

Thermal potential, mechanical instability, and melting entropy

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The concept of the thermal potential, introduced in earlier publications in connection with calculations of elastic properties, thermal expansion, and melting temperatures, is shown to be a unifying principle connecting the thermodynamic properties of the solid and molten states. Recently discovered extrapolations connecting the thermodynamic properties of the solid and molten states are demonstrated to be governed by the characteristics of the thermal potential. A simple model of the melting entropy is presented and combined with previously derived expressions involving parameters of the thermal potential to quantitatively connect the heat of fusion with the volume change at melting. The melting entropy is calculated for a group of cubic crystals with the use of the derived expressions, and good agreement is found with observed values. A principal conclusion of this work is that the shear modulus, heat content, and volume, which are discontinuous at the melting temperature, are continuous functions of each other and related through the parameters of the thermal potential.

I. INTRODUCTION

One of the long-standing problems in physics is developing an understanding of the nature of the first-order phase transformation associated with the melting process. It has been known for a long time that there is a discontinuous change in the heat content of materials (the latent heat of fusion) at the melting temperature T_m . In recent years, more attention has been given to two other discontinuities, namely, the discontinuous changes in shear moduli and volume at the melting temperature. Discontinuities always represent a difficult problem since their existence implies that an interface exists, in this case between solid and liquid phases, which require on each side different physical and mathematical treatments which must somehow be joined at the discontinuity.

One of the early important contributions to the theoretical study of this problem was published by Born.¹ Noting that a crystal is subject to shear while a liquid is not, he proposed that a theory of melting should consist of an investigation of the stability of the lattice under shearing stress. In a cubic crystal, there are two shear moduli, C_{44} and $C' = (C_{11} - C_{12})/2$. Born's mathematical treatment was for the body-centered-cubic lattice (bcc), and he proposed that the cubic crystal would melt when the condition $C_{44} = 0$ is fulfilled. Within a few years, however, it was found that NaCl, which has the face-centered-cubic structure (fcc), behaves as an elastic solid right up to the melting point, and that C_{44} does not vanish. This finding prompted Thompson² to make a detailed theoretical study for the NaCl structure. He arrived at the important result that this

structure becomes unstable because of the condition $C' = 0$ if the lattice parameter is increased by an amount slightly greater than would be achieved by the total thermal expansion from 0 K to T_m in several alkali halide crystals. Subsequent experimental studies³ for individual alkali halide crystals, as well as solid solutions of two different crystals having both fcc and bcc structures, confirmed the results. For those crystals having the fcc structure, C' has the smaller value as the temperature increases, but it maintains a finite value at the melting point; for the crystals having the bcc structure, C_{44} maintains the lower value, but again the value is nonzero at T_m . The latter finding partially confirms Born's conjecture.

In many respects, these results are not surprising. Born, for example, noted a comment by Brillouin⁴ that a theory which considers melting as a vanishing of shearing elasticity does not lead to a latent heat, but concluded that such a theory is not in contradiction with the existence of a latent heat. However, if a shear modulus were to vanish at T_m , then at some arbitrarily small increment of temperature below T_m , the crystal would display an arbitrarily small resistance to a shearing stress. This is in contradiction to all available experimental evidence. Instead, the experimental evidence indicates an underlying connection between the discontinuities in heat content, shear modulus, and volume at T_m .

One important connection of this type was reported by May.⁵ If the shear modulus for fcc metals is plotted versus volume expansion, one finds a nearly linear relationship between the two. More important, May found that if the linear relationship is extrapolated to $C' = 0$, corresponding to the molten state, the

extrapolated value for the volume expansion associated with melting agrees well with experimental values. The importance of this result, then, is that it suggests that measured properties of the solid state (C' and volume expansion) can be used to predict a property of the molten state, namely, the volume change at melting.

This question was subsequently reexamined for the alkali halide crystals by Tallon, Robinson, and Smedley.⁶ Once again, they found that the shear moduli are continuous with respect to volume through the melting expansion, with C' falling continuously to zero for the fcc crystals, and C_{44} displaying the same behavior for the bcc crystals. Tallon⁷ later made a similar examination for a different series of materials and found similar results. This prompted the suggestion that the Born hypothesis is correct if modified to state that the appropriate shear modulus falls to zero for the melt at T_m rather than in the solid.

