

Article

# First principles calculation of the information entropy of liquid aluminum

Michael Widom <sup>1\*</sup>  and Michael Gao <sup>2,3</sup>

<sup>1</sup> Department of Physics, Carnegie Mellon University, Pittsburgh PA, 15217; widom@cmu.edu

<sup>2</sup> National Energy Technology Laboratory, Albany OR, 97321; Michael.Gao@netl.doe.gov

<sup>2</sup> AECOM, P.O. Box 618, South Park, PA 15129

\* Correspondence: widom@cmu.edu; Tel.: +1-412-268-7645

Version January 11, 2019 submitted to Entropy

**Abstract:** The information required to specify a liquid structure equals, in suitable units, its thermodynamic entropy. Hence, an expansion of the entropy in terms of multi-particle correlation functions can be interpreted as a hierarchy of information measures. Utilizing first principles molecular dynamics simulations, we simulate the structure of liquid aluminum to obtain its density, pair and triplet correlation functions, allowing us to approximate the experimentally measured entropy and relate the excess entropy to the information content of the correlation functions. We discuss the accuracy and convergence of the method.

**Keywords:** Gibbs entropy; Shannon entropy; liquid metal

## 0. Introduction

Let  $p_i$  be the probability of occurrence of a state  $i$ , in thermodynamic equilibrium. The Gibbs' and Von Neumann's formulas for the entropy [1,2],

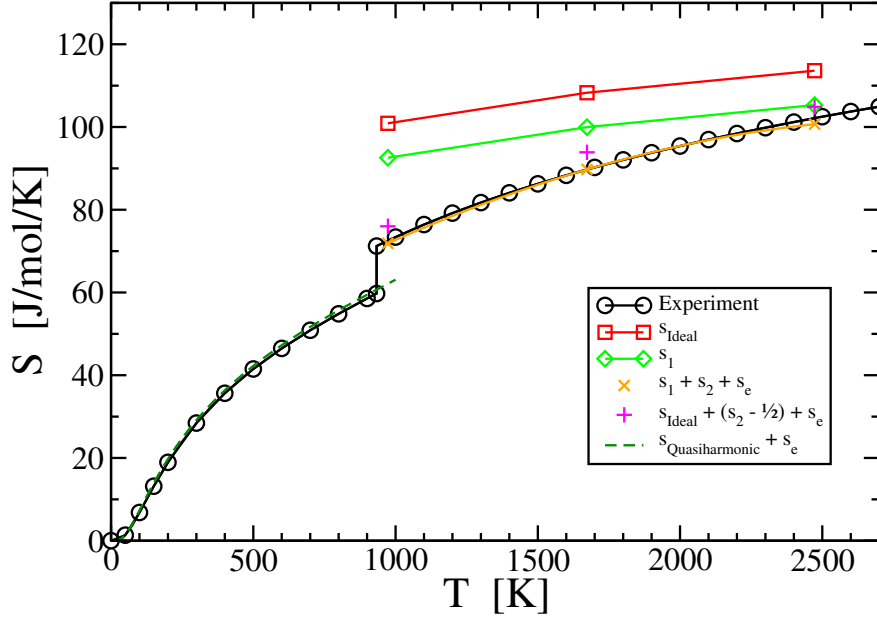
$$S/k_B = - \sum_i p_i \ln p_i, \quad (1)$$

are mathematically equivalent to the information measure defined by Shannon [3]. Entropy is thus a statistical quantity that can be calculated without reference to the underlying energetics that created the probability distribution, as recognized by Jaynes [4]. Previously we applied this concept to calculate the entropy of liquid aluminum, copper and a liquid aluminum-copper alloy binary alloy [5], using densities and correlation functions obtained from first principles molecular dynamics simulations that are nominally exact within the approximations of electronic density functional theory. In this paper we discuss the convergence and principal error sources for the case of liquid aluminum. As shown in Figure 1, we are able to reproduce the experimentally known entropy [6,7] to an accuracy of about 1 J/K/mol, suggesting that this method could provide useful predictions in cases where the experimental entropy is not known.

In a classical fluid [8], the atomic positions  $\mathbf{r}_i$  and momenta  $\mathbf{p}_i$  ( $i = 1, \dots, N$  for  $N$  atoms in volume  $V$ ) take a continuum of values so that the probability becomes a function,  $f_N(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$ , and the entropy becomes

$$S_N/k_B = - \frac{1}{N!} \int_V \prod_i d\mathbf{r}_i d\mathbf{p}_i f_N \ln (h^{3N} f_N) \quad (2)$$

in the canonical ensemble. In this expression, the factor of  $N!$  corrects for the redundancy of configurations of identical particles, and the factors of Planck's constant  $h$  are derived from the



**Figure 1.** Calculated entropies compared with experimental values [6,7].  $s_{\text{Ideal}}$  is from Eq. (12),  $s_1$  is from Eq. (11),  $s_2$  is the pair-correlation correction from Eq. (14), and  $S_e$  is from Eq. (27). We expect the best liquid state result from  $s_1 + s_2 + s_e$ . In the solid state, below melting at  $T_m=933\text{K}$ ,  $s_{\text{Quasiharmonic}}$  is the vibrational entropy in the quasiharmonic approximation.

quantum mechanical expression. For systems whose Hamiltonians separate into additive terms for the kinetic and configurational energies,  $f_N$  factorizes into a product  $\prod_i f_i g_N^{(N)}$  of independent Maxwell-Boltzmann distributions for individual atomic momenta,

$$f_1(\mathbf{p}) = \rho(2\pi mk_B T)^{-3/2} e^{-|\mathbf{p}|^2/2mk_B T}, \quad (3)$$

20 times the  $N$ -body positional correlation function  $g_N^{(1)}(\mathbf{r}_1, \dots, \mathbf{r}_N)$ .

