Pair and Triplet Correlation Entropies of Liquid 3d Transition Metals

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The thermodynamic entropies of liquid 3d transition metals are well explained by the statistical theory of entropy which has recently been rederived by Wallace, and amended by Baranyai and Evans. The pair correlation entropy is computed from measured pair correlation functions, while the triplet correlation entropy is estimated by measured structure factors with the help of the one-component plasma model. The triplet correlation entropy is not small enough to be neglected for the 3d transition metals near the melting point. The details of the entropy arising from the various sources are presented.

Keywords: correlation entropy, liquid, transition metals, structure factor, pair distribution function.

I. Introduction

A statistical theory for the entropy of a classical liquid has recently been rederived by Wallace⁽¹⁾, in which the entropy takes the form of a one-particle (kinetic energy) term, plus a two particle (pair) correlation term, plus a series of higher order correlation terms. Neglecting higher order correlations, Wallace has shown that the theory gives an accurate account of the entropy for nearly free electron metals. The study was limited to 22 nearly free electron metals, because, according to Wallace, only for these is it possible to evaluate the electron-excitation contribution to the total entropy. For the transition metals, on the other hand, the electronic contribution to the entropy plays a rather substantial role because of the high temperature and the high density of states of *d* electrons at the Fermi energy. Recently, Hausleitner and Hafner⁽²⁾, following the work of Meyer et al⁽³⁾, have estimated the *s*- and *d*-electron contributions to the electronic entropy for liquid 3d transition metals. These values have been widely quoted in the works⁽⁴⁾⁽⁵⁾ on the thermodynamic properties of these metals and now believed to be reliable in the liquid phase. Therefore it is quite interesting to investigate whether Wallace's approach is useful for calculating the entropy of these metals too.

The purpose of the present paper is twofold: first, to work out the triplet correlation entropy using experimental structure factors in order to check the convergence of the expansion of the entropy; second, to show the details of the entropy arising from the various sources. In the next section we mention the formalism to be employed. Results of numerical calculations are presented and compared with observed data in section 3. In section 4, discussions will be given regarding the convergence of the entropy series. A conclusion drawn from the present work will be given in the last section.

II. Formalism

1. Correlation expansion of ion motional entropy

Throughout this work it is convenient to work with entropy in units of k_B per particle. According to Wallace, the ion motional entropy S_I has been expressed in the series

$$S_I = S^{(1)} + S^{(2)} + S^{(3)} + \dots \quad (1)$$

where $S^{(1)}$ is the one-particle(kinetic) contribution, $S^{(2)}$ is the pair correlation contribution, $S^{(3)}$ is the triplet correlation contribution, and so on. Because the higher order correlation terms depend on the irreducible parts, the entropy series Eq.(1) is a cumulative expansion, and is expected to converge rapidly for the liquid phase (Ref.(1) and references therein). With the electronic entropy denoted S_{el} , the total liquid entropy is given by

$$S = S_I + S_{el} \quad (2)$$

where S_{el} is, for transition metals,

$$S_{el} = \frac{\gamma_0 z T}{N k_B} + \frac{1}{3} \pi^2 k_B T N_d(E_F) \quad (3)$$

Here $N_d(E_F)$ is the density of states due to the *d*-electron at the Fermi energy and $\gamma_0 z T / N k_B$ is the *s*-electron contribution to the entropy⁽²⁾⁽³⁾. The one-particle contribution is evaluated to give

$$S^{(1)} = 3/2 - \ln \rho \Lambda^3, \quad (4)$$

where Λ is the de Broglie wavelength,

$$\Lambda = \hbar(2\pi / m k_B T)^{1/2}.$$

The two-particle contribution is

$$S^{(2)} = -\frac{1}{2} \rho \int g^{(2)}(r) \ln g^{(2)}(r) dr, \quad (5)$$

where $g^{(2)}(r)$ is the pair correlation function. The three-particle contribution is given in terms of $g^{(3)}$ and $\delta g^{(3)}$

$$S^{(3)} = -\frac{1}{6} \rho^2 \iint g^{(3)}(r_1, r_2, r_3) \ln \delta g^{(3)}(r_1, r_2, r_3) dr_2 dr_3, \quad (6)$$

where $g^{(3)}(r_1, r_2, r_3)$ is the triplet correlation function and the irreducible part $\delta g^{(3)}$ of $g^{(3)}(r_1, r_2, r_3)$ is defined by

$$\delta g^{(3)}(r_1, r_2, r_3) = g^{(3)}(r_1, r_2, r_3) / (g^{(2)}(r_1, r_2) g^{(2)}(r_1, r_3) g^{(2)}(r_2, r_3)). \quad (7)$$

