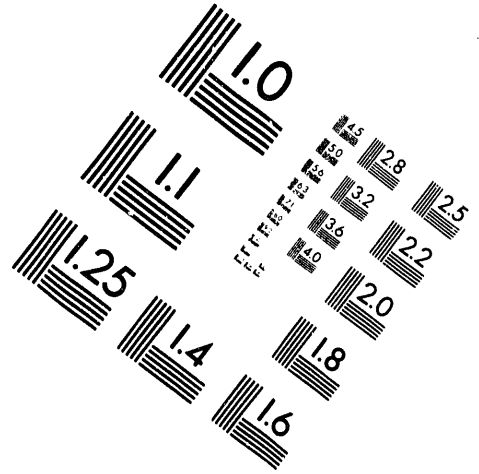
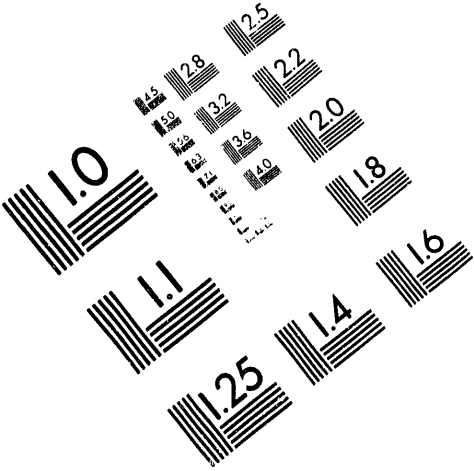




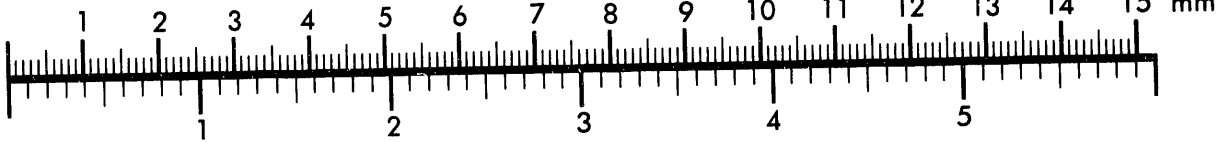
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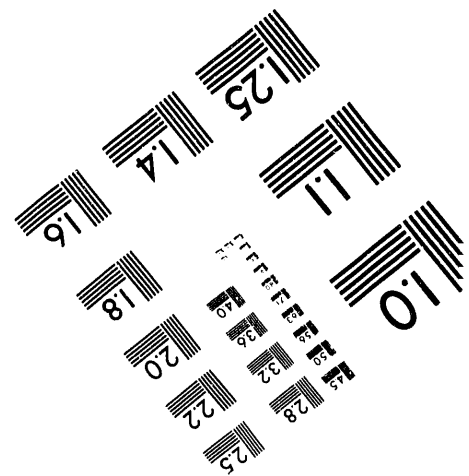
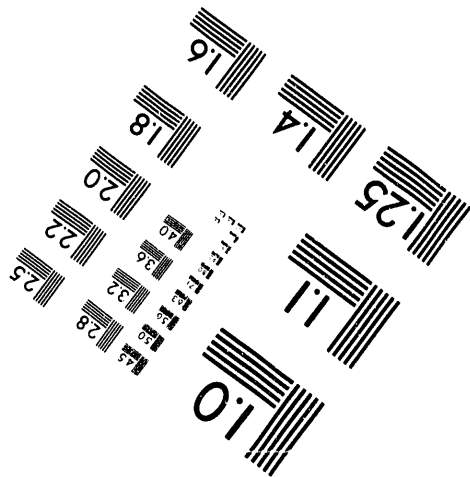
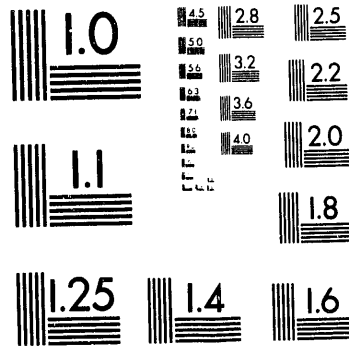
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TITLE: STATISTICAL MECHANICAL THEORY OF LIQUID ENTROPY