Equation (2) can be reexpressed in terms of  $n$ -body distribution functions [8–11],  $g_N^{(n)}$  with  $n < N$ , as

$$S/Nk_B = s_1 + s_2 + s_3 + \dots, \quad (4)$$

where the  $n$ -body terms are

$$s_1 = -\frac{1}{\rho} \int_V d\mathbf{p} f_1(\mathbf{p}) \ln(h^3 f_1(\mathbf{p})) \quad (5)$$

$$s_2 = -\frac{1}{2}\rho^2 \int_V d\mathbf{r}_1 d\mathbf{r}_2 g_N^{(2)} \ln g_N^{(2)}, \quad (6)$$

$$s_3 = -\frac{1}{6}\rho^3 \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_N^{(3)} \ln(g_N^{(3)}/g_N^{(2)} g_N^{(2)} g_N^{(2)}). \quad (7)$$

The subscripts  $N$  indicate that the correlation functions are defined in the canonical ensemble, with a fixed number of atoms  $N$ , and they obey the constraints

$$\rho^n \int_V \prod_i d\mathbf{r}_i g_N^{(n)} = \frac{N!}{(N-n)!}. \quad (8)$$

Each term  $s_n$  can be interpreted in terms of measures of information. Briefly,  $s_1$  is the entropy of a single particle in volume  $V = 1/\rho$ , and hence in the absence of correlations.  $s_2$  is the difference between the information content of the pair correlation function  $g_N^{(2)}$ , and the uncorrelated entropy, which must be added to  $s_1$ . Similarly,  $s_3$  is the difference between the information contents of the three-body correlation  $g_N^{(3)}$  and the two-body correlation  $g_N^{(2)}$ , which must be added to  $s_1 + s_2$ . Notice that the information content of the  $n$ -body is also contained in the  $(n + 1)$ -body and higher-body correlations because of the identity

$$g_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{\rho}{N - n} \int_V d\mathbf{r}_{n+1} g_N^{(n+1)}(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{r}_{n+1}) \quad (9)$$

21 that expresses  $g_N^{(n)}$  as a marginal distribution of  $g_N^{(n+1)}$ .

Mutual information measures how similar a joint probability distribution is to the product of its marginal distributions [12]. In the case of a liquid structure, we may compare the two-body joint probability density [13,14]  $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g_N^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|)$  with its single-body marginal,  $\rho^{(2)}(\mathbf{r})$ . The mutual information per atom

$$I[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)] = \frac{1}{N} \int_V d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \ln(\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) / \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) \quad (10)$$

22 tells us how much information  $g(r)$  gives us concerning the positions of atoms at a distance  $r$  from  
 23 another atom. Mutual information is nonnegative definite. We recognize the term  $s_2$  in Eq. (6)  
 24 as the negative of the mutual information content of  $g_N^{(2)}$ , with the factor of 1/2 correcting for  
 25 double-counting of pairs of atoms.

## 26 1. general theory

### 27 1.1. One-body term

The one-body term  $s_1$  in Eq. (5) can be evaluated explicitly, yielding

$$s_1 = \frac{3}{2} - \ln(\rho\Lambda^3), \quad (11)$$

28 where  $\Lambda = \sqrt{h^2/2\pi mk_B T}$  is the quantum De Broglie wavelength. Both terms in Eq. (11) have simple  
 29 information theoretic interpretations [15]. While an infinite amount of information is required to  
 30 specify the exact position of even a single particle, in practice, due to quantum mechanical uncertainty  
 31 we should only specify position with a resolution of  $\Lambda$ . Consider a volume  $V = 1/\rho$ . In the absence  
 32 of other information, the probability that a single particle is localized within a given volume  $\Lambda^3$  is  
 33  $p = \Lambda^3/V$ . Summing  $-p \ln p$  over the  $(V/\Lambda^3)$ -many such volumes yields  $-\ln(\Lambda^3/V) = -\ln(\rho\Lambda^3)$ .  
 34 Similarly, the 3/2 in Eq. (11) is simply the entropy of the Gaussian momentum distribution, Eq. (3).

Notice that  $s_1$  resembles the absolute entropy of the ideal gas,

$$S_{\text{Ideal}} = \frac{5}{2} - \ln(\rho\Lambda^3). \quad (12)$$

35 The difference lies in the constant term 3/2 in  $s_1$  vs. 5/2 in  $S_{\text{Ideal}}$ . We shall discover that the  
 36 difference  $5/2 - 3/2 = 1$  is accounted for in the many-body terms  $s_2, s_3, \dots$ . Indeed, this is  
 37 clear if we place  $N$  particles in the volume  $V = N/\rho$ . The derivation of Eq. (11) generalizes to  
 38  $s/Nk_B = \frac{3}{2} - \ln(\Lambda^3/V)$ , but this must be corrected [15] by the irrelevant information,  $\ln N!$ , that  
 39 identifies the individual particles in each separate volume  $\Lambda^3$ . The leading term of the Stirling  
 40 approximation  $\ln N! \approx N \ln N - N$  converts  $\ln(\Lambda^3/V)$  into  $\ln(\rho\Lambda^3)$ , while the second term adds  
 41 1 to 3/2 yielding 5/2.

42 Either  $s_1$  or  $s_{\text{Ideal}}$  can be taken as a starting point for an expansion of the entropy in multi-particle  
 43 correlations. Prior workers [11,16–19] tend to favor  $s_{\text{Ideal}}$ , while we shall find it more natural to begin  
 44 with  $s_1$ .

