Evaluation of thermodynamic functions of elemental crystals and liquids

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Techniques are summarized for evaluating thermodynamic functions for pure elements in crystal and liquid phases. An accurate evaluation of the ion-motional free energy is given by quasiharmonic lattice dynamics at quantum temperatures, and computer simulations (e.g., molecular dynamics) at classical temperatures for both crystal and liquid. The computer simulations require knowledge of the effective ion-ion potentials, and since these are not generally available, two approximations for proceeding without them are discussed. First, neglecting anharmonicity in crystals leaves only the quasiharmonic ion-motional free energy, depending almost entirely on the characteristic temperature θ_0, which is the logarithmic moment of the quasiharmonic phonon frequencies. Second, identifying in the constant-density entropy of melting a universal disordering contribution $\Delta \simeq 0.80 Nk$ provides approximate evaluation of the thermodynamic properties of liquids at melt. The errors of these approximations are assessed. [S1063-651X(97)12008-6]

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I. INTRODUCTION

For many practical applications, one needs accurate values of thermodynamic properties of solids and liquids, as functions of temperature and pressure. One such application is the hydrodynamic calculation of high speed deformation processes, such as those calculations done at Los Alamos. This application demands the highest accuracy available for the equilibrium properties of materials, both at modest pressures where experimental data are available, and at high pressures where such data are not available. The purpose of this paper is to describe the procedures we have developed to solve this problem, and to summarize the information both old and new that justifies these procedures. Our discussion is limited to pure elements, where the greatest progress has been made.

The theoretical description of a condensed matter system is based on the physical Hamiltonian and exact statistical mechanics [1,2]. It starts with the adiabatic potential, which is the energy of the system when the ions are fixed at arbitrary positions and the electrons are in their ground state. The motion of ions in this potential is resolved into quasiharmonic phonons and anharmonicity, then the excitation of electrons from their ground state is described by independent electron statistics, and finally, electron-phonon interactions are included. This last step accounts for failure of the adiabatic approximation, and is important for metals. The free energy derived from this theoretical description is written and discussed in the following section.

By now we have developed reliable and accurate techniques to evaluate the various contributions to the total free energy of crystals, with certain exceptions, and these techniques are described in Sec. II. We have long known that anharmonicity is generally a small effect [3-7], and we can now provide a quantitative measure of anharmonicity in crystals, again with specific exceptions, as described in Sec. III. Two recent findings have allowed significant progress in understanding the fusion process [7,8]: (a) Melting of elements is classified into two categories, normal melting in which there is no significant change in the electronic structure (as metal crystal to metal liquid), and anomalous melting in which there *is* a significant change in electronic structure (as polar crystal to metal liquid). (b) The entropy of melting at constant *density*, and not at constant *pressure*, provides information on the disordering entropy in going from crystal to liquid.

The information gained from the fusion process is presented in Sec. IV. The whole of this analysis provides us with a simple representation of the thermodynamic properties of liquids at melt. Our conclusions are summarized in Sec. V.

II. EVALUATION OF THE CRYSTAL FREE ENERGY

Ordinarily, a single element presents us with a number of different crystal phases as temperature and pressure are varied, where each phase has its characteristic crystal structure and bonding type, for example, metallic or covalent. In spite of this diversity, the theoretical description of the partition function and free energy of elemental crystals is universal in form, with only a set of parameters specific to each separate element and phase. We will outline this universal free energy form, and its parameter set, for crystals.

For a system of N-like ions plus their associated electrons, distributed more or less uniformly over a volume V, the Helmholtz free energy F is

$$F = \Phi_0 + F_I + F_E, \tag{1}$$

where $\Phi_0(V)$ is the static lattice potential, i.e., it is the energy of the crystal with ions located at the lattice sites and electrons in their ground state, $F_I(V,T)$ is the ion-vibrational free energy, and $F_E(V,T)$ is the contribution due to thermal excitation of the electrons from their ground state. The ion-vibrational term is based on a set of harmonic normal modes, the phonons, which contribute the quasiharmonic free energy F_H, while the phonon-phonon interactions give rise to the anharmonic free energy F_A, so

$$F_I = F_H + F_A, \tag{2}$$

where qualitatively F_A is small compared to F_H. The electronic free energy is separated into a conduction electron part F_{cond}, and a magnetic part F_{mag},

$$F_E = F_{\text{cond}} + F_{\text{mag}}. \tag{3}$$

At low temperatures the thermal free energy for a metal is dominated by F_E, while otherwise F_E is small compared to F_H. Electron-phonon interactions are supposed to be included in F_E.