AUTHOR(S): Duane C. Wallace

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STATISTICAL MECHANICAL THEORY OF LIQUID ENTROPY

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The multiparticle correlation expansion for the entropy of a classical monatomic liquid is presented. This entropy expresses the physical picture in which there is no free particle motion, but rather, each atom moves within a cage formed by its neighbors. The liquid expansion, including only pair correlations, gives an excellent account of the experimental entropy of most liquid metals, of liquid argon, and the hard sphere liquid. The pair correlation entropy is well approximated by a universal function of temperature. Higher order correlation entropy, due to n -particle irreducible correlations for $n \geq 3$, is significant in only a few liquid metals, and its occurrence suggests the presence of n -body forces. When the liquid theory is applied to the study of melting, we discover the important classification of normal and anomalous melting, according to whether there is not or is a significant change in the electronic structure upon melting, and we discover the universal disordering entropy for melting of a monatomic crystal. Interesting directions for future research are: extension to include orientational correlations of molecules, theoretical calculation of the entropy of water, application to the entropy of the amorphous state, and correlational entropy of compressed argon. We clarify the relation among different entropy expansions in the recent literature.

1. Physical Interpretation of Entropy Formulas

Our goal is to present and evaluate the multiparticle correlation expansion of the entropy of a classical monatomic liquid. Since this entropy formulation is not well known, it is helpful to contrast it with the virial expansion for a classical monatomic gas. Let us consider a system of N like atoms in a volume V , with particle density $\rho = N/V$. The entropy S in the classical canonical ensemble is¹

$$S = -kV \int f^{(1)} \ln(h^3 f^{(1)}) d\mathbf{p} - k(\rho^N/N!) \int \dots \int g^{(N)} \ln g^{(N)} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (1)$$

Here k is Boltzmann's constant, h is Planck's constant, $f^{(1)} = f^{(1)}(\mathbf{p})$ is the one-particle momentum distribution, where \mathbf{p} = momentum, and $g^{(N)} = g^{(N)}(\mathbf{r}_1 \dots \mathbf{r}_N)$ is the N -particle correlation function, where \mathbf{r}_i = particle positions. Equation (1) is valid at all temperatures T and densities ρ . However, the N -particle correlation integral in (1) is generally intractable, so it is useful to develop approximations for this integral, appropriate to the gas and liquid regimes.

Henceforth we work with entropy in units of k per particle. The one-particle term in (1) is S_1 ,

$$S_1 = -\rho^{-1} \int f^{(1)} \ln(h^3 f^{(1)}) d\mathbf{p}, \quad (2)$$

and the integral can be done because $f^{(1)}(\mathbf{p})$ is the normalized Boltzmann distribution, yielding¹

$$S_1 = \frac{3}{2} - \ln(\rho \Lambda^3), \quad (3)$$

where $\Lambda = h(\beta/2\pi M)^{1/2}$ is the deBroglie wavelength, and $\beta = (kT)^{-1}$.

The N -particle correlation entropy in (1) is S_N . The correlation function $g^{(N)}(\mathbf{r}_1 \dots \mathbf{r}_N)$ depends on the total system potential $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N)$, which may contain n -particle potentials for $n = 2, 3, \dots$. In the physically realistic case, where Coulomb forces are screened, and where there are no infinite hard cores, all of these n -particle potentials are spatially integrable, and this means the gas regime is reached both at low density ($\rho \rightarrow 0$), and at high temperature ($\beta \rightarrow 0$).

Let us examine S_N for the gas regime. In the partition function, the expansion can be made $\exp[-\beta\Phi(\mathbf{r}_1\dots\mathbf{r}_N)] = 1 + \dots$, where equivalence of the expansion at $\rho \rightarrow 0$ and at $\beta \rightarrow 0$ has been discussed.² This leads to $g^{(N)}(\mathbf{r}_1\dots\mathbf{r}_N) = (N!/N^N) + \dots$, and hence

$$S_N = 1 - \dots, \quad (4)$$

where $-\dots$ represents a power series in ρ , which is the virial series. The complete gas entropy is therefore

$$S_{gas} = S_1 + 1 - \dots \quad (5)$$

The value 1 expresses that each particle moves freely throughout the entire system volume; the series $-\dots$ expresses interference of this free motion, from the atomic interactions, and is negative, hence reduces the entropy from the ideal gas value $S_1 + 1$. The virial expansion has a radius of convergence,³ which presumably does not extend to the liquid regime.