Similarly, $S^{(4)}$ depends on the irreducible correlation $\delta g^{(4)}$, and so on. In principle, examination of the separate terms of the liquid entropy series will give us information on the multiparticle interactions in the liquid phase.

Concerning Wallace's expression for the entropy of a canonical ensemble, however, we must quote the key remarks made by Baranyai and Evans^{(6),(7)}. These authors have pointed out that Wallace's method contains some conceptual errors regarding the ensemble dependence of the entropy expansion. These authors, taking the correct long-range behavior of the correlation functions, have obtained

$$S_I = S_{PG} + S^{(2)} + \frac{1}{2}\rho \int (g^{(2)} - 1)dr + S^{(3)} + \frac{1}{6}\rho^2 \iint [g^{(3)} - 3g^{(2)}g^{(2)} + 3g^{(2)} - 1]dr^2 + \dots \quad (8)$$

where $g^{(2)}$ and $g^{(3)}$ are, respectively, the two- and three-particle correlation functions, and S_{PG} is the total entropy per particle of a perfect gas, i.e., $S_{PG} = S^{(1)} + 1$. Equation (8) is both a local and ensemble-invariant expansion of the entropy and is more accurate for numerical computations of the canonical ensemble entropy. In the present work we employ Eq.(8) for evaluation of the entropy instead of using Eq.(1). The two integrals in Eq.(8) can be carried out explicitly⁽⁸⁾ as we shall show in section 3.

2. Evaluation of the triplet correlation entropy

In considering the higher-order correlational entropy, it is natural to assume that the three-particle term is dominant. By the use of the relative positions $r = r_2 - r_1$, $s = r_3 - r_1$ and $t = s - r$ of three particles in a liquid (isotropic and homogeneous system), the three-particle entropy is given by

$$S^{(3)} = -\frac{1}{6}\rho^2 \iint g^{(3)}(r,s,t) \ln \delta g^{(3)}(r,s,t) dr ds. \quad (9)$$

The evaluation of $S^{(3)}$ necessitates the calculations of the three-particle correlation function $g^{(3)}(r,s,t)$. This is rather cumbersome and extremely time consuming if we use a molecular dynamics simulation. The reason is that an accurate determination of $g^{(3)}(r,s,t)$ requires the large number of configurations needed for acceptable statistics⁽⁷⁾. In the present work we employ an approximate method for evaluation of $S^{(3)}$.

We define a function $H(r,s,t)$, following Egelstaff et al⁽⁹⁾, as follows:

$$H(r,s,t) = g^{(3)}(r,s,t) - g(r)g(s)g(t) \quad (10)$$

where $g(r)g(s)g(t)$ is the superposition approximation term proposed by Kirkwood⁽¹⁰⁾. With this new function $H(r,s,t)$, Eq.(7) can be written as

$$\begin{aligned} \delta g^{(3)}(r,s,t) &= \frac{g^{(3)}(r,s,t)}{g(r)g(s)g(t)} \\ &= \frac{g(r)g(s)g(t) + H(r,s,t)}{g(r)g(s)g(t)} = 1 + \frac{H(r,s,t)}{g(r)g(s)g(t)}. \end{aligned} \quad (11)$$

Using this relation, Eq.(9) is now approximated by

$$\begin{aligned} S^{(3)} &= -\frac{1}{6}\rho^2 \iint \{g(r)g(s)g(t) + H(r,s,t)\} \\ &\quad \ln \{1 + \frac{H(r,s,t)}{g(r)g(s)g(t)}\} dr ds \\ S^{(3)} &\approx -\frac{1}{6}\rho^2 \iint \{g(r)g(s)g(t) + H(r,s,t)\} \\ &\quad \{ \frac{H(r,s,t)}{g(r)g(s)g(t)} \} dr ds \\ S^{(3)} &\approx -\frac{1}{6}\rho^2 \iint H(r,s,t) dr ds. \end{aligned} \quad (12)$$

