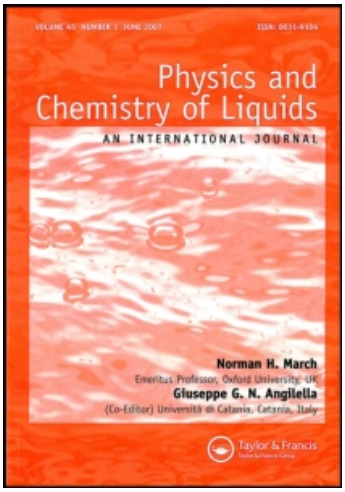

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic Properties of Liquid Metals: One-Component Plasma (OCP) Model

K. N. Khanna[a]; G. Shanker[a]
[a] Department of Physics, V.S.S.D. College (Kanpur University), Kanpur, India

To cite this Article Khanna, K. N. and Shanker, G.(1985) 'Thermodynamic Properties of Liquid Metals: One-Component Plasma (OCP) Model', Physics and Chemistry of Liquids, 15: 1, 69 — 73
To link to this Article: DOI: 10.1080/00319108508081005
URL: http://dx.doi.org/10.1080/00319108508081005

Phys. Chem. Liq., 1985, Vol. 15, pp. 69–73
0031-9104/85/1501–0069$18.50/0

Printed in the United Kingdom

Letter

Thermodynamic Properties of Liquid Metals: One-Component Plasma (OCP) Model

K. N. KHANNA and G. SHANKER

Department of Physics, V.S.S.D. College (Kanpur University), Kanpur 208002, India.

(*Received January 2, 1985*)

It is shown that the plasma parameter obtained by fitting the entropy of the system to observed one can reasonably reproduce thermodynamical properties of liquid metals. A simple method is proposed to calculate specific heat C_p of liquid metals in OCP system.

Recently it has been shown that liquid metals can be treated successfully as a system consisting of classical point like ions embedded in a uniform neutralizing background.[1] Several authors have recently reported thermodynamic properties of liquid metals, most of the approaches limited to alkali metals and discussed the usefulness of this system in comparison to the hard sphere reference system.[2–6] However, there remains an important question regarding the magnitude of the plasma parameter Γ.[7] It is noticed that the theoretical value of Γ which corresponds to the freezing point of the metals at atmospheric pressure lies above the value ($\Gamma = 155$ for alkali metals) at which the computer simulation indicates that the OCP is crystallizing. In view of this, in this communication, we demonstrate how the approach, to evaluate the value of Γ by fitting the entropy of the system to observe one, can be applied to improve the value of Γ and to calculate the thermodynamical properties of alkali and polyvalent liquid metals successfully. This fitting approach was successful in hard sphere system.[8] The Helmholtz free energy of a liquid metal can be assumed as

$$F = F_{\mathrm{OCP}} + F_{eg} \tag{1}$$

where F_{OCP} is the Helmholtz free energy in the OCP system and F_{eg} is the

difference in the free energy in the reference system (OCP) and the real liquid. F_{OCP} can be written like in the hard sphere system

$$F_{OCP} = F_{gas} + \Delta F_{OCP} \tag{2}$$

here, F_{gas} is the gaseous motion of N identical particles with mass M in the volume V.

$$F_{gas} = -NK_BT \ln\left[\Omega\left(\frac{MK_BT}{2\pi\hbar^2}\right)^{3/2}\right] - NK_BT \tag{3}$$

ΔF_{OCP} which includes the Coulomb interaction energy, can be described in terms of the Plasma parameter Γ[9]

$$\Delta F_{OCP} = NK_BT(A\Gamma + B\Gamma^{1/4} + C \ln \Gamma + D) \tag{4}$$

where $A = -0.896434$; $B = 3.447408$; $C = -0.555130$
$D = -2.995974$; K_B is the Boltzmann's constant.

$$\Gamma = (Ze)^2/aK_BT; a = \left(\frac{3\Omega}{4\pi}\right)^{1/3}$$

The contribution from the non reference liquid, F_{eg} can be assumed as

$$F_{eg} = \left[\frac{2.21}{a^2} - \frac{0.916}{a} - (0.115 - 0.031 \ln a)\right]Z + \frac{A}{\Omega} + F_{el} \tag{5}$$

the first three terms are the kinetic, exchange and correlation energies of the electron gas. A is an adjustable parameter to achieve the condition $P = -(\partial F/\partial\Omega)_T = 0$.