Before we can derive the correlation entropy for a liquid, we need to recognize the physically spurious long-range correlations present in constant- N ensembles. First, in any ensemble, there exists a correlation length l_c , normally a few nearest neighbor distances, beyond which the two-particle correlation vanishes, as indicated by the condition $g^{(2)}(r) = \text{constant}$ for $r > l_c$. In the grand canonical ensemble this constant is 1, and the normalization of $g^{(2)}$ is

$$\rho \int [g^{(2)}(r) - 1] d\mathbf{r} = -1 + \alpha, \quad (6)$$

where $\alpha = \rho \kappa kT$, and κ is the isothermal compressibility. α is a measure of density fluctuations; α is positive, and for a liquid $\alpha \ll 1$. In the canonical ensemble, $g^{(2)}(r)$ has a nonphysical long range correlation because, given a particle at any position, the number of remaining particles is exactly $N-1$. Thus $g^{(2)}(r) = 1 - (\alpha/N)$ for $r > l_c$, and the normalization of $g^{(2)}$ is

$$\rho \int [g^{(2)}(r) - 1] d\mathbf{r} = -1. \quad (7)$$

To obtain the same normalization in any ensemble, we limit the integration to $r \leq l_c$, denoted by $\int_c d\mathbf{r}$, and find

$$\rho \int_c [g^{(2)}(r) - 1] d\mathbf{r} = -1 + \alpha + O(N^{-1}). \quad (8)$$

This result is valid for all ensembles, since $g^{(2)}(r)$ is the same to order N^{-1} in all ensembles.⁴ Analogous properties hold for the higher order correlation functions $g^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n)$.

To establish the correct approximation for S_N for a liquid, we first note that the motion of particles in a liquid represents an opposite extreme from a gas. In a liquid there is no free particle motion; instead, each particle moves within a cage formed by its neighbors. Hence in a liquid, the important correlation information is contained in the $g^{(n)}$ for small n , specifically for $n = 2, 3, \dots$. This concept led H. S. Green⁵ to the multiparticle correlation expansion of $\ln g^{(N)}$ in the canonical ensemble, in which the first term is $\frac{1}{2}N(N-1)\ln g^{(2)}$. However, the spatial integral of Green's expansion contains the nonphysical long range correlations resulting from the constant- N condition. In the past we have corrected this problem by using grand canonical correlation functions.^{1,6} Here we will limit the integrations to within the correlation length, giving results valid in all ensembles:

$$S_N = S_2 + S_3 + \dots, \quad (9)$$

where

$$S_2 = -\frac{1}{2}\rho \int_c g^{(2)}(r) \ln g^{(2)}(r) d\mathbf{r}, \quad (10)$$

and where S_n contains only n -particle correlation functions. The complete liquid entropy is then

$$S_{liq} = S_1 + S_2 + S_3 + \dots \quad (11)$$

As shown in the next Section, experimental data confirm that the series (11) is rapidly converging for liquids. For a monatomic liquid at melt, $S_1 \approx 10$, $S_2 \approx -2.6$, and the higher order terms, if significant, are negative. Hence as the atoms move in a liquid, the interatomic potentials interfere with the kinetic energy, and reduce the entropy from the one-particle (kinetic) contribution S_1 .

2. Comparison with Experiment for Liquids

For real monatomic liquids, it is currently possible to evaluate the entropy contributions S_1 and S_2 , but no higher order contributions can be directly evaluated, because the higher order correlation functions are not available. S_1 depends only on density and temperature. To evaluate S_2 , we used experimental data for $g^{(2)}(r)$, from neutron scattering and x-ray scattering. A representative curve of $g^{(2)}(r)$ is shown in Figure 1; the integral S_2 , equation (10), depends mainly on $g^{(2)}(r)$ in the neighborhood of the first two peaks and valleys. Let us denote the higher order correlation entropy by S_X ,

$$S_X = S_3 + S_4 + \dots \quad (12)$$

For the liquid metals there is also an electronic excitation contribution S_E , so that the total theoretical entropy is

$$S = S_1 + S_2 + S_X + S_E. \quad (13)$$

We have compared this theory with the experimental entropy for liquid argon,⁷ the hard sphere liquid,¹ and for 22 nearly free electron liquid metals.⁸

The first important finding is that S_2 displays approximately universal behavior for most liquids. The range $S_2 = -2.6 \pm 0.3$ at the melting temperature T_m includes argon, the hard sphere liquid, and all the metals except for six which undergo anomalous melting (described in the next Section). The temperature dependence of S_2 is also universal, as shown in Figure 2. The trend of S_2 with temperature is easily understood: as temperature increases, thermal kinetic energy increasingly overcomes the caging effect of the interatomic potentials, hence the magnitude of S_2 decreases.