Generally, then, F_H dominates the temperature dependence of the crystal free energy. The behavior of F_H is conveniently expressed in terms of a few phonon characteristic temperatures θ_n, defined by

$$\ln(k\theta_0) = \langle \ln(\hbar\omega) \rangle_{\text{BZ}}, \tag{4}$$

$$k\theta_1 = \tfrac{4}{3}\langle \hbar\omega \rangle_{\text{BZ}}, \tag{5}$$

$$k\theta_2 = [\tfrac{5}{3}\langle (\hbar\omega)^2 \rangle_{\text{BZ}}]^{1/2}, \tag{6}$$

where $\langle \cdots \rangle_{\text{BZ}}$ indicates a Brillouin zone average of a function of the phonon frequencies ω. At $T=0$, F_H reduces to the phonon zero-point energy F_{HO},

$$F_{\text{HO}} = \tfrac{1}{2}\sum \hbar\omega = \tfrac{9}{8}Nk\theta_1. \tag{7}$$

The leading low-temperature dependence of F_H is T^4/θ_D^3, where θ_D is the Debye temperature, which depends on the acoustic phonon velocities. The high-temperature expansion of F_H is

$$F_H = -3NkT[\ln(T/\theta_0) - \tfrac{1}{40}(\theta_2/T)^2 + \cdots], \tag{8}$$

where $+\cdots$ represents terms in T^{-4}, T^{-6}, and so on. The expansion (8) is extremely useful, since only the two terms shown leave an error $\lesssim 1\%$ for $T \gtrsim \theta_2$, and θ_2 is usually much less than the melting temperature T_m.

Currently, one can obtain highly accurate values of the most important free energy contributions, Φ_0 and F_H. Diamond-cell measurements give the pressure $P(V)$ on the room-temperature isotherm, to pressures in the Mbar range. The function $\Phi_0(V)$ can be obtained from this $P(V)$ curve, self-consistently with the complete free energy, through the relation $P = -(\partial F/\partial V)_T$. Also, electronic band structure calculations give $\Phi_0(V)$ directly, at any desired density, and these calculations steadily become more accurate [9,10]. Phonon frequencies are measured by inelastic neutron scattering, and extensive tables of moments of the frequency distribution have been compiled [11]. The corresponding characteristic temperatures θ_n, which are accurate to around 1%, and the density ρ_N at which the neutron scattering measurements were made, are listed in Table I for 25 elements. When neutron scattering measurements are not available, as is the case for compressed crystals, band structure calculations of frozen phonons can be used to construct the phonon spectrum, and hence the phonon characteristic temperatures. As examples of the procedures just mentioned, $\Phi_0(V)$ was obtained from the room temperature isotherm for Fe [12], and frozen-phonon calculations were used in an *ab initio* calculation for Al [13].

TABLE I. Phonon characteristic temperatures at density ρ_N, and Grüneisen parameters γ, for 25 elements. A more extensive table, and the data sources, are given in Refs. [5] and [7].

Element	ρ_N(g/cm^3)	θ_0 (K)	θ_1 (K)	θ_2 (K)	γ
Li	0.546	265.5	388	400	0.88
Na	1.005	113.3	163	166	1.24
K	0.904	68.9	99.4	102.1	1.24
Rb	1.616	42.2	61.9	63.9	1.26
V	6.1	250			1.5
Nb	8.57	198			1.6
Ta	16.75	162			1.6
Cr	7.19	338			(1.5)
Mo	10.24	273			1.6
W	19.3	225			1.6
Al	2.731	283.5	399	404	2.25
Pb	11.55	64.1	91.3	93.4	2.65
Cu	9.018	225.3	315	317	2.02
Ag	10.49	150.1	211	213	2.42
Au	19.27	124.5	179.3	184	2.95
Ni	8.90	275			1.9
Pd	12.05	200			2.3
Pt	21.56	163.5			2.6
Mg	1.74	229.4	319	320	1.5
Zn	7.270	161	235	242	2.2
In	7.43	85.3	128	(138)	2.4
β-Sn	7.30	103.4	154	172	2.2
Hg	14.46	64.7	106	(124)	2.5
Si	2.34	421	645	685	(0.5)
Ge	5.32	245	373	396	0.8