#### 45 1.2. Two- and three-body terms

Translational symmetry allows us to replace the double integral over positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in Eq. (6) for  $s_2$  with the volume  $V$  times a single integral over the relative separation  $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ . A similar transformation applies to the integral for  $s_3$ . However, the canonical ensemble constraint Eq. (8) leads to long-range (large  $r$ ) contributions to the remaining integrations. Nettleton and Green [16] and Raveche [17,18] recast the distribution function expansion in the *grand*-canonical ensemble and obtained expressions that are better convergent. We follow Baranyai and Evans [11] and apply the identity

$$\rho^2 \int_V d\mathbf{r}_1 d\mathbf{r}_2 g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \quad (13)$$

to rewrite the two-body term as

$$s_2 = S_{\text{Fluct}}^{(2)} + S_{\text{Info}}^{(2)} \quad (14)$$

$$S_{\text{Fluct}}^{(2)} = \frac{1}{2} + \frac{1}{2}\rho \int d\mathbf{r} [g^{(2)}(r) - 1] \quad (15)$$

$$S_{\text{Info}}^{(2)} = -\frac{1}{2}\rho \int d\mathbf{r} g^{(2)}(r) \ln g^{(2)}(r). \quad (16)$$

The combined integrand  $\{[g^{(2)}(r) - 1] - g^{(2)}(r) \ln g^{(2)}(r)\}$  of  $s_2$  falls off rapidly, so that the sum of the two integrals converges rapidly as the range of integration extends to large  $r$ . Furthermore, the combined integral is ensemble invariant, which allowed us to substitute the grand canonical ensemble radial distribution function  $g(r)$  in place of the canonical  $g_N^{(2)}$ . The same trick applies to the three-body term,

$$s_3 = S_{\text{Fluct}}^{(3)} + S_{\text{Info}}^{(3)} \quad (17)$$

$$S_{\text{Fluct}}^{(3)} = \frac{1}{6} + \frac{1}{6}\rho^2 \int d\mathbf{r}^2 (g^{(3)} - 3g^{(2)}g^{(2)} + 3g^{(2)} - 1) \quad (18)$$

$$S_{\text{Info}}^{(3)} = -\frac{1}{6}\rho^2 \int d\mathbf{r}^2 g^{(3)} \ln (g^{(3)}/g^{(2)}g^{(2)}g^{(2)}). \quad (19)$$

The contribution of  $1/2$  in  $s_2$  as given by Eq. (14), together with an added  $1/6 + 1/12 + \dots = 1/2$  from the three-body Eq. (17) and higher terms, reconciles the one-body entropy with the ideal gas. For consistency with previous workers [11,16–19] who omit the  $1/2$  from  $S_{\text{Fluct}}^{(2)}$  and the  $1/6$  from  $S_{\text{Fluct}}^{(3)}$ , and to make connection with the ideal gas, we can add the entire series  $1/2 + 1/6 + 1/12 + \dots = 1$  to  $s_1$  and write

$$S/Nk_B = S_{\text{Ideal}} + (s_2 - 1/2) + (s_3 - 1/6) + \dots \quad (20)$$

46 which is equivalent to Eq. (4).

In the grand-canonical ensemble, the  $S_{\text{Fluct}}^{(2)}$  term in Eq. (14) arise from fluctuations in the number of atoms,  $N$ , and can be evaluated in terms of the isothermal compressibility  $\chi_T$  as

$$S_{\text{Fluct}}^{(2)}/k_B = \frac{1}{2}\gamma, \quad (21)$$

where

$$\gamma = \rho k_B T \chi_T \quad (22)$$

is the dimensionless compressibility. Note that  $\chi_T$ , and hence also  $\mathfrak{S}_{\text{Fluct}}^{(2)}$ , are positive definite. The remaining term is the entropy reduction due to the two-body correlation. As noted above, the mutual information content of the radial distribution function  $g^{(2)}(r)$  reduces the entropy by

$$S_{\text{Info}}^{(2)}/k_B \equiv -\frac{1}{2}\rho \int d\mathbf{r} g^{(2)}(r) \ln g^{(2)}(r). \quad (23)$$

47 The complete two-body term is now  $s_2 = S_{\text{Fluct}}^{(2)} + S_{\text{Info}}^{(2)}$ .

The three-body fluctuation term (see Eq. (16)) also relates to isothermal compressibility [18], with

$$S_{\text{Fluct}}^{(3)} = \frac{1}{2}\gamma - \frac{1}{3}\gamma^2 + \frac{1}{6}\rho\gamma \left. \frac{\partial\gamma}{\partial\rho} \right|_{\beta}. \quad (24)$$

48 The final term in Eq. (17) reduces to a difference of three- and two-body entropies, and its sign  
49 is not determined. Essentially, the  $g^{(3)} \ln(g^{(3)}/g^{(2)}g^{(2)}g^{(2)})$  term adds back the two-body mutual  
50 information  $I[g^{(2)}]$  and then subtracts the information contained in the three-body correlation  $g^{(3)}$ .  
51 Note that  $g^{(3)}$  necessarily contains all the information in  $g^{(2)}$  because of the identity Eq.(9).

52 The pattern illustrated in Eqs. (21) and (24) holds for the analogous higher-body correlations  
53 as well, because integrals of the correlation function  $g^{(n)}$  can be written in terms of integrals and  
54 density derivatives of  $g^{(n-1)}$ . One limit of special interest is the incompressible limit, where the initial  
55 terms of Eqs. (14) and (17) vanish and only the information-derived  $g \ln g$  terms survive. This limit  
56 should apply to dense fluids at low temperatures. Another limit occurs at high temperature, where  
57 the density drops and the correlation functions approach 1. In this limit all integrals involving  $g^{(n)}$   
58 vanish so that  $S_{\text{Info}}^{(n)} = 0$  and all the  $S_{\text{Fluct}}^{(n)}$  terms sum to  $1/2 + 1/6 + 1/12 + \dots = 1$ .