The second important finding is that the theoretical entropy, with $S_X = 0$, is accurate for most liquids.⁸ For Li, Na, K, Rb, Cs, Al, Mg, and Si, the quantity $S_1 + S_2 + S_E$ agrees with the experimental entropy to approximately ± 0.1 , which is around 1% of the experimental entropy, and which is the magnitude of the combined errors in the analysis. Hence for these metals, the

theory with $S_X = 0$ is essentially exact. The comparison for liquid sodium is shown in Figure 3.⁹

In general, then, it makes sense to use equation (13), together with the experimental entropy, to infer the value of S_X . For the liquid metals, this procedure tells us that S_X , when it is significant, is negative. For Cd, Pb, and Ge, S_X at T_m is around -0.3, which is small. But the six elements Sb, Bi, In, Hg, Ga, and Sn have large negative values of S_X , suggesting the operation of strong many-body potentials in these liquids. However, as shown in Figure 4, the magnitude of S_X decreases with increasing temperature. The physical process here is the same as in the pair correlation entropy S_2 : increasing the thermal kinetic energy overcomes more of the confining effect of the interatomic potentials, hence decreases the magnitude of S_X .

The remaining liquid metals Cu, Ag, Au, Zn, and Tl, and the hard sphere liquid, fall into the category of $S_X = 0$ within error estimates. Only one instance of a positive S_X has been found. An accurate analysis of argon, at 85K on the liquid-vapor equilibrium curve, yielded $S_X = 0.38$.⁷ But argon at this point is a highly expanded liquid. It would therefore be of interest to measure $g^{(2)}(r)$, and calculate S_2 , for argon at a pressure of say 10 kbar, where we expect $S_X \approx 0$.

3. Application to Melting

Having an accurate theory for the entropy of a classical monatomic liquid allows us to learn much about the processes involved in the melting of elements.^{10,11} Here we present some of the interesting results of the melting analysis.

Consider the entropy of melting. $\Delta S^* = \Delta S^*(P_m, T_m)$ is measured at constant pressure and temperature, and corresponds to $S_a - S_c$ in Figure 5. The entropy change at constant volume is $\Delta S = \Delta S(V_{lm}, T_m)$, corresponding to $S_a - S_b$ in Figure 5. We have evaluated ΔS from the measured ΔS^* , by calculating the thermodynamic correction $S_b - S_c$, for all the elements for which accurate data are available.¹⁰ Note ΔS and ΔS^* are significantly different quantities, and only ΔS provides direct understanding of the melting process.

Figure 6 shows a graph of S_2 at $T \approx T_m$, as a function of ΔS . The cluster of points at the smallest ΔS represents elements which are simple metals in both crystal and liquid phases. Of the six separated points, we know that Si and Ge melt from a polar crystal to a metal liquid, Sb and Bi melt from a semimetal crystal to a metal liquid, and we assume that Sn and Ga likewise have a change in electronic structure upon melting. This leads to our most important classification of melting processes:¹⁰

(a) Normal elements have no significant change in electronic structure upon melting, and have ΔS in the narrow range 0.80 ± 0.17 .

(b) Anomalous elements have a significant change in electronic structure upon melting, and have ΔS much larger than normal. For the six anomalous elements in Figure 6, $\Delta S = 1.48 - 3.85$.

Let us consider specifically the normal elements, and use the empirical value of ΔS to construct a melting rule. The liquid entropy, denoted by a superscript l , is from (13),

$$S^l = S_1^l + S_2^l + S_X^l + S_E^l. \quad (14)$$

The crystal entropy is denoted by a superscript c , and from lattice dynamics theory at high temperatures,

$$S^c = 3 [\ln(T/\theta_0) + 1] + S_A^c + S_E^c, \quad (15)$$

where the first term is the quasi-harmonic contribution, S_A^c is the anharmonic contribution, and S_E^c is the electronic contribution. The characteristic temperature θ_0 is defined in terms of the quasi-harmonic phonon frequencies $\omega_{\mathbf{k}}$,

$$\ln(k\theta_0) = \langle \ln \hbar \omega_{\mathbf{k}} \rangle_{BZ}, \quad (16)$$

where $\langle \rangle_{BZ}$ represents a Brillouin zone average. From (14) and (15), along with (3) for S_1^l , we find for $\Delta S = S^l - S^c$,

$$\Delta S = \frac{3}{2} \ln L - \frac{3}{2} + S_2^l + S_X^l - S_A^c + S_E^l - S_E^c, \quad (17)$$

where

$$L = Mk\theta_0^2 / 2\pi\hbar^2 \rho^{2/3} T_m. \quad (18)$$

Now for normal melting, where crystal and liquid have essentially the same electronic structure, we have $S_E^l - S_E^c \approx 0$, $\Delta S \approx 0.8$, and $S_2^l \approx -2.6$ at T_m . With these results, (17) becomes the normal melting rule,

$$\frac{3}{2} \ln L = 4.9 + S_A^c - S_X^l. \quad (19)$$

For most elements we expect the further simplification $S_A^c \approx 0$, and $S_X^l \approx 0$.