Here we assumed that $|H(r,s,t)/g(r)g(s)g(t)| < 1$ and $H(r,s,t)^2/g(r)g(s)g(t) < 1$ for all range of particle configurations. On the other hand, the relation between the pair correlation function $g(r)$ and the triplet correlation function $g^{(3)}(r,s,t)$ in the grand canonical ensemble can be expressed in the following form⁽⁹⁾:

$$\begin{aligned} \rho \int [g^{(3)}(r,s,t) - g(r)] ds \\ + 2g(r)[1 - k_B T (\frac{\partial \rho}{\partial P})_T] - \rho k_B T (\frac{\partial g(r)}{\partial P})_T = 0, \end{aligned} \quad (13)$$

where P is the pressure and ρ is the number density of particles. Then, one can get the Fourier transform of $H(r,s,t)$ in terms of the relation in Eq.(13) in the following form⁽⁹⁾⁽¹¹⁾:

$$\begin{aligned} \tilde{H}(Q) &\equiv \rho^2 \int e^{iQr} dr \int H(r,s,t) ds \\ &= \frac{1}{(2\pi)^3 \rho} [S(Q) - 1] * [S(Q) - 1]^2 \\ &\quad + [S(Q) - 1][S(0) + S(Q) - 1] - \rho k_B T (\frac{\partial S(Q)}{\partial P})_T, \end{aligned} \quad (14)$$

where $A*B$ means a convolution between A and B , and $S(Q)$ is the structure factor. For convenience of discussion, $\tilde{H}(Q)$ is separated into three parts in the following form⁽¹¹⁾:

$$\tilde{H}(Q) = H_1(Q) + H_2(Q) + H_3(Q), \quad (15)$$

where

$$\begin{aligned} H_1(Q) &= \frac{1}{(2\pi)^3 \rho} [S(Q) - 1] * [S(Q) - 1]^2 \\ &= \frac{2\pi}{(2\pi)^3 \rho} \int_0^\infty [S(Q') - 1]^2 Q'^2 \times I(Q, Q') dQ' \end{aligned} \quad (16)$$

$$\begin{aligned} I(Q, Q') &= \frac{1}{QQ'} \int_{|Q-Q'|}^{Q+Q'} x [S(x) - 1] dx \\ H_2(Q) &= [S(Q) - 1][S(0) + S(Q) - 1], \end{aligned} \quad (17)$$

and

$$H_3(Q) = -\rho k_B T (\frac{\partial S(Q)}{\partial P})_T. \quad (18)$$

Hence, comparing Eq.(12) with Eq.(14),

$$S^{(3)} = -\frac{1}{6}\rho^2 \int dr \int H(r,s,t) ds = -\frac{1}{6}\tilde{H}(0) \quad (19)$$

A change in the structure factor on application of the pressure is required for $H_3(Q)$ but this is generally not available in the literature. In order to determine $H_3(Q)$ or $(\frac{\partial S(Q)}{\partial P})_T$ we have employed the one-component plasma (OCP) model⁽¹²⁾⁻⁽¹⁵⁾ which has been successfully used in the discussion of the thermodynamic properties of the liquid 3d transition metals⁽⁴⁾⁽⁵⁾⁽¹⁶⁾⁽¹⁷⁾.

