Comments on Heat Capacity at Constant Volume of Liquid Metals Calculated from Hard-Sphere Model

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ABSTRACT

In this paper, comments have been given with respect to the heat capacity at constant volume C_V of liquid metals calculated from the hard-sphere model. The method, in which the packing fraction ξ is determined by taking into account the entropy contribution arising from the softness of the interatomic forces, enables us to predict C_V value for Zn, Cd, Ga, Tl, Sn, Pb and Bi. On the other hand, the predicted value of C_V for alkali metals is smaller by 8 ~ 11 % than the experimental values, although the definite origin for difference is not certainly identified at the present time.

Keywords: Heat capacity, Excess entropy, Liquid metal, Hard-sphere model

1. INTRODUCTION

A modified hard-sphere model /1-4/, which includes the soft force contribution of the interatomic forces, is capable of describing some thermodynamic, transport and surface properties of liquid metals. In the course of such works, there is still a puzzling problem regarding the heat capacity at constant volume calculated from the hard-sphere model shown in Table 1 using the results given by Shimoji /5/, as an example. It is seen from this table that the experimental values of C_V/Nk_B of liquid metals are close to 3. The C_V values of liquid polyvalent metals are moderately well predicted by the simple hard-sphere model, while those of liquid alkali metals are always larger by 20~30 % than the experimental values.

The purpose of this paper is to give comments on the puzzling problem in terms of a modified hard-sphere model, in which the packing fraction ξ is determined by taking into account the entropy contribution arising from the softness of the interatomic forces.

2. HARD-SPHERE MODEL

The heat capacity at constant volume C_V is given by

$$C_V = (\partial E/\partial T)_V = T(\partial S/\partial T)_V = -T(\partial^2 F/\partial T_2)_V \qquad (1)$$

where T is the absolute temperature and V is the volume. E, S and F denote the internal energy, the entropy and the Helmholtz free energy, respectively. The pressure p is given by

$$p = -(\partial F/\partial V)_T \qquad (2)$$

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If the equation of state by Carnahan-Starling /6 / is applied to Eq.(2),

$$p_H = nk_BT(1 + \xi + \xi^2 - \xi^3)(1 - \xi)^{-3} \quad , \tag{3}$$

the Helmholtz free energy takes the form

$$F = Nk_BT(- \ln(\Lambda^3(1/n)) + (3-2\xi)(1-\xi)^{-2} - 4), \tag{4}$$

where N is the number of particles confined in the volume V, n is the number density (i.e., N/V), k_B is the Boltzmann constant. Λ is defined by

$$\Lambda = ((2\pi m\, k_B\, T)/h^2)^{1/2}, \tag{5}$$

where m is the mass of a particle and h is the Planck constant. ξ is the packing fraction

defined by

$$\xi = \pi n\sigma^3/6 , \tag{6}$$

where σ stands for a diameter of the hard-sphere. Then substituting Eq. (4) into Eq. (1), we obtain after some algebraic calculations

$$C_I/Nk_B = 3/2 - 4((2-\xi)/(1-\xi)^3)T(\partial\xi/\partial T)_V - 2((5-2\xi)/(1-\xi)^4)T^2((\partial\xi/\partial T)_V)^2 - 2((2-\xi)/(1-\xi)^3)T^2(\partial^2\xi/\partial T^2)_V \tag{7}$$

The experimental values of C_I/Nk_B of liquid metals, as mentioned in the previous section, are close to 3, which indicates a necessity of introducing the temperature dependence of ξ or σ when the hard-sphere model is employed. This is easily seen from Eq.(7) because we will only obtain 3/2 when $(\partial\xi/\partial T)_V$ and $(\partial^2\xi/\partial T^2)_V$ are set to be zero. Assuming $(\partial^2\xi/\partial T^2)_V = 0$, using $\xi = 0.46$ and the values of $(\partial\xi/\partial T)_V$ given in Ref. /5/, we obtain the values of C_I/Nk_B listed in the column 4 of Table 1. The negative sign of $(\partial\xi/\partial T)_V$ (see Ref. /5/) clearly indicates that $\sigma(T)$ decreases with increasing temperature. The results of Shimoji /5/ suggest that liquid alkali metals are much softer (or $|\xi(\partial\xi/\partial T)_V|$ is larger) than the other liquid metals, although the values of $(\partial\xi/\partial T)_V$ were determined by fitting the calculated thermal pressure coefficients to the experimental values. In this work the value of $(\partial\xi/\partial T)_V$ is, for all metals, uniquely determined from Eq. (10).

