Defect Melting Models for Cubic Lattices and Universal Laws for Melting Temperatures

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We set up simple harmonic lattice models for elastic fluctuations in bcc and fcc lattices and the excitation of dislocations and disclinations. From these we derive, in a lowest approximation, universal formulas which predict melting temperatures in good agreement with the experiments. This new theory is more precise than Lindemann's rule by factor 2, and more predictive, since the size of the Lindemann number has to be fixed by experiments. In addition, our theory allows for systematic improvements.

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Melting transitions [1–4] are important phenomena of both technical and theoretical interest [5–13]. A hundred years ago, Sutherland [14] found an empirical rule, that the product $bT_mM^{\frac{1}{6}}$ is nearly constant for metals, where T_m is the melting temperature, b the mean coefficient of expansion, and M the atomic mass. In the following year, he advanced a kinetic theory of solids [15], in which he postulated that melting would occur when the space between atoms reaches a certain value relative to the atomic diameter, so that atoms are able to escape from the imprisonment by their neighbors. He carried out a hard-sphere simulation experiment by shaking a box containing one layer of marbles, and noting by removing marbles one at a time that the apparent solid-liquid transition occurs when a free volume of 25-33% is reached. From the vibration amplitude and the thermal kinetic energy, together with the above empirical melting rule, Sutherland [15] calculated the period of vibrations of metal atoms at the melting temperature, and found that the ratio of vibration amplitude to atomic spacing is nearly the same for all elements at melting.

In 1910, Lindemann [16] combined Sutherland's ideas with the Debye theory of specific heat in solids, and derived his famous rule according to which a quasi-universal parameter, the Lindemann number, should be the same for all melting transitions. The number is usually stated in the form

$$L = \theta v^{1/3}(M/T_m)^{1/2}$$

where θ is the Debye temperature and v the volume per atom. Subsequent extensive tests of this rule were carried out by Gschneidner [17], Ross [18], and Crawford [19] who found, however, that Lindemann's rule is not very reliable. First, the Debye temperature cannot be precisely specified since the Debye theory of specific heat is itself approximate. Second, extracting θ from the data by a best fit of the Debye theory, the Lindemann number varies considerably from material to material, as emphasized by Wallace [20].

The most unsatisfactory feature of the Lindemann rule is that its size is unknown and has to be extracted from an average of many melting transitions. Thus, the Sutherland-Lindemann approach to melting has remained a purely phenomenological rough description of the transition. In spite of its roughness, it is often used even today in many works to estimate melting temperature, this being due to a lack of a more precise melting theory.

During the past two decades, several other melting theories have been developed. One is based on density functionals [21, 22], and has provided us with an alternative insight into the melting transition. This work, however, describes satisfactorily only the long-wave length limit of fluctuations, and neglects the important role of the lattice structure, thus requiring essential corrections, which sometimes have been inserted these heuristically [23–25]. Another theory of melting is based on a Landau expansion in a symmetric tensor order parameter of rank four [26]. This theory is purely phenomenological and thus only descriptive, not predictive.

For a proper description for the melting transition, it seems necessary to incorporate information of the lattice structure and the associated crystal defects into the theory. About 15 years ago, one of the authors (HK) did this successfully by constructing lattice models of the melting transition [3, 4]. The important progress of these models [27] was that they started out from the lattice version of the elastic lattice energy which allow for the thermal creation and annihilation of dislocations and disclinations and keeps track of their lattice elastic energy [27]. They are included by means of discrete-valued defect gauge fields, the disclinations being essential for explaining the first-order nature of transition [28], which otherwise would be of second order, as in the vortex-line induced λ-transition of superfluid helium.

In this respect, the older models went beyond those of more recent authors [24, 29] who considered only the proliferation of dislocation lines which, if properly treated, would have produced only second-order phase transitions

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[30], thus being unable to describe the melting transition.