The quasiharmonic phonon frequencies depend on density, but not on temperature [2]. To evaluate the corresponding density dependence of θ_n, we introduce the thermodynamic Grüneisen parameter $\gamma = V\beta B_S/C_P$, where β is the thermal expansion coefficient, B_S is the adiabatic bulk modulus, and C_P is the constant-pressure specific heat. At temperatures $T \gtrsim \theta_2$, γ is (to a very good approximation [2,6])

$$\gamma \approx d \ln \theta_0/d \ln \rho. \tag{9}$$

High-temperature values of γ are also listed in Table I. An approximate relation among the characteristic temperatures, suitable for estimates, is

$$\theta_2 \approx \theta_1 \approx e^{1/3}\theta_0. \tag{10}$$

This implies the useful approximation $d \ln\theta_n/d \ln \rho \approx \gamma$ for $n=1$ and 2 also. Note the Debye temperature θ_D is quite different in value from θ_n for $n=0,1,2$, and F_H cannot be expressed in terms of θ_D at $T=0$, or at high temperatures.

The electronic free energy F_E includes a number of complications. First note $F_E = 0$ at $T=0$. For the nearly-free-electron elements, one has $kT/\epsilon_F \ll 1$ for temperatures to melting, where ϵ_F is the Fermi energy, so the bare conduction electron free energy is $-\tfrac{1}{6}\pi^2 N(kT)^2 n(\epsilon_F)$, where $n(\epsilon)$ is the electron density of states per atom. This low-temperature expansion is not accurate for the transition metals, so for them one has to calculate the electron density of

states via band structure theory, then do the appropriate integral of independent electron statistics over the density of states [6]. In either case, the bare conduction electron free energy is renormalized at low temperatures by electron-phonon interactions. This renormalization can in principle be calculated theoretically [2,14], or extracted from experimental data [15], and the effect presumably disappears for $T \gtrsim \theta_2$. At the present time, no accurate theory exists for the magnetic free energy; nevertheless, we were able to use an empirical representation of this term for ferromagnetic iron [12].

We consider finally the anharmonic free energy F_A. This is most important at high temperatures, say $T \gtrsim \theta_2$, and here the ion motion is classical, so F_A can be evaluated from molecular dynamics calculations, if one knows the ion-ion interaction potentials. These potentials are well described for simple metals by pseudopotential perturbation theory, and on this basis we were able to calculate accurate thermodynamic properties of metallic sodium [16–18], and theoretically extract the anharmonic contributions for $\theta_2 \lesssim T \lesssim T_m$ [3,4]. At quantum temperatures, say $T \lesssim \frac{1}{2}\theta_2$, F_A is extremely difficult to evaluate, but here it is negligible for most elements. Hence the most accurate yet practical treatment of anharmonicity is to neglect it in the quantum regime, and evaluate it via computer simulation in the classical regime.

III. ON NEGLECTING THE ANHARMONICITY

We now ask to what level of accuracy one can neglect entirely the anharmonic contributions to thermodynamic functions of elemental crystals. For the classical temperature range $T \gtrsim \theta_2$, and for the principal thermodynamic functions, entropy S, and internal energy U, it is possible at last to give a definite answer to this question. We do this by extracting the anharmonic contributions directly from experimental data for S and U, at temperatures $T \gtrsim \theta_2$.