3. Evaluation of $H_3(0)$ based on the OCP model

The isothermal pressure derivative of the liquid structure factor $(\frac{\partial S(Q)}{\partial P})_T$ is related to the isothermal density derivative of $S(Q)$ so that the function $H_3(Q)$ can be rewritten as

$$\begin{aligned} H_3(Q) &= -\rho k_B T (\frac{\partial S(Q)}{\partial P})_T = -\rho k_B T \rho \kappa_T (\frac{\partial S(Q)}{\partial \rho})_T \\ H_3(Q) &= -S(0) \rho (\frac{\partial S(Q)}{\partial \rho})_T \end{aligned} \quad (20)$$

From Refs.(16) and (17), $S(Q)$ in the low wavenumber region is given by

$$S(Q) = \left[\frac{k_{DH}^2}{k_i^2} + \frac{k_{DH}^2(4 + 4k_e^2 r_c^2 - k_e^2 r_c^4 Q^2)}{4(k_e^2 + Q^2)} \right]^{-1} \quad (21)$$

where r_c is the radius of the empty-core pseudopotential⁽¹⁸⁾ and

$$k_{DH} = (4\pi z_s^2 \rho / k_B T)^{1/2} \quad (22)$$

is the Debye-Hückel inverse screening length with z_s being the effective valency and k_i is the "inverse screening length

" of the OCP given by

$$k_{DH}^2 / k_i^2 = 1 - 0.398415\Gamma + 0.31122\Gamma^{1/4} - 0.1850 \quad (23)$$

where Γ is a plasma parameter. On the other hand, the quantity k_e in Eq.(21) is the inverse screening length of the electron gas and is related to the electronic screening function $\varepsilon(Q, \rho)$ as

$$\lim_{Q \rightarrow 0} \varepsilon(Q, \rho) = 1 + k_e^2 / Q^2. \quad (24)$$

Here k_e is given by

$$k_e^2 = \frac{4\pi k_F^3}{(\pi k_F)^2 - \pi k_F - 0.153} \quad (25)$$

for the Geldart-Vosko expression⁽¹⁹⁾ describing many electron effects and k_F stands for the Fermi wavenumber. Differentiation of Eq.(21) with respect to ρ leads to

$$\rho \left(\frac{\partial S(Q)}{\partial \rho} \right)_T = - (B + C) [S(Q)]^2 \quad (26)$$

where

$$B = \frac{1}{3} (-0.398415\Gamma + 0.077805\Gamma^{1/4})$$

and

$$C = \frac{k_{DH}^2}{4(k_e^2 + Q^2)} \{ 4 + 4k_e^2 r_c^2 - k_e^2 r_c^4 Q^2 + \frac{k_e^2 r_c^2}{3} [-4(1 + \frac{\pi k_F + 0.306}{(\pi k_F)^2 - \pi k_F - 0.153}) + 3r_c^2 Q^2 (1 + \frac{\pi k_F / 3 + 0.102}{(\pi k_F)^2 - \pi k_F - 0.153})] \} - \frac{k_{DH}^2 k_e^2}{12(k_e^2 + Q^2)^2} [1 - \frac{(\pi k_F + 0.306)}{(\pi k_F)^2 - \pi k_F - 0.153}] (4 + 4k_e^2 r_c^2 - k_e^2 r_c^4 Q^2)$$

Therefore, the limiting value of the function $H_3(Q)$ based on the OCP model is expressed as

$$H_3(0) = [S(0)]^3 (B + \lim_{Q \rightarrow 0} C). \quad (27)$$

As an example, we take liquid Co at 1823 K for evaluation of the entropy arising from this source. Using input data (taken from Ref.(16)) such as $T = 1823$ K, $r_c = 1.232$ (a.u.), $z_s = 1.32$, $\Gamma = 110$, mass density 7.70 (g/cm³), atomic weight 58.93 and employing the Geldart-Vosko screening function to describe the electron gas, we obtain $S(0) = 0.0198$, $B = -14.5245$, $\lim_{Q \rightarrow 0} C = 46.2376$, $H_3(0) = 0.0198^3 (-14.5245 + 46.2376) \approx 0.000246$ and therefore, $S^{(3)} = -H_3(0)/6 \approx -0.00004$. This value of the entropy is negligibly

Fig. 1 Convolution terms $H_1(Q)$ for 7 metals near the melting points ($1 \text{ a.u.}^{-1} \approx 1.89 \text{ \AA}^{-1}$).

small in the present entropy analysis. This story is absolutely true for all 3d metals presently studied.