The last term represents the electronic term. All these terms except F_{el} do not contribute to entropy being exclusively volume dependent terms.

$$S = -\left(\frac{\partial F}{\partial T}\right)_\Omega = S_{gas} + S_{OCP} + S_{el}$$

$$\frac{S}{NK_B} = \frac{5}{2} + \ln\left[\Omega\left(\frac{MK_BT}{2\pi\hbar^2}\right)^{3/2}\right] + \left[-\frac{3}{4}B\Gamma^{1/4} - C(\ln\Gamma - 1) - D\right] + \frac{1}{3}\pi^2K_BTN(E_F) \tag{6}$$

S_{el} term is negligibly small for simple metals and is considered on the lines of Yokoyama *et al.*[10] Neglecting electronic term, the excess entropy in OCP system can be expressed as

$$\frac{\Delta S}{NK_B} = -\frac{3}{4}B\Gamma^{1/4} - C(\ln\Gamma - 1) - D \tag{7}$$

For comparison, the results of Slattery *et al.*[11] can be written as

$$\frac{\Delta S}{NK_B} = -2.83632\Gamma^{1/4} + 0.89770\Gamma^{-1/4} + 0.80049 \ln \Gamma + 1.78559 \tag{8}$$

We now turn to calculate specific heats C_v and C_p. The method to evaluate C_p is the same as proposed earlier in hard sphere system [12].

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_\Omega = \frac{3}{2} + \frac{3}{16}B\Gamma^{1/4} + C + \frac{1}{3}\pi^2 K_B T N(E_F) \tag{9}$$

and

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \frac{3}{2} + \frac{3}{16}B\Gamma^{1/4} + C + \alpha T + \frac{\alpha T}{3}\left(\frac{3B}{16}\Gamma^{1/4} + C\right) + \frac{1}{3}\pi^2 K_B T N(E_F) \tag{10}$$

here α represents coefficient of thermal expansion. To test the validity of our Γ values, we also calculate the structure factor at long wavelength by using the expression of compressibility proposed by Evans and Sluckins.[13]

$$\frac{K_{id}}{K_{\text{OCP}}} = -0.3989\Gamma + 0.3414\Gamma^{1/4} + 0.0549\Gamma^{-1/4} + 0.7332 \tag{11}$$

where $K_{id}^{-1} = nK_B T$. Comparing with Ornstein–Zernike relation

$$\lim_{K \to 0} S(K) = nK_B T K_{\text{OCP}} \tag{12}$$

we find structure factor at long wavelength.

Table I shows that the calculated values of Γ are well below the values of Γ at which OCP is believed to melt. We also remark that the fitting of Z^* as done by most of the workers to achieve the reasonable value of Γ is not done here. We now proceed to calculate the excess entropy by feeding these values of Γ in Eqs (7) and (8) that almost give same numerical values. The results are then compared with existing theoretical values and experiments.[14] Two promising results in this regards are $\Gamma = 140$, $\Delta S/NK_B = -3.75$ for Na[2] and $\Gamma = 130.5$ $\Delta S/NK_B = -3.64$ for Li[5] at their melting temperatures. Recently Montella *et al.*[4] have also calculated the excess entropy varying from -2.9 to -3.8 for alkali metals using variational approach. Table I shows the general improvement of the excess entropy by using our Γ values. The calculated values of C_v and C_p by using these Γ values are lower than experimental value.[14] Unfortunately, reliable experimental values of thermal

TABLE 1

Specific heats and excess entropy (in units of NK_B) of liquid metals at their melting points