The problem with this suggestion is that it defeats Born's original idea of characterizing the thermodynamics of materials in terms of a microscopic lattice dynamical theory, since the relationship between the solid and molten states is left unanswered. In this work, a characterization of properties for both liquid and solid phases will be made using the model developed earlier for calculations of elastic properties, thermal expansions, and melting temperatures. In the next section, it will be demonstrated that the concept of the thermal potential, introduced as part of the model, explains the extrapolation discussed above, as well as other related ones which have not previously been presented. Next, an expression for the melting entropy will be derived from a simple model, which involves the parameters of the thermal potential. This will be used to quantitatively demonstrate the connection between the heat of fusion and the volume expansion at melting. Finally, the melting entropy will be calculated for a group of cubic crystals and found to agree favorably with observation. These results suggest that there is a simple underlying principle, the thermal potential, describing the thermodynamic properties of materials, including the melting process.

II. THERMAL POTENTIALS AND THE EXTRAPOLATION OF SOLID STATE PROPERTIES TO THE MOLTEN STATE

The extrapolation of shear moduli to the molten state discussed above implies a connection between the properties of the solid material and the changes that take place upon melting. For example, in the case of the fcc metals, the consistent ability of a linear plot of C' versus volume expansion to predict the volume expansion at melting with good accuracy

indicates that there should be a unifying principle governing these and all related material properties. An analysis of the temperature dependence of the shear moduli in the cubic metals has been made by means of the localized-continuum model.⁸ Initially, the motivation behind this model was to follow the spirit of the approach suggested by Born,¹ who described a demonstration by Debye that the thermal expansion can be viewed as the shift of the mean position due to the asymmetry of the amplitude of oscillation in an anharmonic potential. The vibration about the shifted mean position can, however, be considered harmonic. Therefore the model retains as much as possible of the usual picture of harmonic vibrations between atoms in the crystal, while at the same time introducing an anharmonic potential whose descriptive parameters characterize both thermal expansions and elastic properties. The potential was chosen to have the form of the Morse potential $V(r) = D [1 - \exp[-a(r - r_0)]]^2$ since the quantum-mechanical solutions are known. The parameters of the potential were originally determined for the cubic metals from low temperature elastic data.⁸ Subsequently, the model was applied to the calculation of thermal expansion in insulators⁹ with empirical rules set forth for the determination of the relevant potential-well parameters without experimental data.¹⁰ In contrast with the earlier works on elastic properties, these calculations identified the interatomic potential with a thermal potential maintaining the stability of the solid, with the potential depth given by $D = Q_s + Q$, where Q_s is the heat content of the solid at T_m relative to 0 K and Q is the latent heat of fusion. A check of this concept was made for the cubic metals,¹¹ and the values of D calculated from low-temperature elastic data were found to compare well, within the limitations of the calculations, with experimental values of $Q_s + Q$.

Since the analysis of the temperature dependence of the shear moduli in the cubic metals indicates that to a first approximation, there is a linear dependence of the shear moduli on the volume expansion,⁸ the linear extrapolations of May suggest that the thermal potential can describe the properties of the molten state as well as those of the solid state. In particular, if one uses the linear Eq. (16) of Ref. 8 for $C'(T)$ versus linear expansion for the fcc metals, sets $\Delta C'(T) = C'(0)$, since the total change in C' from 0 K to the melt at T_m is just $C'(0)$, and uses the calculated values of the Morse potential parameters, one obtains a value for the total linear expansion going from the solid at 0 k to the melt at T_m . The values so obtained agree fairly well with observation for aluminum but the agreement is rather poor for the other fcc metals. The reason for this is that this equation and the others derived in Ref. 8 are approximate, since they include only nearest-neighbor interactions, and the Morse potential is not an exact fit

to the real interatomic potential. Consequently, the calculated Morse potential parameters are a compromise fit to the low-temperature thermal data, and give $C'(T)$ curves that differ from the experimental curves. However, somewhat different values of the Morse potential parameters can be chosen which give an accurate fit to the $C'(T)$ curves, thus giving semiquantitative agreement with May's extrapolations.