III. Results

Figure 1 displays the convolution terms $H_1(Q)$ for liquid Ti, V, Cr, Mn, Fe, Co and Ni near the melting point. In the present work all calculations were performed using the experimental data due to Waseda⁽²⁰⁾, and Waseda and Ueno⁽²¹⁾

Table 1 Details of entropy (in units of Nk_B) calculated from Eqs.(2),(3) and (8). The values of the electronic contributions S_{el}^s and S_{el}^d are taken from Ref.(2). Experimental data, S_{expt} , are due to Hultgren et al⁽²²⁾.

	$T(K)$	S_{PG}	$S^{(2)}$	$S^{(3)}$	Eq.(29)	Eq.(30)	S_{el}^s	S_{el}^d	S_{calc}	S_{expt}	$(S_{calc}/S_{expt}) (\%)$
Ti	1973	14.06	-1.85	-0.49	-0.49	-0.16	0.38	0.92	12.37	12.01	103
V	2173	14.10	-1.98	-0.58	-0.49	-0.15	0.37	0.91	12.18	12.08	101
Cr	2173	14.00	-2.11	-0.56	-0.49	-0.16	0.33	0.94	11.95	11.58	103
Mn	1533	13.66	-1.88	-0.81	-0.49	-0.15	0.25	0.78	11.36	12.05	94
Fe	1833	13.84	-2.40	-0.58	-0.49	-0.16	0.27	1.08	11.56	12.07	96
Co	1823	13.84	-2.32	-0.63	-0.49	-0.16	0.27	1.19	11.70	12.08	97
Ni	1773	13.79	-2.27	-0.58	-0.49	-0.16	0.26	1.33	11.88	11.72	101

. It is readily recognized from Fig.1 that $H_1(Q)$ has a broad negative minimum around $Q=0.8\text{a.u.}^{-1}(\approx 1.5\text{\AA}^{-1})$, and the depth of the minimum is rather shallow for Ti and V, but seems to get deeper, clearly except Cr, with increasing number of d -electron. What we are interested in the present work is the $Q = 0$ value of these functions. The value of $H_1(0)$ is the smallest for Ti, while the largest for Mn. Other metals appear to have the values slightly higher than 2. All $H_1(0)$ values are displayed in Fig.2 for comparison. Obviously, no systematic change in magnitude can be seen among the metals. Incidentally, these $H_1(0)$ values were obtained by using the exact limiting formula

$$H_1(0) = -\frac{2}{(2\pi)^2 \rho} \int_0^\infty [S(Q)-1]^3 Q^2 dQ \quad (28)$$

Since the value of $H_2(0)$ is around 1 for all metals, the value of $H_1(0)$ is predominant in evaluating $S^{(3)}$.

Before going to show numerical details of the entropy calculations, we present, for reader's convenience, the results of the two integrals which appeared in Eq. (8). This is well documented in the paper of Mountain and Raveche (8):

$$\frac{1}{2}\rho \int [g(r) - 1] d\mathbf{r} = \frac{1}{2}[\gamma - 1] \quad (29)$$

and

$$\begin{aligned} \frac{1}{6}\rho^2 \iint [g^{(3)}(r,s,t) - g(r)g(s) - g(s)g(t) \\ - g(r)g(t) + g(r) + g(s) + g(t) - 1] d\mathbf{r}ds \\ = -\frac{1}{6} + \frac{1}{2}\gamma - \frac{1}{3}\gamma^2 + \frac{1}{6}\rho \left(\frac{\partial \gamma}{\partial \rho} \right)_T \end{aligned} \quad (30)$$

where γ is defined by $\gamma = \rho k_B T \kappa_T$, κ_T being the isothermal compressibility. Hence, γ is equal to the long-wavelength limit of the structure factor, $S(0)$. Since experimental data as well as theoretical values of $S(0)$ based on the OCP model are summarized in Ref.(16), it is quite easy to get the entropy contribution from this source.

Numerical details of the entropy calculated in this work are given in Table 1. The two-particle term $S^{(2)}$ is evaluated from the measured radial distribution function, while the three-particle term $S^{(3)}$ is evaluated by the measured structure factors. $S^{(2)}$ is of order of -2, being 15~16% of the perfect gas term S_{PG} . On the other hand, $S^{(3)}$ is of order of -0.6, being 4~5% of S_{PG} .