The general theoretical expressions for S and U, from the free energy, are

$$S = S_H + S_A + S_E , \qquad (11)$$

$$U = \Phi_0 + U_H + U_A + U_E . \qquad (12)$$

At $T = 0$ the energy is U_0,

$$U_0 = \Phi_0 + \tfrac{9}{8}Nk\theta_1 + U_{A0} , \qquad (13)$$

where the term in θ_1 is $U_H(T=0)$, and U_{A0} is $U_A(T=0)$. The high-temperature expansions of the harmonic contributions are

$$S_H = 3Nk[\ln(T/\theta_0) + 1 + \tfrac{1}{40}(\theta_2/T)^2 + \cdots], \qquad (14)$$

$$U_H = 3NkT[1 + \tfrac{1}{20}(\theta_2/T)^2 + \cdots]. \qquad (15)$$

To evaluate θ_n at densities ρ not far from the measurement density ρ_N (see Table I), we use

$$\theta_n(\rho) \approx \theta_n(\rho_N)(\rho/\rho_N)^\gamma . \qquad (16)$$

From Eq. (11), S_A can be obtained by subtracting accurate theoretical harmonic and electronic contributions from the experimental entropy. The same can be done for the energy,

TABLE II. Anharmonic contributions to entropy and energy of crystals at melt. The first column is nearly-free-electron elements; the second column is transition metals.

Element	S_A^*	$U_A^* - U_{A0}^*$	Element	S_A^*	$U_A^* - U_{A0}^*$
Li	0.03	0.08	V	(0.16)	(0.22)
Na	0.09	0.07	Nb	−0.10	0.04
K	0.15	0.09	Ta	−0.09	−0.01
Rb	0.08	0.09	Cr	0.8[a,b]	
Al	0.04	−0.02	Mo	0.6[a]	
Pb	−0.04	−0.07	W	0.5[a]	
Cu	0.00	−0.03	Ni	0.27[a,b]	
Ag	−0.07	−0.11	Pd	−0.04	−0.05
Au	−0.07	−0.12	Pt	−0.17	−0.09
Mg	0.13	0.06			
Zn	−0.05	−0.06			
In	0.00	−0.02			
β-Sn	0.02	0.10			
Hg	0.08	0.08			
Si	0.23	0.17			
Ge	0.20	0.13			

[a]To avoid uncertainties in the density correction of θ_0, Cr, Mo, W, and Ni are analyzed at $\rho = \rho_N$.
[b]Tabulated values for Cr and Ni include magnetic contributions.

from Eq. (12), with the aid of Eq. (13) to eliminate Φ_0. In solving Eq. (12) for U_A at say $P = 1$ bar, the density becomes a variable because of thermal expansion, and the corresponding density dependence of U_0 is accounted for in straightforward ways [7]. Also note that U_{A0} cannot be eliminated, so Eqs. (12) and (13) can only be solved for the quantity $U_A - U_{A0}$.

Let us define reduced entropy S^*, and reduced energy U^*, by

$$S^* = S/Nk, \qquad (17)$$

$$U^* = U/NkT. \qquad (18)$$

The magnitudes of harmonic and electronic contributions to these reduced quantities, for $T \gtrsim \theta_2$, are

$$S_H^* \approx 4-10, U_H^* \approx 3,$$

$$S_E^* \approx 2U_E^* \lesssim \begin{cases} 0.1 & \text{for nearly-free-electron elements} \\ 0.5-1.0 & \text{for transition metals} \end{cases}$$

$$(19)$$

The relative importance of anharmonic contributions for $T \gtrsim \theta_2$ is revealed in the magnitudes of S_A^* and $U_A^* - U_{A0}^*$ at the melting temperature, and these quantities are listed in Table II for all the elements for which accurate values can be obtained at present. The first column lists 16 nearly-free-electron elements [19], for which the electronic contributions are very small, and are evaluated from band structure densities of states, or from free electron theory. Errors of ±0.05 are expected in the anharmonic quantities for the nearly-free-electron elements; the means and variances for the 16 elements are given by [19]

$$S_A^* = 0.05 \pm 0.09, \qquad (20)$$

$$U_A^* - U_{A0}^* = 0.03 \pm 0.09.$$

Comparing Eq. (20) with Eq. (19) tells us that anharmonicity in the entropy and energy at classical temperatures is very small for the 16 nearly-free-electron elements.