Table 1

Heat capacity of liquid metals at the melting point. Experimental values of C_P and C_V are taken from Kleppa's data(1950). The quantities CV' are calculated from Eq.(7), in which $(\partial^2\xi/\partial T^2)_V = 0$ is assumed and the value of $(\partial\xi/\partial T)_V$ is referred to the results of Shimoji /5/

Metal	C_P/C_V	C_V/Nk_B	C_V/Nk_B
Na	1.12	3.4	4.4
K	1.11	3.5	4.2
Rb	1.15	3.4	4.1
Zn	1.25	3.1	3.3
Cd	1.23	3.1	2.9
Ga	1.08	3.2	2.7
Tl	1.21	3.0	3.1
Sn	1.11	3.0	2.5
Pb	1.20	2.9	2.7
Bi	1.15	3.1	3.0

3. RESULTS

The value of C_V was estimated using the empirical formula proposed by Protopapas *et al.* /7/. According to Protopapas *et al.*, the temperature dependence of σ is estimated by

$$\sigma(T) = 1.126\sigma_m\,[1 - 0.112(T/T_m)^{1/2}], \tag{8}$$

or

$$(\partial \ln\sigma/\partial \ln T)_V = - (0.056\sigma_0/\sigma(T))(T/T_m)^{1/2} \tag{9}$$

where the relation $\sigma_m = 0.888\sigma_0$ is used, and $\sigma_0 = 1.0878(n_m)^{-1/3}$ with n_m being the number density of ions at the melting point. Since the packing fraction ξ is defined by $\xi - \pi n\sigma^3/6$, the temperature dependence of ξ is obtained as

$$(\partial\xi/\partial T)_V = -\pi\, n \times 3.545667 \times 10^{-2} (n_m^{-1})(TT_m)^{-1/2}(1-0.112(T/T_m)^{1/2})^2. \tag{10}$$

At or near the melting point, putting $T \simeq T_m$ and $n \simeq n_m$ in Eq.(10), we obtain

$$(T(\partial\xi/\partial T)_V)\, T \simeq T_m \simeq -8.78\times10^{-2}. \quad (11)$$

Likewise, since $(\partial^2\xi/\partial T^2)_V = (\pi n/2)(2\sigma((\partial\sigma/\partial T)_V)^2 + \sigma^2(\partial^2\sigma/\partial T^2)_V)$, the temperature derivative of $(\partial\xi/\partial T)_V$ at constant volume is

$$(\partial^2\xi/\partial T^2)_V = (\pi n/2)\,(7.942294\times10^{-3}\,(n_m^{-1})T_m^{-1}T^{-1} \times (1-0.112(T/T_m)^{1/2}) +3.545667\times10^{-2}(n_m^{-1})T_m^{-1/2}T^{-3/2}(1-0.112(T/T_m)^{1/2}) \quad (12)$$

At or near the melting point, putting $T \simeq T_m$ and $n \simeq n_m$ in Eq.(12), we obtain

$$(T^2(\partial^2\xi/\partial T^2)_V)\, T \simeq T_m \simeq 5.50\times10^{-2}. \quad (13)$$

On the other hand, as reported in Ref. /2/, the excess entropy of liquid metals S_E is given by

$$S_E = S_{pack} + S_S, \quad (14)$$

in which S_{pack} is the excess entropy due to the finite packing of the hard spheres, best described via the negative Carnahan-Starling expression

$$S_{pack}/Nk_B = -\xi(4-3\xi)/(1-\xi)^2 \quad (15)$$

S_S is an entropy contribution arising from the softness of the interatomic forces/1/, given by

$$S_S/Nk_B = \pi n_m f(\sigma_0-\sigma_m)\,(T/T_m)^{1/2}\sigma^{-2}g(\sigma), \quad (16)$$

where f is a parameter related to the soft-force part of the pair potential and is approximated as ~ 0.35 for all systems at all temperatures. As shown in Ref. /8/, we take the value of S_S to be 0.60 in units of Nk_B. Then if we set $S_E/Nk_B = -3.60$ in Eq.(14), as mentioned in Ref./2/, we obtain $S_{pack}/Nk_B = -4.1$ and we can extract the value of ξ through Eqs.(14)-(16). The extracted value of ξ is 0.463, with which the hard-sphere structure factor moderately well describes the experimental structure factor data of liquid metals near the melting point /9/. Without neglecting the last term of Eq. (7), the value of C_V is calculated as

$$\begin{aligned} C_V/Nk_B &= 3/2-4((2-0.463)/(1-0.463)^3) \\ &\times(-8.78\times10^{-2})-2((5-2\times0.463)/ \\ &(1-0.463^4)\times(-8.78\times10^{-2})^2-2((2-0.463)/ \\ &(1-0.463^3)\times(5.50\times10^{-2}) \\ &= 1.5 + 3.486 - 0.755 - 1.092 \\ &= 3.14\,. \end{aligned}$$

Hence, the value of C_V for all metals is predicted as $C_V/Nk_B = 3.14$ at or near the melting point. This value is in good agreement with the experimental values for Zn, Cd, Ga, Tl, Sn, Pb and Bi, but is smaller by 8 ~ 11 % than the experimental values of alkali metals.

