{\sigma}^{\infty} u(r, n) g_0(r, n) r^2 dr)_{V,T}\right] + \frac{S^{el}}{N} \end{aligned}$$

It is easy to show that

$$\frac{1}{2\pi n g_0(\sigma, n)\sigma^2}\left(\frac{\partial F^{hs}}{\partial \sigma}\right)_{V,T} = k_B T \tag{A5}$$

So we have

$$\begin{aligned} \frac{S}{N} &= \frac{S^{hs}}{N} + \frac{S^{el}}{N} - 2\pi n g_0(\sigma, n)\sigma^2 \left(\frac{\partial \sigma}{\partial T}\right)_V k_B T \\ &\times \left[1 + \frac{1}{\sigma^2 g_0(\sigma, n)}\left(\frac{\partial}{\partial \sigma}\left\{\sigma^3 \int_1^{\infty} \frac{u(r^*, n)}{k_B T} g_0(r^*, n) r^{*2} dr^*\right\}\right)_{V,T}\right] \end{aligned}$$

where, $r^* = r/\sigma$. The integral is clearly a negative constant $(-A)$. Thus,

$$\frac{S}{N} = \frac{S^{hs}}{N} - 2\pi n g_0(\sigma, n)\sigma^2 \left(\frac{\partial \sigma}{\partial T}\right)_V k_B T\left[1 - \frac{3A}{g_0(\sigma, n)}\right] + \frac{S^{el}}{N} \tag{A6}$$

The soft force contribution is thus given by

$$\frac{S^{sf}}{N} = -2\pi n g_0(\sigma, n)\sigma^2\left(\frac{\partial\sigma}{\partial T}\right)_V k_B T\left(1 - \frac{3A}{g_0(\sigma, n)}\right) \tag{A7}$$

In the variational method one chooses η so as to make this term vanish and entropy of the system is then given by Eq. (A4). It is however possible to estimate A for L-J potential in Laplace transformed space and for liquid metal potentials in Fourier transformed space within PY theory. The value of A comes out to be almost one in most cases at the m.p. Further at higher temperature both A and $g_0(\sigma, n)$ decrease slowly and the ratio remains almost constant. Under these circumstances we put the soft force parameter, $f = 1 - 3A/g_0(\sigma, n) \simeq 0.35$ for all systems at all temperatures.

Now, following the prescription by Protopapas *et al.*[10] concerning the average distance of closest approach for repulsive collisions, the pair potential in the close vicinity of minimum at $r = \sigma_0$ is approximated by a parabola and this gives

$$\left(\frac{\partial\sigma}{\partial T}\right)_v = -\frac{\sigma_0 - \sigma_m}{2\sqrt{T_m}\,T} \tag{A8}$$

where, we use $\sigma_0 = 1.0878\,(n_m)^{-1/3}$ as given by Protopapas *et al.*[10] and n_m refers to the density at m.p. Using (A8) in (A7) we have the soft forcce contribution to the entropy given by

$$\frac{S^{sf}}{Nk_B} = \pi n f(\sigma_0 - \sigma_m)\left(\frac{T}{T_m}\right)^{1/2}\sigma^2 g_0(\sigma, n) \tag{A9}$$