Truncation of the series of terms  $S_{\text{Info}}^{(n)}$  is accurate if higher many-body correlation functions can be approximated by products of fewer-body correlations. That is, if the higher correlation functions contain no new information. For example, the Kirkwood superposition approximation

$$\delta g_N^{(3)}(r, s, t) \equiv g^{(3)}(r, s, t) / g_N^{(2)}(r) g_N^{(2)}(s) g_N^{(2)}(t) \approx 1 \quad (25)$$

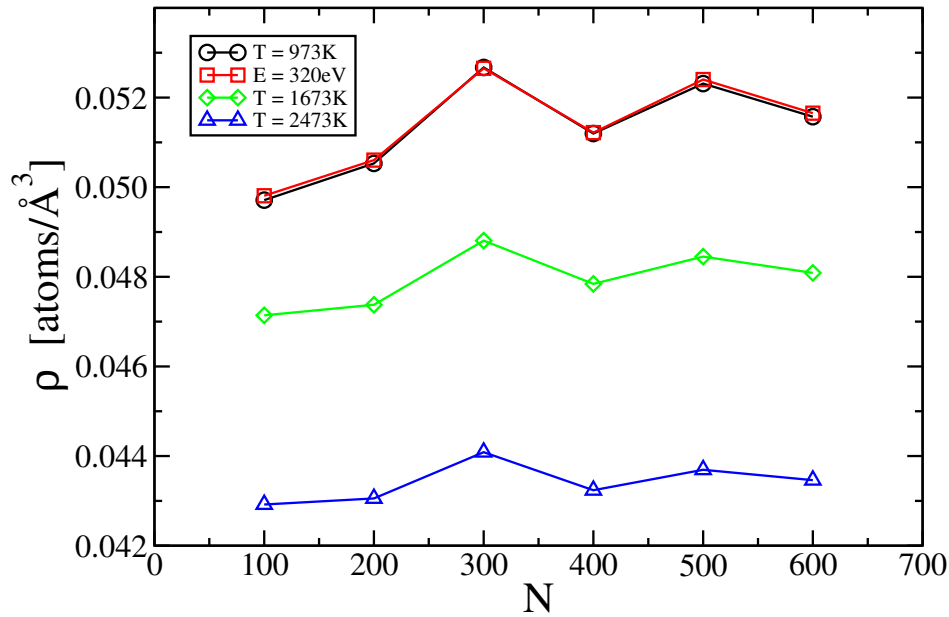
59 causes  $S_{\text{Info}}^{(3)}$  to vanish.

## 60 2. Results

61 To provide the liquid state correlation functions needed for our study we perform *ab-initio*  
62 molecular dynamics (AIMD) simulations based on energies and forces calculated from first principles  
63 electronic density functional theory (DFT). We apply the plane-wave code VASP [20] in the  
64 generalized gradient approximation [21]. Simulations are performed at fixed volume for each  
65 temperature. In order to determine the proper volumes (*i.e.* liquid densities  $\rho$ ) we performed  
66 simulations at several volumes to identify the volume at which the pressure (including the kinetic  
67 term) vanished. Most runs were performed using Normal precision FFT grids, however the smallest  
68 system (N=100 atoms) was found to require accurate precision.

69 Figure 2 shows the result of convergence studies in both volume and plane-wave cutoff  
70 energy. Briefly, we found minimal dependence on the plane wave energy cutoff, but strong and  
71 non-monotone dependence on the number of atoms. We accept  $N = 500$  atoms as a suitable target  
72 for convergence of the volume and we use the same condition for collecting our correlation functions.  
73 Our calculated density at 973K falls below the experimentally assessed value by about 1%, similar to  
74 the discrepancy for solid Al in the limit of low temperature. From the volume-dependence of pressure  
75 we obtain estimates of the dimensionless compressibility  $\gamma$  ranging from 0.008 at T=973K up to 0.015  
76 at T=2473K.

77 Pair correlation functions  $g^{(2)}(r)$  are collected as histograms in  $\Delta = 0.01 \text{ \AA}$  bins, normalized to  
78  $4\pi r^2 \Delta N^2 / V$  and subsequently smeared with a Gaussian of width  $\sigma = 0.025 \text{ \AA}$ . Triplet correlation



**Figure 2.** Calculated aluminum density *vs.* number of atoms  $N$  at various temperatures. All results hold for the default energy cutoff of 240 eV except for red squares that hold for 320 eV.

79 functions  $g^{(3)}(r, s, t)$  utilize bin widths of  $\Delta = 0.10 \text{ \AA}$ , normalized to  $8\pi^2rst\Delta^3N^3/V^2$ , and are  
 80 not smeared. Our run durations for data collection were 10 ps. All structures were thoroughly  
 81 equilibrated prior to data collection.