4. DISCUSSION

From Eq.(16), the heat capacity arising from S_S is given by

$$\begin{aligned} (C_V/Nk_B)^{S_S} &= T(\partial(S_S/Nk_B)/\partial T)_V \\ &= (1/2)(S_S/Nk_B)(1+(2(4+9\xi-4\xi^2)/(3\xi(1-\xi)(2-\xi))) \\ &\times(T(\partial\xi/\partial T)_V)). \end{aligned} \quad (17)$$

This equation was originally derived by Bari *et al.* /1/. Since $S_S/Nk_B \simeq 0.60$ for alkali metals /8/, we obtain $(C_V/Nk_B)^{S_S} \simeq 0.30$ if the second term of Eq. (17) is completely neglected. Then the heat capacity at constant volume is considered to be given by

$$C_V/Nk_B = (C_V/Nk_B)^{HS} + (C_V/Nk_B)^{S_S} + (C_V/Nk_B)^{elec} \quad (18)$$

where $(C_V/Nk_B)^{HS}$ denotes the ion motional contribution (hard-sphere term) which is given by Eq. (7), and $(C_V/Nk_B)^{elec}$ stands for the contribution from the electron excitation entropy which is typically 0.05 for alkali metals. Therefore, the total C_V for alkali metals should be given as $C_V/Nk_B = 3.14 + 0.30 + 0.05 = 3.49 \simeq 3.5$. This value of C_V/Nk_B is in excellent agreement with the experimental values of alkali metals shown in Table 1. However, this is not the true story as we show below:

$$(C_V/Nk_B)^{S_S} = (1/2)\times 0.60(1 + (2(4 + 9\times 0.463 - 4\times 0.463^2)/(3\times 0.463(1-0.463)(2-0.463)))\times(-8.78\times 10^{-2}))$$
$$\simeq 0.30(1 - 1.12) \simeq -0.04 .$$

The negative value of $(C_V/Nk_B)^{S_S}$ is not unphysical since S_S decreases with increasing temperature as suggested by Bari *et al.* /1/ for liquid Na. Obviously, the second term of Eq.(17) is much the same as the first term in magnitude and plays an important role in proper evaluation of $(C_V/Nk_B)^{\breve{S}S}$. Thus, the total C_V/Nk_B is given as C_V/Nk_B = 3.14 + (-0.04) + 0.05 = 3.15 for liquid alkali metals.

Incidentally, here we would like to refer to the heat capacity calculations by Bari *et al.* /1/. These authors used Eq. (19) below, which is obtained by the Gibbs-Bogoliubov variational calculation /5/,

$$(C_V/Nk_B)^{HS} = 3/2 - 2\xi((2-\xi)/(1-\xi)^3)(\partial \ln\xi/\partial \ln T)_V . \quad (19)$$

Including $(C_V/Nk_B)^{S_S}$ and $(C_V/Nk_B)^{elec}$, using ξ = 0.46 and $(\partial \ln\xi/\partial \ln T)_V$ = - 0.203 listed in Ref. /1/, they obtain (C_V/Nk_B) = 3.323 for liquid Na. For the other metals such as K, Rb, Cs, Zn, Hg, Pb, Al and Cu, using ξ = 0.46 and $(\partial \ln\xi/\partial \ln T)_V$ = - 0.20, they obtain (C_V/Nk_B) = 3.345, 3.349, 3.358, 3.346, 3.308, 3.386, 3.385 and 3.364, respectively. As seen from their results, there is very good agreement with the observed values for liquid alkai metals, while there is disagreement for liquid Zn, Hg, Pb, Al and Cu .

5. CONCLUSIONS

The heat capacity at constant volume of liquid metals is not always explainable even by the use of the modified hard-sphere model. The contribution arising from the softness of the interatomic interactions $(C_V/Nk_B)^{\breve{S}S}$ is negligibly small for all liquid metals at or near the melting point. The conclusions drawn from the present work are summarized as follows.

(1) The term $(\partial^2\xi/\partial T^2)_V$ in Eq.(7) is not negligible for evaluation of the heat capacity at constant volume of liquid metals.

(2) The value of (C_V/Nk_B) of liquid alkali metals calculated from Eq.(7) is smaller by about 10 % than the experimental values. Even if the contributions $(C_V/Nk_B)^{\breve{S}S}$ and $(C_V/Nk_B)^{elec}$ are taken into account, the calculated C_V/Nk_B value undershoots the experimental value. The definite origin for this difference has not yet been established for certain.

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