IV. Discussion

As we have mentioned at the beginning of section 2, the entropy series Eq.(1) is expected to converge rapidly for the liquid phase.

Fig. 2 Values of $H_1(0)$ for 7 metals near the melting points.

Actually Wallace has performed calculations for 22 nearly free electron metals and has shown that the theory gives an accurate account of the entropy within the framework of the pair correlation function. In order to take a look at this for liquid 3d metals, we present, in Table 2, the entropy results calculated by the method of Wallace. As can be seen from the last column of Table 2, the thermodynamic entropy is accurately given by his liquid statistical theory. This surprising result suggests to us that the three- and more-particle entropy terms are generally negligible. Or, it is conceivable that there must be some cancellation of the higher-particle terms at the liquid densities leading to a fortuitous estimate of the entropy from the two-particle term alone. This is the reason why we performed calculations of $S^{(3)}$ in this work. As is seen from Table 1, the magnitude of $S^{(3)}$ is about a quarter of that of $S^{(2)}$ (again except Mn) and is not small enough to be neglected. An entropy contribution of the same order as $S^{(3)}$, judging from the comparison between theory and experiment in Table 1, appears to arise from the higher-order expansion terms.

At first, we expected that theoretical values of the entropy should be a little larger than experimental data. This expectation stems from the role of higher order correlations. The presence of n -body interaction potentials, for $n \geq 3$,

Table 2 Details of entropy (in units of Nk_B) calculated from Eqs.(1),(2) and (3). The values of the electronic contributions S_{el}^s and S_{el}^d are taken from Ref. (2). Experimental data, S_{expt} , are due to Hultgren et al (22).

	$T(K)$	$S^{(1)}$	$S^{(2)}$	S_{el}^s	S_{el}^d	S_{calc}	S_{expt}	$(S_{calc}/S_{expt}) (\%)$
Ti	1973	13.06	-1.85	0.38	0.92	12.51	12.01	104
V	2173	13.10	-1.98	0.37	0.91	12.40	12.08	103
Cr	2173	13.00	-2.11	0.33	0.94	12.16	11.58	105
Mn	1533	12.66	-1.88	0.25	0.78	11.81	12.05	98
Fe	1833	12.84	-2.40	0.27	1.08	11.80	12.07	98
Co	1823	12.84	-2.32	0.27	1.19	11.98	12.08	99
Ni	1773	12.79	-2.27	0.26	1.33	12.10	11.72	103

gives rise to higher-order irreducible correlations, and hence to a higher-order correlation entropy. The effect is to decrease the freedom of the particle motion and to bring more order into a liquid, hence to decrease the entropy. This is why the correlation entropies are negative. Therefore, we thought that our calculated values would decrease by about a half of $S^{(3)}$ by inclusion of the higher order terms for $n \geq 4$, and that this would lead to a good agreement between theory and experiment. However, favorable results to support our speculation were not always borne out in the present analysis. Apparently, liquid Mn, Fe and Co destroy our expectation. This is probably because our evaluation of $S^{(3)}$ contains some approximations in the method of analysis and relies solely on the experimental data which might contain some errors.

On comparing Table 1 with Table 2, both Eq.(1) and Eq.(8) provide the same degree of description of entropy. However, Eq.(8) reduces to the correct perfect gas term in the low-density limit, or in the high-temperature limit, but Eq.(1) reduces merely to the one-particle term which is given by Eq.(4).

V. Conclusion

We have attempted an evaluation of $S^{(3)}$ in order to check the convergence of the expansion of the entropy. The conclusion drawn from the present study is as follows:

- (1) The thermodynamic entropies of liquid 3d transition metals are well explained by the statistical theory of entropy given by Eqs.(2),(3) and (8).
- (2) The present results show that the expansion of the entropy converges less rapidly than might have been expected from an analysis of the two-body term alone.

Acknowledgments

The authors are grateful to Mr. H. Ito and Mr.T. Kawamoto for their assistance in numerical calculations of Eqs.(5) and (16). Discussions with Professor Y.Waseda were also helpful to the authors.

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