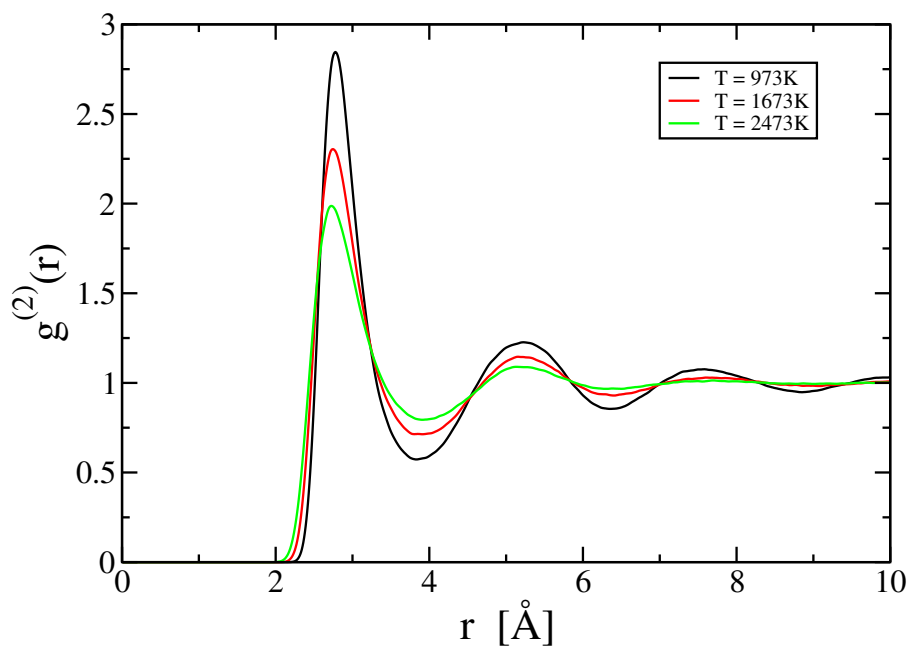
82 Figure 3 illustrates the pair correlation function  $g^{(2)}(r)$  at various temperatures. Note the  
 83 oscillations that extend to large  $r$ ; presumably these oscillations are responsible in part for the  
 84 oscillations in  $\rho$  as a function of  $N$ . Note also the decreasing amplitude of oscillation with increasing  
 85 temperature. Figure 4 illustrates the three-body correlation function for the special case of equilateral  
 86 triangles with  $r = s = t$ . The inset displays the ratio  $\delta g^{(3)}(r, r, r)$  (see Eq.( 25)). Notice that  $\delta g^{(3)}$   
 87 is nearly a step function, with small decaying oscillations that diminish with increasing temperature.

### 88 2.1. One-body term

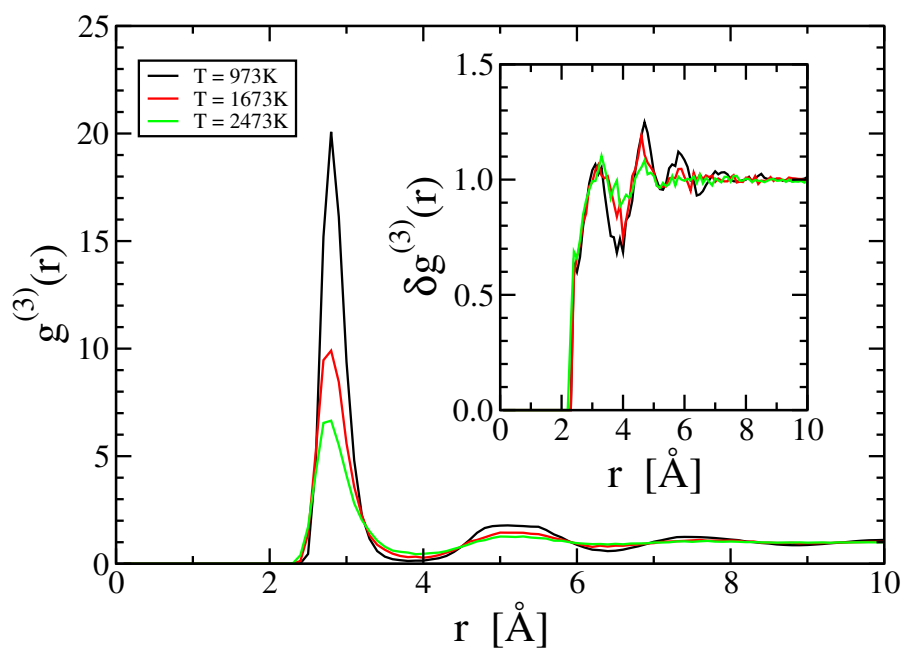
89 The one-body term explicitly depends on density, and also depends implicitly on temperature  
 90 through the De Broglie wavelength  $\Lambda$ . Taking our calculated densities, and evaluating  $\Lambda$ ,  $s_1$ , and  $s_{\text{Ideal}}$ ,  
 91 we note that  $s_1$  and  $s_{\text{Ideal}}$  are greater than, but rather close to, the experimental liquid entropies [6,7],  
 92 as shown in Fig. 1. The differences drop as the temperature grows, as expected because nonideality  
 93 of the liquid metal becomes less important at high temperature.