Element	$T(K)$	Γ	C_v	C_p	C_p (Exp) [14]	$-\Delta S$ Theo. Eq. (7)	$-\Delta S$ Value using Exp [14] Eq. (8)	
Li	453	120	3.15	3.25	3.65	3.46	3.49	3.61
Na	371	124	3.16	3.31	3.82	3.51	3.55	3.45
K	337	120	3.15	3.30	3.86	3.46	3.50	3.45
Rb	312	126	3.19	3.35	3.78	3.54	3.58	3.63
Cs	301	123	3.18	3.36	3.84	3.50	3.54	3.56
Mg	953	104	3.12	3.36	3.90	3.24	3.27	—
Cd	623	146	3.20	3.46	3.57	3.47	3.51	4.00
Zn	723	162	3.25	3.54	3.78	3.96	4.01	3.78
Al	943	121	3.20	3.37	3.52	3.78	3.83	3.49
In	433	199	3.44	3.53	3.55	4.33	4.39	4.34
Pb	613	152	3.33	3.46	3.68	3.85	3.90	3.91
Ga	303	212	3.52	3.47	3.35	4.45	4.51	4.62
Sn	523	173	3.38	3.46	3.57	4.08	4.13	4.08
Cu	1356	105	3.11	3.58	3.78	3.25	3.29	3.59

expansion are not available. The values of C_v are almost the same as obtained by Percus–Yevick phonon theory.[10] The values of C_p for Zn, Sn, Ga, Pb and Bi are adequately better than in hard sphere system.[15,16] The present values of Γ also seem useful to predict the structure factor of liquid metals at long wavelength as displayed in Table II.

In conclusion, OCP model discussed here is able to reproduce thermodynamical properties of liquid metals despite its crude form. Further, our results revealed that OCP model can be extended to polyvalent liquid metals with reasonable accuracy.

TABLE II

Structure factor at long wave length for liquid metals

Element	$T(K)$	Γ	$S(0)$ Ours	Ref. [6]	Expt. [17, 18]
Li	453	120	0.0217	0.0201	—
Na	371	124	0.0210	0.0215	0.0233
K	337	120	0.0217	0.0212	0.0225
Rb	312	126	0.0207	0.0207	0.0220
Cs	301	123	0.0212	0.0202	0.0237
Mg	953	104	0.0252	—	0.025[a]
Al	943	121	0.0216	—	0.0202
Pb	613	152	0.017	—	0.009, 0.014

[a] From McAlister (1974).

References

1. M. Baus and J. P. Hansen, *Phys. Rep.*, **59**, 1 (1980).
2. K. K. Mon, R. Gann and D. Stroud, *Phys. Rev.*, **A24**, 2145 (1981).
3. W. H. Young, *J. Phys. F*, **21**, L 19 (1982).
4. N. Montella, G. Senatore and M. P. Tosi, *Physica B*, **124**, 22 (1984).
5. M. Ross, H. E. DeWitt and W. B. Hubbard, *Phys. Rev.* **A24**, 1016 (1981).
6. D. K. Chaturvedi, M. Rovere, G. Senatore and M. P. Tosi, *Physica B*, **111**, 11 (1981).
7. M. Iwamatsu, R. A. Moore and S. Wang, *Phys. Lett*, **101A**, 97 (1984).
8. K. N. Khanna, *J. Phys. F*, **14**, 1827 (1984).
9. S. Galam and J. P. Hansen, *Phys. Rev.* **A14**, 816 (1976).
10. I. Yokoyama, I. Ohkoshi and W. H. Young, *Phys. Chem. Liq.*, **10**, 273 (1981).
11. W. L. Slattery, G. D. Doolen and H. E. Dewitt, *Phys. Rev.* **A21**, 2087 (1980).
12. K. N. Khanna, *Phys. Chem. Liq.* **13**, 151 (1983).
13. R. Evans and T. Sluckin, *J. Phys. C*, **14**, 3137 (1981).
14. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman. Selected values of the Thermodynamic Properties of the Elements 1973 (Metals Park, Ohio, Am. Soc. Met.).
15. I. Ohkoshi, I. Yokoyama, Y. Waseda, B. P. Alblas and W. Van der Lugt, *Physica B*, **113**, 195 (1982).
16. I. Yokoyama, M. J. Stott, I. H. Umar and W. H. Young, *Inst. Phys. Conf. Ser.* **30**, p. 95 (1977).
17. G. M. B. Webber and R. W. B. Stephens in: Physical Acoustics, Vol. IV B, W. P. Manson ed. (Academic Press, New York, 1968), p. 53.
18. S. P. McAlister, E. D. Crozier and J. F. Cochran, *Can. J. Phys.* **52**, 1847 (1974).