In our melting study of 36 elements,¹⁰ for which sufficient data are available, all of the normal elements follow the melting rule (19). It is therefore clear that we have a quantitative understanding of the normal melting process. The constant-volume entropy difference, $\Delta S \approx 0.8$, is identified as the entropy required to dissolve the long range order of the crystal, leaving the short range order about the same in crystal and liquid.

We have also achieved a quantitative understanding of the anomalous melting process.¹⁰ In this case, ΔS contains the universal long range disordering entropy of 0.8, plus a large positive contribution corresponding to the change of electronic groundstate, at the melting temperature T_m . As an exercise, use Figure 7 to figure out why anomalous melting requires ΔS larger than normal, and $|S_2|$ smaller than normal, as observed in Figure 6.

4. Directions for Future Research

When you learn something new, questions for further investigation spring up like mushrooms. Let me mention three interesting applications of the liquid entropy theory.

(a) It would be valuable to consider molecular liquids, and extend the entropy theory to include angular correlations among molecules. Lazaridis and Paulaitis¹² have made a good beginning in this direction, studying the entropy of solution of simple molecules in water. Of course, water itself is a most interesting molecular liquid, and apparently the entropy of water is not well understood.¹³ An application of the liquid correlation expansion to water would be very revealing.

(b) When a liquid is cooled, it can sometimes pass into an amorphous state. Does the multiparticle correlation expansion remain valid for the amorphous state? This is an ideal problem to study by computer simulations, since the amorphous state is easily achieved, and the correlation functions are directly accessible. Such a study might shed light on the nature of the glass transition.

(c) As mentioned in Section 2, it would be of interest to measure the pair correlation function, and calculate S_2 , for liquid argon at a pressure of around 10 kbar. This would provide an important check on the property $S_x \approx 0$ for liquids without strong n -particle forces, for $n \geq 3$.

5. Relation Among Different Entropy Expansions

Concerning entropy expansions, the recent literature contains a number of errors, hence a clarification of the relation among different expansions is needed.

In H. S. Green's original expansion,⁵ the one-particle term is undefined,⁶ while the multiparticle terms contain the physically spurious long range correlation of the canonical ensemble. To eliminate this long range correlation, Nettleton and M. S. Green¹⁴ constructed a grand canonical expansion in powers of the density, and in the process they fixed the one-particle term at the ideal gas value S_1+1 . This expansion was also discussed by Yvon.¹⁵ An alternate derivation was given by Raveché,¹⁶ and was evaluated for liquid models by Raveché and Mountain.¹⁷ The Nettleton M. S. Green-Raveché (NGR) expansion is reducible, in the sense that S_n contains correlation of all orders $\leq n$. The NGR expansion has the correct limit in the gas regime. In the liquid regime, aside from some very small terms in α , the NGR expansion differs by the amount n^{-1} , in order n , from the liquid correlation expansion.¹ Hence while the two expansions converge to the same limit, the difference n^{-1} is crucial in any practical application; note the liquid correlation expansion in second order is often accurate to around ± 0.1 .

I. Z. Fisher¹⁸ derived an entropy expansion in which the one-particle term is S_1+1 , while the two-particle term is S_2 . Faber¹⁹

tested this expansion for Al and Hg, and concluded correctly that it is inaccurate. Baranyai and Evans^{20,21} express the opinion that the liquid correlation expansion must be wrong, because it differs term by term from the NGR expansion. Indeed, the liquid correlation expansion is correct, precisely because of this difference.