We have recently carried out band structure calculations of the electron density of states, and of the corresponding conduction electron entropy, in order to determine the anharmonic entropy for 11 transition metals [6]. This analysis turns out to be quite informative, especially when combined with our analysis of nearly-free-electron elements. Anharmonic quantities for the crystal at melt are listed in the second column of Table II for nine of these transition metals (Ti and Zr will be discussed shortly). The data for V are uncertain because of a large discrepancy among primary sources of experimental entropy [20]. For the magnetic metals we are not able to separate S_A and S_{mag}, so only their sum is listed in Table II. The reduced entropy of 0.27 for Ni is consistent with a small anharmonic contribution; if we estimate $S_{mag}^* = 0.33$, then $S_A^* = -0.06$ for Ni at melt [6]. The three metals Cr, Mo, and W are clearly exceptional, in that their anharmonic entropies are *much* larger than any other element listed in Table II. Again reduced entropy for Cr includes the magnetic contribution, and Grimvall *et al.* [21] have estimated that S_{mag} from spin fluctuations is significant in Cr. The qualitative conclusion for V, Nb, Ta, Ni, Pd, and Pt is that anharmonicity is about the same magnitude as it is for the nearly-free-electron elements, while for Cr, Mo, and W it is much larger.

The transition metals Ti and Zr each undergo a phase transition, from hcp to bcc, at around $0.6T_m$. The phonons, as observed by inelastic neutron scattering at high temperatures, show considerable softening as the transition is approached, both from below and from above [22,23]. This means the anharmonicity is significant, and is strongly temperature dependent. But the phonon frequencies measured at high temperatures are renormalized, i.e., they include anharmonicity, hence they provide renormalized characteristic temperatures $\hat{\theta}_n$, which are explicitly temperature dependent. To leading order perturbation, the renormalized harmonic entropy $\hat{S}_H = S_H(\hat{\theta}_n)$ includes anharmonicity correctly, that is [2,24],

$$\hat{S}_H = S_H + S_A. \qquad (21)$$

It was pleasing to see that the experimental entropy agrees with $\hat{S}_H + S_E$ to high accuracy for both phases of Ti and Zr, from room temperature to the melting point [6].

IV. INFORMATION FROM THE FUSION PROCESS

Melting is commonly observed at a fixed value T_m of the temperature, and a fixed value P_m of the pressure, where the crystal and liquid have densities ρ_{cm} and ρ_{lm}, respectively. The entropy of melting $\Delta S(P_m, T_m)$ is the difference between the liquid entropy $S^l(\rho_{lm}, T_m)$ and the crystal entropy $S^c(\rho_{cm}, T_m)$, so this experimental melting entropy contains two contributions, one due to the change in density on melting, the other due to disordering from crystal to liquid. We

TABLE III. Entropy of melting at constant density for 34 elements. Melting is normal in the first two columns, anomalous in the third.

Element	ΔS^*	Element	ΔS^*	Element	ΔS^*
Li	0.75	V	0.90	Sn	1.48
Na	0.73	Nb	0.97	Ga	2.37
K	0.73	Ta	1.1	Sb	2.68
Rb	0.73	Cr	(0.9)	Bi	2.62
Cs	0.73	Mo	(1.2)	Si	3.77
Ba	0.90	W	(1.1)	Ge	3.85
Fe	0.68	Pd	0.74		
Al	0.88	Pt	0.79		
Pb	0.68	Ti	0.70		
Cu	0.86	Zr	0.93		
Ag	0.73				
Au	0.64				
Ni	0.88				
Mg	0.96				
Zn	0.97				
Cd	0.93				
In	0.76				
Hg	0.90				

wish to separate out the disordering contribution, i.e., the difference between liquid and crystal entropies at the same density, for example, at density ρ_{lm}. We first extrapolate the crystal entropy from ρ_{cm} to ρ_{lm}, via the Taylor expansion at constant temperature,

$$S^c(\rho_{lm}) = S^c(\rho_{cm}) + \eta \gamma C_V(\rho_{cm}) + \cdots, \qquad (22)$$

where C_V is the constant-volume specific heat, and

$$\eta = \frac{\rho_{cm}}{\rho_{lm}} - 1, \qquad (23)$$

and where $+\cdots$ represents terms of order η^2 and higher. Hence

$$\Delta S(\rho_{lm}, T_m) \equiv S^l(\rho_{lm}, T_m) - S^c(\rho_{lm}, T_m) = \Delta S(P_m, T_m)$$
$$- \eta \gamma C_V(\rho_{cm}, T_m) + \cdots. \qquad (24)$$

We define the reduced entropy of melting at constant density as ΔS^*,

$$\Delta S^* = \frac{\Delta S(\rho_{lm}, T_m)}{Nk}. \qquad (25)$$

For all the elements for which we are currently able to make a reliable estimate of ΔS^*, the result is listed in Table III.