If this analysis is correct, then different but related extrapolations should be possible. For example, as discussed in earlier papers, there is generally an intimate connection between heat content and thermal expansion, so that a plot of heat content versus $C'(T)$ for the fcc metals should also be approximately linear. Moreover, the extrapolation to the molten state should this time predict the heat of fusion. This turns out to be true for the fcc metals as is illustrated in Fig. 1 for the case of lead. The $C'(T)$ data used in Fig. 1 was published by Vold *et al.*,¹² while the heat content data was taken from the Bureau of Mines tables.¹³ We note here that the linear extrapolation to the molten state ($C' = 0$) gives a heat content H_1 such that $H_1 - H_m \approx 2Q$, where H_m is the value for the solid at T_m . This same result is obtained with fairly good accuracy in all of the fcc metals.

The explanation of this somewhat surprising result is fairly straightforward. In the fcc metals, $C'(T)$ diminishes somewhat more than 50% in value from 0 K to T_m , while the total volume expansion of the solid from 0 K to T_m is somewhat greater than the volume expansion on melting. In contrast, as discussed earlier,^{9,11} the heat content of the solid at T_m relative to that at 0 K is about 70% of $D = Q_s + Q$,

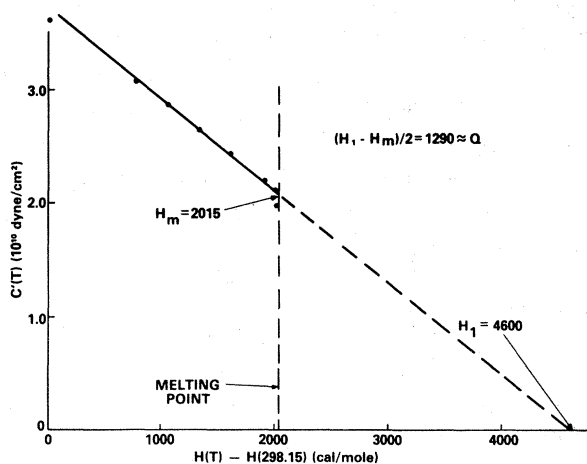


FIG. 1. Elastic shear modulus $C'(T)$ vs heat content for lead. Linear extrapolation beyond the melting point gives a value H_1 corresponding to $C' = 0$ (the molten state). The difference between H_1 and the heat content at the melting point H_m is approximately twice the latent heat of fusion.

while Q is about 30% of the total. This means that in the plot of $H(T)$ vs $C'(T)$, $(H_1 - H_m)$ is slightly less than $[H_m - H(0)]$ so that $H_1 - H_m \approx 2Q$. In Ref. 11, the condition for melting was derived in cubic crystals from the condition $Q_s = 0.7D$, which is based on empirical observation. We can see that this condition is consistent with the analysis here. However, while this has resulted in a semiquantitative explanation of the related linear extrapolations and the role of the thermal potential in the melting process, a quantitative description requires a specific model for the entropy of fusion.

III. MELTING ENTROPY AND THE THERMAL POTENTIAL

It is evident that a theoretical confirmation of the analysis of Sec. II as well as the previously determined condition for melting in cubic crystals, requires an explanation of the conditions $Q_s \approx 0.7D$ and $Q \approx 0.3D$ on other than empirical grounds. This in turn requires a quantitative description of the melting entropy. One of the early suggestions concerning the entropy of fusion was made by Hirschfelder, Stevenson, and Eyring.¹⁴ Their model, which has since become known as the so-called communal entropy, results from the idea that in a solid, the N atoms are confined to small compartments, equal in volume. The liquid with the same volume corresponds to the situation where the compartments no longer exist, and each atom is free to move to any part of the total volume. If one further assumes that the atoms in the liquid behave as a perfect gas, then one can use the partition function for a perfect gas to calculate the entropy of the liquid. The partition function for the solid differs because there are $N!$ ways that the N atoms can be permuted among the N compartments. It is an easy matter to show from these simple arguments that the entropy difference is $\Delta S_f = Nk = R$ for a mole of a monatomic material, or more generally nR if there are nN atoms per mole.