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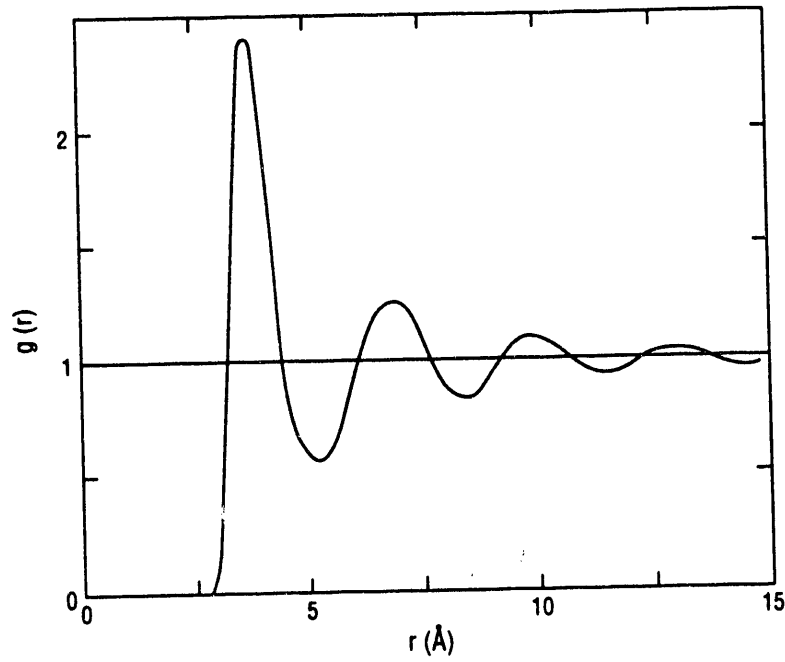


FIG. 1. The pair correlation function for liquid sodium at 378 K (T_m is 371 K).

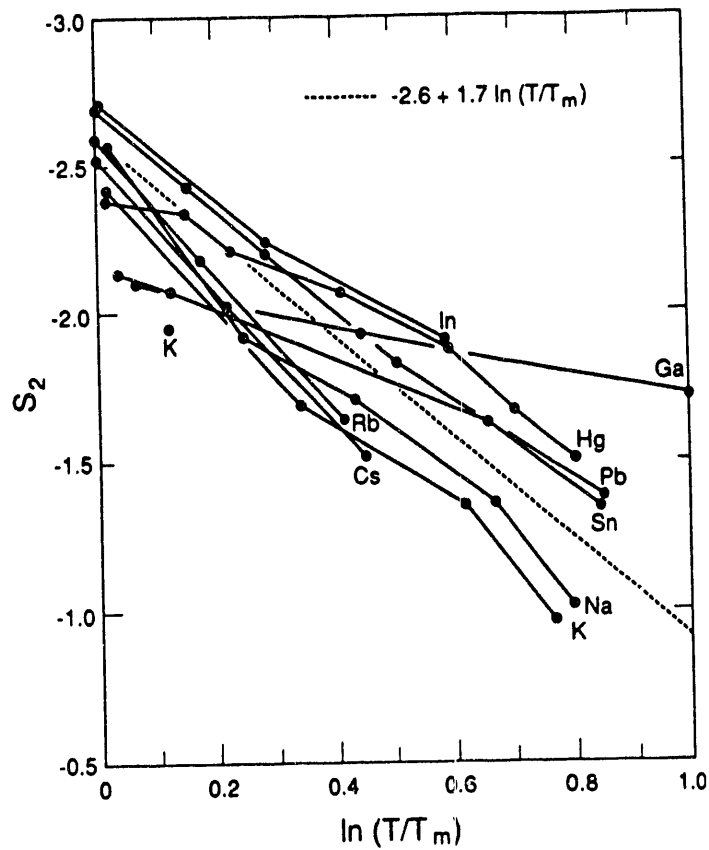


FIG. 2. Pair correlation entropy S_2 against $\ln(T/T_m)$, showing approximately universal behavior, as represented by the dotted line. Sn and Ga are anomalous. [Proc. R. Soc. Lond. **A433**, 615 (1991)].