### 94 2.2. Two-body term

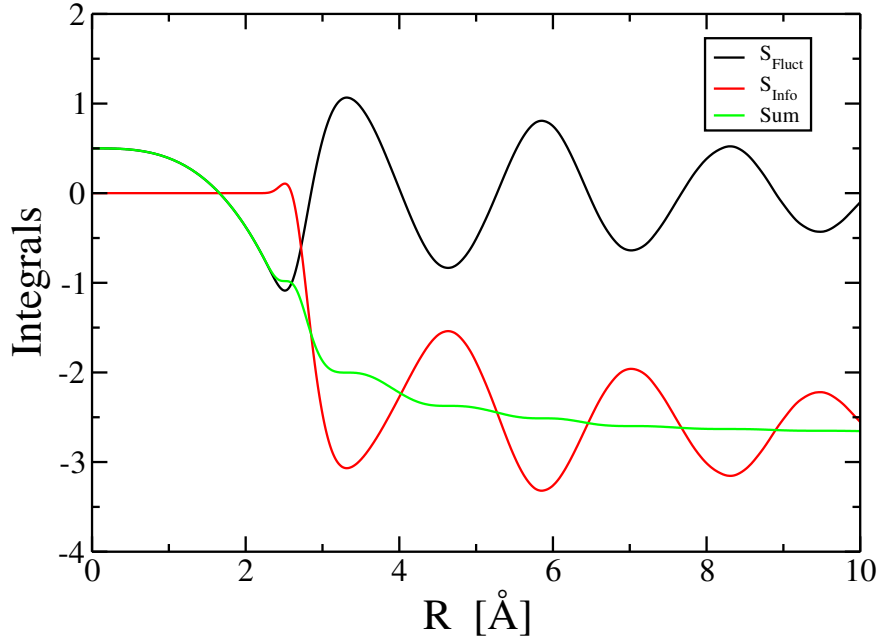
95 In figure 5 we plot the terms  $S_{\text{Fluct}}^{(2)}$  and  $S_{\text{Info}}^{(2)}$  as defined by Eqs. (21) and (23), respectively, where  
 96 we integrate from zero separation up to a cutoff of  $R$ . Owing to the  $R^2$  increase of the volume  
 97 differential  $dr$ , oscillations of  $g^{(2)}$  are magnified at large  $R$ . The fluctuation term appears to converge  
 98 towards a value close to 0, consistent with the low compressibility of the liquid metal, while the  
 99 information term converges towards a negative value. Note that the oscillations are nearly opposites,  
 100 so that their sum converges rapidly towards a negative value of  $s_2$ .



**Figure 3.** Pair correlation function  $g^{(2)}(r)$  at various temperatures.



**Figure 4.** Triplet correlation function  $g^{(3)}(r,r,r)$  at various temperatures. Inset: Kirkwood ratio Eq.(25).



**Figure 5.** Two-body terms  $S_{\text{Fluct}}$  and  $S_{\text{Info}}$  and their sum from simulated pair correlation function  $g^{(2)}$  at  $T=973\text{K}$ .

101 Adding the entropy reduction  $s_2$  to the single-particle entropy  $s_1$  yields values that are close to  
 102 experiment but lie slightly below, as is evident in Fig. 1 (blue triangles). However we know that  
 103 liquid metals have an electronic entropy (see Sec. 2.3),  $S_{\text{Elec}}$ , and when we include that term (Fig 1,  
 104 orange crosses) the values lie within 1 J/K/mol of the experimental values. Had we chosen to add  
 105  $s_2 - 1/2 + S_{\text{Elec}}$  to  $s_{\text{Ideal}}$  instead of adding  $s_2 + S_{\text{Elec}}$  to  $s_1$  the values would have been greater by  
 106  $R/2 = 4.157 \text{ J/K/mol}$ , resulting in poorer agreement (Fig. 1 magenta + signs). In section 2.4 we  
 107 explain why  $s_1 + s_2 + \dots$  is a more suitable starting point for an expansion in multiparticle correlation  
 108 functions than  $s_{\text{Ideal}} + (s_2 - 1/2) + \dots$  is.

### 109 2.3. Electronic entropy

The electronic density of states  $D(E)$ , which comes as a byproduct of first principles calculations, determines the electronic entropy [22]. At low temperatures, all states below the Fermi energy  $E_F$  are filled and all states above are empty. At finite temperature, single electron excitations vacate states below  $E_F$  and occupy states above, resulting in the Fermi-Dirac occupation function

$$f_T(E) = \frac{1}{\exp[(E - \mu)/k_B T] + 1}. \quad (26)$$

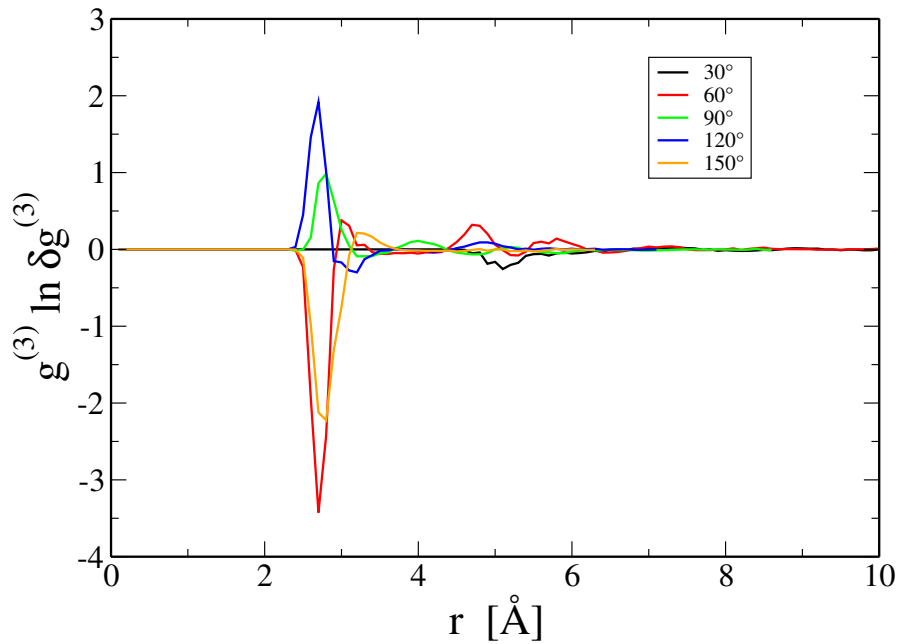
Fractional occupation probability creates an electronic contribution to the entropy,

$$S_{\text{Elec}} = -k_B \int D(E) [f_T(E) \ln f_T(E) + (1 - f_T(E)) \ln 1 - f_T(E)]. \quad (27)$$

110 We apply this equation to representative configurations drawn from our liquid metal simulations,  
 111 with increased  $k$ -point density in order to converge the density of states.