For some time, there was doubt that the communal entropy accurately represents the melting process. First, even though the communal entropy can be shown to arise when using a partition function for the liquid different from that for a perfect gas, there was uncertainty as to whether every part of the total volume is equally accessible to each atom of the liquid at T_m . Second, hard-sphere calculations had not yielded such a result. However, recent Monte Carlo calculations for liquid KCl by Woodcock and Singer,¹⁵ using a realistic interatomic potential, indicate that in contrast with hard-sphere liquids, the entire communal entropy appears at fusion. In addition, there is a well-known empirical rule known as Richard's rule¹⁶ which states that the entropy of fusion is given by $\Delta S_f \approx 2$ cal/g-at. K. This value is,

of course, just the communal entropy.

A closer examination of heat content data reveals, however, that Richard's rule is generally a lower bound to the melting entropy rather than an accurate value. The reason for this is rather obvious. The communal entropy does not allow for any volume expansion at melting. Such expansion, of course, increases the entropy. This contribution can be accounted for quantitatively by a simple extension of the argument discussed above. If the volume of the solid is Nv where v is the cell or compartment volume, then the increase in volume can be interpreted as an increase in the number of compartments each of which maintains the volume v . If the fractional increase in volume is β , then the total increased volume is $Nv(1+\beta)$, and the number of compartments in the larger volume increases by a factor $(1+\beta)$.

According to our previous discussion, the N compartments associated with the volume of the cell at T_m are filled, each with one atom. After melting, the volume expansion produces additional $N\beta$ compartments, according to this model, which are not filled. For each arrangement of these $N\beta$ holes, there are $N!$ ways of permuting the atoms among the remaining compartments. There is an additional factor of W arrangements for the holes associated with the number of ways of arranging N objects of one type, $N\beta$ of another in $N(1+\beta)$ compartments, one to a compartment, where

$$W = \frac{[N(1+\beta)]!}{N!(N\beta)!}$$

Using Stirling's formula $N! \approx (N/e)^N$, one gets

$$W = \left(\frac{(1+\beta)^{1+\beta}}{\beta^\beta} \right)^N$$

The entropy difference between the liquid having the volume Nv and that having the volume $Nv(1+\beta)$ is then given by $S_v = k \ln W$ or

$$S_v = Nk [(1+\beta) \ln(1+\beta) - \beta \ln \beta] \quad (1)$$

For fractional volume changes $\ln(1+\beta) \approx \beta$, so that

$$S_v \approx Nk \beta (1+\beta - \ln \beta) \quad (2)$$

Therefore, according to this model, the melting entropy per mole for a material having nN atoms per mole is

$$\Delta S_f = nR [1 + \beta(1 + \beta - \ln \beta)] \quad (3)$$

In an earlier publication,¹¹ the heat content of the solid at T_m relative to 0 K was set equal to a fixed fraction K of the depth of the thermal potential. In particular, the universal constant $K = 0.7$ was used to calculate the melting temperatures of a wide range of cubic monatomic and binary crystals. Recalling the relation $D = Q_s + Q$, this implies that the heat of fusion is given by $Q = (1-K)D$. If the earlier analysis is correct, then Q should be approximately $0.3D$ at least for many cubic crystals. Equation (3) can be used to check this conclusion. Expressing the quantities in units of energy per atom, then

$$Q = T_m \Delta S_f = (1-K)D = kT_m [1 + \beta - \ln \beta] \quad (4)$$

Equation (4) can be used to calculate $(1-K)$ from experimental values of β and the previously determined values⁸⁻¹¹ of D . These are compared in Table I with values determined from experiment.¹³ The experimental values of β used are those reported by Schinke and Sauerwald¹⁷ for binary cubic crystals, and deduced from the volume data of Borelius¹⁸ for the cubic metals. Both calculated and observed values of $(1-K)$ are generally quite close to the value 0.3. Moreover, the average of both sets of

TABLE I. Calculated versus observed values of $(1-K)$ for various cubic crystals.