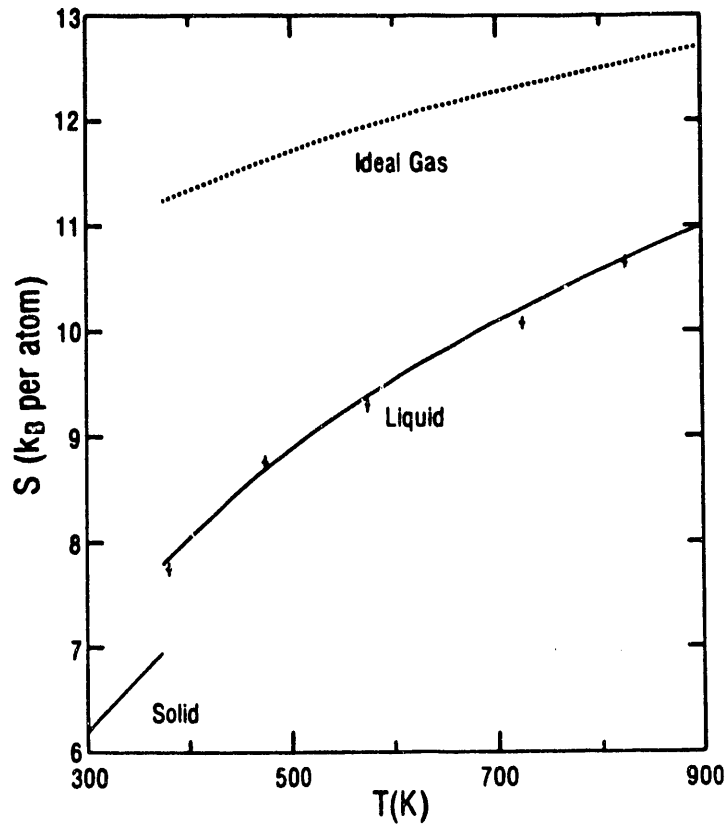


FIG. 3. Entropy of sodium. Solid line is experiment, and crosses are the theoretical expression $S_1 + S_2 + S_E$. [Phys. Lett. A122, 418 (1987)].

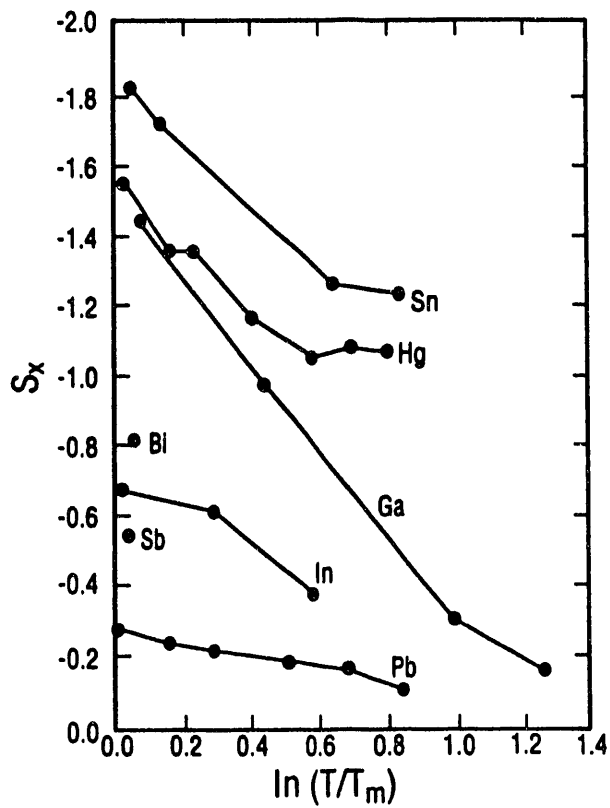


FIG. 4. Higher order correlation entropy S_x against $\ln(T/T_m)$. [Proc. R. Soc. Lond. A433, 615 (1991)].

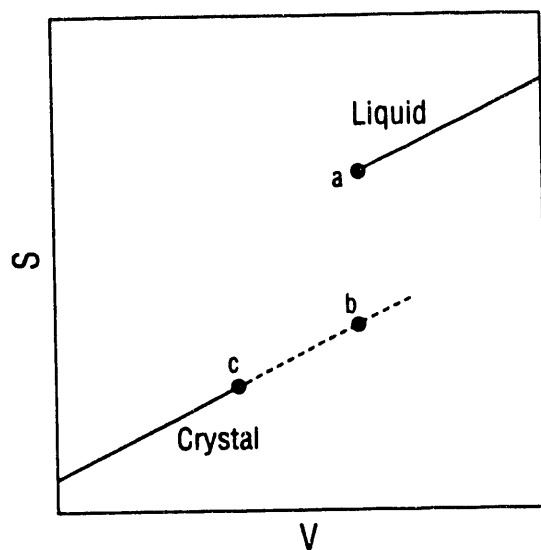


FIG. 5. $S(V)$ at the constant temperature T_m . At constant pressure, $\Delta S^* = S_a - S_c$, while at constant volume, $\Delta S = S_a - S_b$.