A. Normal melting

Normal melting is defined qualitatively as melting without significant change in the electronic structure. It turns out ΔS^* provides a quantitative identification of melting as normal or anomalous. The first column in Table III lists 18 normal melting elements [25], with errors in ΔS^* expected to be around ± 0.05. For these 18 elements, ΔS^* has little

variation: the values range from 0.64 to 0.97, and the distribution has mean and variance given by $\Delta S^* = 0.80 \pm 0.10$. Further, the compression dependence of melting shows that ΔS^* remains essentially constant for normal melting at any density [8]. This apparent universality of ΔS^* can be explained by the two-part hypothesis: (a) Since the electronic structure changes little on normal melting, the electronic entropies of liquid and crystal are the same, within the experimental scatter of ΔS^*. (b) Since the crystal has long range order, and the liquid does not, there exists a universal disordering entropy Δ of the liquid, not present in the crystal, and of approximate value

$$\Delta/Nk \equiv \Delta^* \approx 0.80. \tag{26}$$

We will continue our analysis in the light of this hypothesis.

The first column of Table III includes two transition metals, Fe and Ni. From continued data analysis, we can add 10 more transition metals, listed in the second column of Table III. Here the errors in ΔS^* are expected to be larger, say around ± 0.1, and the experimental values of $\Delta S(P=1 \text{ bar})$ are uncertain for Mo and W, while the density correction in Eq. (24) is uncertain for Cr. Hence within expected errors, ΔS^* for these transition metals lies in the distribution of the first column elements. This confirms the universality of ΔS^* for normal melting, and supports our hypothesis.

B. Anomalous melting

In anomalous melting, there is a significant change in the electronic structure, from crystal to liquid. This change is quite apparent for the two most anomalous elements, Si and Ge, which melt from polar crystal to metallic liquid. It is also obvious in Sb and Bi, which melt from semimetal to metal, but the nature of the electronic structure change is not so obvious in the two least anomalous elements, Sn and Ga. Nevertheless, for all six elements, which comprise all the anomalous-melting elements we have been able to analyze, ΔS^* is very large, far removed from the normal-melting distribution established above. The anomalous ΔS^* are listed in the third column of Table III [7] and are in the range 1.48–3.85.

To gain insight into anomalous melting, let us consider a material with the phase diagram in Fig. 1, and generalize an argument that Jayaraman *et al.* [26] applied to Cs. As the material is compressed from low pressure, there is a relative shifting of bands near the Fermi energy, hence a change in the electronic structure, which is the underlying reason for the presence of two crystal phases, α and β. When the liquid is compressed, the electronic structure change can proceed more or less continuously, but the solid is constrained by crystal symmetry, which interferes with the electronic structure change, hence the electronic structure is discontinuous across the α-β phase boundary. This means the electronic structure in the liquid is different from *either* crystal phase, in the vicinity of the triple point, so we should generally expect anomalous melting in the vicinity of a triple point. This conclusion is supported by experiment, since all six of the anomalous elements identified in Table III have triple points on the melting curve at modest pressures. An even more striking example is provided by evaluation of ΔS^* along the melt curve for Cs [8]. As pressure is increased,
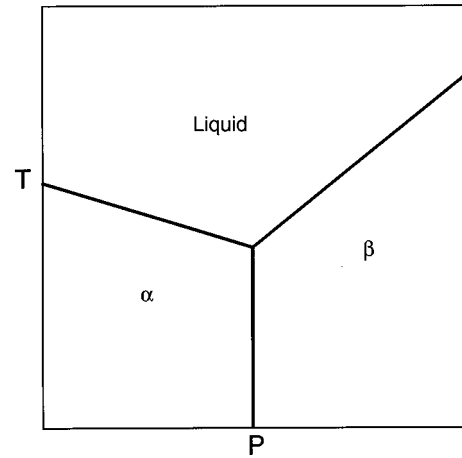

FIG. 1. Representative phase diagram possessing a triple point on the melting curve.