	kT_m (eV)	D (eV per ion)	β (%)	$(1-K)$ (calc)	$(1-K)$ (obs)
Cu	0.117	0.55	5.7	0.26	0.28
Al	0.080	0.19	6.4	0.52	0.33
Au	0.115	0.71	6.2	0.20	0.27
Pb	0.052	0.35	3.0	0.17	0.27
Ag	0.106	0.49	5.8	0.27	0.28
LiF	0.096	0.52	29.4	0.32	0.35
NaF	0.109	0.47	27.4	0.38	0.35
NaCl	0.093	0.39	25.0	0.39	0.35
KF	0.088	0.41	17.2	0.32	0.35
KCL	0.090	0.36	17.3	0.38	0.34
AgCl	0.063	0.40	8.9	0.21	0.28
AgBr	0.061	0.38	8.2	0.21	0.21
Average				0.30	0.30

TABLE II. Calculated vs observed melting entropy for various cubic crystals. The values are expressed in calories per degree mole.

	β (%)	$\frac{0.3D}{T_m}$	$\Delta S_f(\text{calc})$	$\Delta S_f(\text{obs})$
Cu	5.7	2.80	2.43	2.30
Al	6.4	1.41	2.47	2.76
Au	6.2	3.67	2.46	2.21
Pb	3.0	4.03	2.26	1.90
Ag	5.8	2.74	2.44	2.31
LiF	29.4	6.44	6.92	5.77
NaF	27.4	5.15	6.77	6.25
NaCl	25.0	5.02	6.59	6.38
KF	17.2	5.56	5.98	5.97
KCl	17.3	4.75	5.99	5.85
AgCl	8.9	7.60	5.21	4.23
AgBr	8.2	7.43	5.14	3.12

values is 0.30. These results confirm the earlier conclusions and the role of the thermal potential in connecting the heat of fusion and the volume change at melting as indicated by the extrapolations discussed in Sec. II.

Equation (3) can also be used to calculate the melting entropy. Comparison of these calculated values versus the observed values¹³ is presented in Table II, and the agreement is generally quite good. In addition, values of the quantity $0.3D/T_m$ are included. This should approximate the melting entropy based on a universal constant $(1 - K) = 0.3$ if the ideas presented here are correct. As can be seen from the table, these values do not agree as well with observation as those calculated from Eq. (3) because of uncertainties in the values of D and fluctuations in the values of K about the mean value. However, the agreement is good enough to confirm the ideas presented here on the role of the thermal potential in the melting process.

IV. CONCLUSIONS

The primary conclusion reached in this paper is that a single unifying principle, the thermal potential, governs the thermodynamic properties of the solid and molten states. In a previous paper,¹¹ the maximum thermal expansions and melting temperatures of a wide range of monatomic and binary cubic crystals were calculated in terms of a model involving the thermal potential. However, the use of the universal constant $K = 0.7$ remained empirically based and somewhat mysterious.

In this work, the picture is now completed. Melt-

ing occurs when the sum of the harmonic and elastic energies and the heat of fusion equal the depth of the thermal potential D . The heat of fusion arises from the contribution of the communal entropy and the volume expansion at melting, which in turn is determined by the value of $(1 - K)D$, while the solid-state heat content at T_m is DK . Empirical observation, as well as the calculations presented above, indicate that for at least a wide range of cubic monatomic and binary crystals, $K \approx 0.7$. Further, we can now see how the underlying action of the thermal potential explains the extrapolations of the solid to the molten state from which properties of the solid state can predict parameters associated with the change of state at melting.

One of the advantages of a unifying principle is the degree of simplicity that it introduces. By means of the thermal potential, a wide range of thermodynamic properties of materials can be explained quantitatively, and in a simple and straightforward manner. The only remaining question is whether or not the thermal potential is in fact "real." This concept is a surprising one, and differs considerably from the interatomic pair potential. The melting transition is generally explained in terms of the action of the free energy, which in turn is determined by the values of the entropy and the internal energy. However, this paper and the previous publications strongly suggest that the aggregate of atoms in the condensed phases behave as if subject to a thermal potential which governs the elastic, expansion, and melting properties. Demonstrating the existence of this potential from first principles may prove to be quite difficult, but the evidence accumulated so far strongly suggests that it is real.

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