112 At low temperatures, the electronic entropy approaches  $(\pi^2/3)D(E_F)k_B^2 T$ , which depends only  
 113 on the density of states at the Fermi level. However, at the high temperatures of liquid metals the





**Figure 6.** Three-body integrand  $g^{(3)}(r, r, t) \ln (g^{(3)}(r, r, t) / g^{(2)}(r)g^{(2)}(r)g^{(2)}(t))$  for isosceles triangles of angle  $\theta$  and sides  $(r, r, t = 2r \cos \theta)$  at  $T=973\text{K}$ .

114 electronic entropy requires the full integral as given in Eq. (27), rather than its low temperature  
 115 approximation.

#### 116 2.4. three- and higher-body terms

117 We saw in Fig. 5 that the integral in Eq. (21) converges slowly to the dimensionless  
 118 compressibility  $\gamma$  which is a positive but very small value. Accordingly, the same must be true  
 119 for the integral of the three-body fluctuation term, Eq. (24), and all higher-body terms as well.  
 120 Thus all fluctuation terms are essentially negligible contributions to the entropy at the temperatures  
 121 considered here. This observation must break down at sufficiently high temperatures, because in  
 122 the limit of very high temperature all correlation functions approach 1, so that all integrals vanish.  
 123 As noted by Baranyai and Evans [11],  $s_2 \rightarrow 1/2$ ,  $s_3 \rightarrow 1/6$ ,  $s_4 \rightarrow 1/12$  and  $s_3 + s_4 + \dots \rightarrow 1$ .  
 124 This limit only holds at extreme high temperatures and low densities, however the small shortfall in  
 125  $s_1 + s_2 + S_{\text{Elec}}$  at  $T=2473\text{K}$  could reflect a need to include a small fluctuation contribution due to the  
 126 many-body terms  $S_{\text{Fluct}}^{(n)}$  at high temperatures.

127 We still need to discuss the three-body information term,  $S_{\text{Info}}^{(3)}$  (Eq. (17)). Previous studies have  
 128 discussed this term for model Lennard-Jones and hard-sphere fluids [23,24]. This term vanishes  
 129 within the Kirkwood superposition approximation,  $\delta g^{(3)} = 1$ , and as seen in Fig. 4 this approximation  
 130 is quite accurate even at  $T=973\text{K}$ . Presumably the nearly free electron character of aluminum, which  
 131 causes its interactions to be well described by a nearly hard-sphere pair potential [25], leads to the  
 132 weak form of  $\delta g^{(3)}$ . The deviations of  $\delta g^{(3)}$  from 1 are oscillatory, both in radial dependence as seen  
 133 in Fig. 4, and in angle as shown in Fig. 6. We lack sufficient resolution in  $g^{(3)}$  to evaluate the complete  
 134 integral, however integrating over  $r$  at fixed angle the terms are of magnitude 0.1 or less, and they  
 135 reverse sign as a function of angle, leading to further cancellation.

### 136 3. Discussion

137 We find that the entropy of liquid aluminum is described rather accurately using the first two  
 138 terms in an expansion of the entropy in multiparticle correlations. We show in particular that it  
 139 is advantageous to start the series with  $s_1$  rather than  $s_{\text{Ideal}}$ , and in compensation to include the  
 140 terms  $1/2, 1/6, \dots$  within  $s_{\text{Fluct}}^{(2)}, s_{\text{Fluct}}^{(3)}, \dots$ , respectively, because each of these terms then becomes  
 141 of the order of the small dimensionless compressibility  $\gamma$ . The remaining terms,  $S_{\text{Info}}^{(n)}$ , each have  
 142 a simple information-theoretic interpretation, with  $s_1$  being the information to specify individual  
 143 particle positions with resolution  $\Lambda^3$ ,  $S_{\text{Info}}^{(2)} = -I[g^{(2)}]$  being the mutual information content of the pair  
 144 correlation function, and the corresponding higher order terms reflecting the additional information  
 145 contained in  $g^{(n)}$  that is not already present in the lower order terms.

146 In terms of accuracy, obtaining an accurate density is important. The difference between  
 147 densities predicted at different system sizes  $N$  can shift the value of  $s_1$  by about 0.5 J/K/mol, with  
 148 greater density reducing  $s_1$ . More significant is the impact of density on  $s_2$ , with the same difference in  
 149 density increasing the mutual information  $I[g^{(2)}]$  by up to 6 J/K/mol. Both of these potential sources  
 150 of error substantially exceed the truncation error due to neglect of multiparticle correlations, a finding  
 151 that may hold generally for nearly-free-electron metals, while transition metals with angle-dependent  
 152 forces may require additional terms.

153 **Funding:** This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting  
 154 Technology Research Program. MCG was supported by NETL's Research and Innovation Center's Innovative  
 155 Process Technologies (IPT) Field Work Proposal. MW was supported by the Department of Energy under grant  
 156 DE-SC0014506. Please add: "This research received no external funding" or "This research was funded by NAME  
 157 OF FUNDER grant number XXX." and and "The APC was funded by XXX". Check carefully that the details given  
 158 are accurate and use the standard spelling of funding agency names at <https://search.crossref.org/funding>, any  
 159 errors may affect your future funding.