ΔS^* remains constant at the normal value of 0.75 for pressures to 1.4 GPa, then ΔS^* increases dramatically and passes out of the normal range at 1.9 GPa, and a triple point on the melting curve follows at 2.3 GPa.

If we consider a material can exist in either of two electronic structure forms, for example, covalent and metal, and describe anomalous melting as the equilibrium between the crystal in one form and the liquid in the other, then we can write down all the terms that contribute to $\Delta S(\rho_{lm}, T_m)$. Among these terms we can identify the normal melting terms, and setting these equal to the disordering entropy Δ we find [7]

$$\Delta S^* = \Delta^* + \Delta \Phi_0^* + (\text{small terms}), \tag{27}$$

where $\Delta \Phi_0$ is the (positive) difference in static lattice potentials for the two electronic structure forms, at density ρ_{lm}, and the small terms include contributions from U_E, from U_{H0}, and a term of order η^2. An evaluation of Eq. (27) for Si and Ge shows agreement with experiment [7], and strengthens our confidence in the universality of the disordering entropy Δ^* of elemental liquids.

V. SUMMARY

Suppose one wants to calculate thermodynamic functions, including the phase diagram, of an element in solid and liquid phases, under conditions where little or no experimental data are available; what techniques can be used, and what kind of accuracies are to be expected? Answering this will provide a summary of the present study.

To begin, one needs the static lattice potential $\Phi_0(V)$ for every relevant crystal phase, and this is obtainable from isothermal compression measurements, or from band structure calculations. For thermal motion of the ions, an accurate procedure is to use quasiharmonic lattice dynamics at quantum temperatures ($T \lesssim \frac{1}{2}\theta_2$), and molecular-dynamic calculations at classical temperatures ($T > \frac{1}{2}\theta_2$). The electron excitation contributions require theoretical evaluation, from the electron density of states, together with electron-phonon renormalization at quantum temperatures. Following these procedures, and with the aid of a pseudopotential model for

sodium fitted to the energy and its first two volume derivatives at $T=0$ [27], we have calculated to excellent accuracy the thermodynamic properties of the crystal to melt [2,3] the room-temperature isotherm to high pressures [4], the melting temperature to modest pressures [18], and thermodynamic properties of the liquid to high temperatures [16]. Also, based on no experimental data but the atomic weight and number, we have calculated to excellent accuracy the melting temperature, and the crystal and liquid entropies, of Al [13].

The molecular-dynamic calculations require a knowledge of the effective ion-ion interactions in every phase of interest. Two approximations, of lesser accuracy but requiring much less information, are to neglect anharmonicity in the crystal, and to approximate the constant-density entropy of normal melting by a universal constant. Assessment of these approximations follows.

For crystal phases, neglect of anharmonicity leaves only the quasiharmonic free energy for the ion motion, and at classical temperatures this depends *almost entirely* on the single phonon characteristic temperature $\theta_0(V)$, which can be obtained from inelastic neutron scattering experiments, or from frozen phonon calculations. Neglecting anharmonicity introduces errors at classical temperatures of roughly ± 0.1 in the reduced energy and entropy, errors very small compared to the quasiharmonic energy and entropy, and even small compared to the energy and entropy changes on melting ($\Delta S^* \approx 0.80$). Exceptional elements, where the anharmonicity is not so small, are Cr, Mo, W, Ti, and Zr. Finally, the quasiharmonic approximation is also capable of giving the correct shape of the equilibrium boundary between the α and ϵ phases of iron [12].

Together with the thermodynamics of crystals, whether accurate or approximate, a separate approximation will specify all the thermodynamic properties of the liquid at melt, again to an accuracy of roughly ± 0.1 in the reduced energy and entropy: for crystal and liquid of the same electronic structure form, and at the same density, the reduced entropy difference is $\Delta^* \approx 0.80$. Both normal and anomalous melting are contained in this statement, where to treat anomalous melting it is only necessary to apply the approximation separately to two different electronic structure forms. In addition, the approximation can be transformed into an estimator for the melting temperature [7].

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