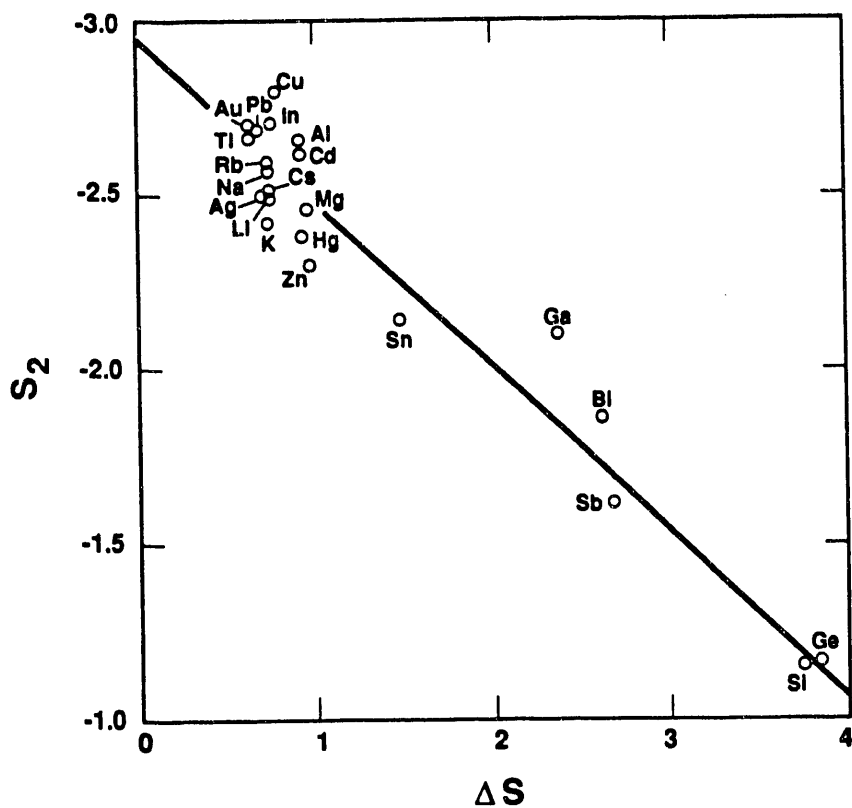


FIG. 6. The correlation between S_2 at $T \approx T_m$, and ΔS . The points in the cluster are normal elements, and the six separated points are anomalous elements. [Proc. R. Soc. Lond. A433, 631 (1991)].

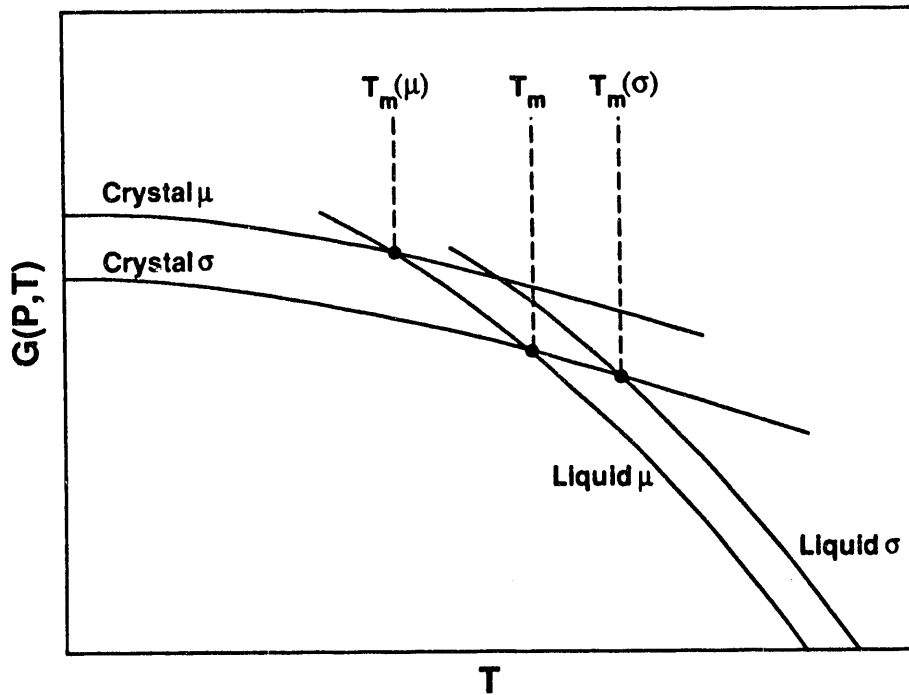


FIG. 7. The Gibbs free energy G as function of T , at a constant P . Anomalous melting occurs at T_m , from the crystal with electronic structure σ , to the liquid with electronic structure μ . [Proc. R. Soc. Lond. A433, 631 (1991)].

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