160 **Conflicts of Interest:** Disclaimer: This project was funded by the Department of Energy, National Energy  
 161 Technology Laboratory, an agency of the United States Government, through a support contract with AECOM.  
 162 Neither the United States Government nor any agency thereof, nor any of their employees, nor AECOM, nor any  
 163 of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility  
 164 for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or  
 165 represents that its use would not infringe privately owned rights. Reference herein to any specific commercial  
 166 product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily  
 167 constitute or imply its endorsement, recommendation, or favoring by the United States Government or any  
 168 agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of  
 169 the United States Government or any agency thereof. Declare conflicts of interest or state "The authors declare  
 170 no conflict of interest." Authors must identify and declare any personal circumstances or interest that may be  
 171 perceived as inappropriately influencing the representation or interpretation of reported research results. Any  
 172 role of the funders in the design of the study; in the collection, analyses or interpretation of data; in the writing  
 173 of the manuscript, or in the decision to publish the results must be declared in this section. If there is no role,  
 174 please state "The funders had no role in the design of the study; in the collection, analyses, or interpretation of  
 175 data; in the writing of the manuscript, or in the decision to publish the results".

- 176
- 177 1. Gibbs, J.W. *Elementary principles in statistical mechanics*; Dover, New York, 1960.
  - 178 2. von Neumann, J. Thermodynamik quantenmechanischer Gesamtheiten. *Nachrichten von der Gesellschaft*  
 179 *der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse* **1927**, 1927, 273–291.
  - 180 3. Shannon, C.E. A Mathematical Theory of Communication. *Bell System Technical Journal* **1948**, 27, 379–423.  
 181 doi:10.1002/j.1538-7305.1948.tb01338.x.
  - 182 4. Jaynes, E.T. Information Theory and Statistical Mechanics. *Physical Review* **1957**, 106, 620–630.  
 183 doi:10.1103/PhysRev.106.620.
  - 184 5. Gao, M.; Widom, M. Information entropy of liquid metals. *J. Phys. Chem. B* **2018**, 122, 3550–3555.
  - 185 6. Hultgren, R.R. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals,  
 186 Ohio, 1973.
  - 187 7. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; McDonald, R.; Syverud, A. <http://kinetics.nist.gov/janaf/>,  
 188 1985.

- 189 8. Green, H.S. *The molecular theory of fluids*; North-Holland, Amsterdam, 1952.
- 190 9. Yvon, J. *Correlations and entropy in classical statistical mechanics*; Pergamon, Oxford, 1969.
- 191 10. Wallace, D.C. On the role of density fluctuations in the entropy of a fluid. *J. Chem. Phys.* **1987**,  
192 87, 2282–2284.
- 193 11. Baranyai, A.; Evans, D.J. Direct entropy calculation from computer simulation of liquids. *Physical Review*  
194 *A* **1989**, 40, 3817–3822. doi:10.1103/PhysRevA.40.3817.
- 195 12. Cover, T.M.; Thomas, J.A. *Elements of information theory*; Wiley, New Jersey, 2006.
- 196 13. McQuarrie, D.A. *Statistical Mechanics*; Harper & Row, New York, 1973; chapter 5-3, 10-7 and 13-2.
- 197 14. Rowlinson, J.S.; Widom, B. *Molecular theory of capillarity*; Oxford, 1982.
- 198 15. Ben-Naim, A. An informational theoretical approach to the entropy of liquids and solutions. *Entropy*  
199 **2018**, 20, 514.
- 200 16. Nettleton, R.E.; Green, M.S. Expression in Terms of Molecular Distribution Functions for the Entropy  
201 Density in an Infinite System. *Journal of Chemical Physics* **1958**, 29, 1365. doi:10.1063/1.1744724.
- 202 17. Raveche, H.J. Entropy and Molecular Correlation Functions in Open Systems. I. Derivation. *The Journal*  
203 *of Chemical Physics* **1971**, 55, 2242–2250.
- 204 18. Mountain, R.D.; Raveche, H.J. Entropy and Molecular Correlation Functions in Open Systems. II Two-  
205 and Three-Body Correlations. *The Journal of Chemical Physics* **1971**, 55, 2250–2255. doi:10.1063/1.1676400.
- 206 19. Laird, B.B.; Haymet, A.D.J. Calculation of the entropy of binary hard sphere mixtures from pair  
207 correlation functions. *The Journal of Chemical Physics* **1992**, 97, 2153–2155. doi:10.1063/1.463103.
- 208 20. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys.*  
209 *Rev. B* **1999**, 59, 1758–75.
- 210 21. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*  
211 **1996**, 77, 3865–3868.
- 212 22. Widom, M. Modeling the structure and thermodynamics of high-entropy alloys. *J. Mater. Resch.* **2018**,  
213 33, 2881–2898.
- 214 23. Baranyai, A.; Evans, D.J. Three-particle contribution to the configurational entropy of simple fluids. *Phys.*  
215 *Rev. A* **1990**, 42, 849–857.
- 216 24. Laird, B.B.; Haymet, A.D.J. Calculation of the entropy from multiparticle correlation functions. *Phys. Rev.*  
217 *A* **1992**.
- 218 25. Moriarty, J.A.; Widom, M. First Principles Interatomic Potentials for Transition Metal Aluminides. Theory  
219 and Trends Across the 3d Series. *Phys. Rev. B* **1997**, 56, 7905–7917.

220 © 2019 by the authors. Submitted to *Entropy* for possible open access publication  
221 under the terms and conditions of the Creative Commons Attribution (CC BY) license  
222 (<http://creativecommons.org/licenses/by/4.0/>).