A simple universal melting formula was obtained from the above lattice defect models in a lowest-order approximation which combines the properties of the high-temperature expansion of the defect contributions with the low-temperature expansion of the free energy density. From the intersection of these two curves, one can obtain a formula for the melting temperature in accordance with Lindemann's rule, but with a *prediction* of the absolute size of the Lindemann number [3].

This successful theory has, however, one important drawback: For simplicity, it was constructed only for the physically somewhat exotic case of simple cubic lattices. This makes it strictly applicable only to very few materials—there are almost no simple cubic lattices in nature. If the derived formulas are applied to other cubic crystal structures such as body center cubic (bcc) lattices and face center cubic (fcc) lattices, the accuracy must necessarily be bad. Hence there is an obvious need to generalize the theory to physically more prolific crystal structures.

The purpose of this letter is to present such a generalization of the melting model to fcc and bcc lattices. When generalizing the previous melting model to other cubic lattices, We shall see in the high-temperature limit, that for all cubic crystals the free energy density is only related to the elastic constants of the crystals and does not depend on the lattice structure of the system. This is in contrast to the low-temperature limit, where the free energy density involves integrals over the lattice momenta K_i and $\overline{K}_i$ which strongly depend on the detailed lattice structure of the crystals. It is therefore important to give a proper description of the low-temperature limit of the free energy density for different lattice structures.

The lattice model for the cubic crystals will be based on the elastic energy

$$\begin{aligned} E &= \frac{a^3}{n} A \sum_x \Bigg\{ \frac{1}{4} \sum_{l \neq m} \left[\nabla_{(l)} u_{(m)} + \nabla_{(m)} u_{(l)} \right]^2 \\ &+ C \sum_l \left[\nabla_{(l)} u_{(l)} \right]^2 + \frac{B}{2A} \left[\sum_l \nabla_{(l)} u_{(l)} \left(\vec{x} - \vec{e}_{(l)} \frac{a}{2} \right) \right]^2 \Bigg\} \\ &= -\frac{a^3}{n} A \sum_{x,i,j,l,n} \frac{1}{2} u_i(x) \Bigg[e^i_{(l)} e^j_{(l)} \sum_m \overline{\nabla}_{(m)} \nabla_{(m)} \\ &\qquad + 2(C-1) e^i_{(l)} e^j_{(l)} \nabla_{(l)} \overline{\nabla}_{(l)} \\ &\qquad + \left(\frac{B}{A} + 1 \right) e^i_{(l)} \nabla_{(l)} \overline{\nabla}_{(n)} e^j_{(n)} \Bigg] u_j(x), \end{aligned} \quad (1)$$

where n is the number of atoms per unit cell, $\vec{e}_{(l)}$ are *oriented link vectors* of cubic lattice pointing from any lattice site to its nearest neighbors along the *positive* direction, and u_i denote the Cartesian displacement field, $u_{(l)} = u_i e^i_{(l)}$ their components along the link directions. For fcc lattices, there are six link vectors:

$$\begin{aligned} &\vec{e}_{(1)} = (1,1,0), \quad \vec{e}_{(2)} = (1,0,1), \quad \vec{e}_{(3)} = (0,1,1) \\ &\vec{e}_{(4)} = (1,-1,0), \; \vec{e}_{(5)} = (0,1,-1), \; \vec{e}_{(6)} = (-1,0,1), \end{aligned} \quad (2)$$

each lattice site $\mathbf{x}$ having twelve nearest neighbors at $\mathbf{x} \pm \vec{e}_{(l)} a/2$. For bcc lattices, there are four link vectors

$$\begin{aligned} &\vec{e}_{(1)} = (1,1,1), \quad \vec{e}_{(2)} = (1,1,-1), \\ &\vec{e}_{(3)} = (1,-1,1), \; \vec{e}_{(4)} = (-1,1,1), \end{aligned} \quad (3)$$

and each lattice site possesses eight nearest neighbors. The symbols $\nabla_{(l)}$ and $\overline{\nabla}_{(l)}$ denote lattice derivative, defined by $\nabla_{(l)} f(\vec{x}) = \left[f\left(\vec{x} + \vec{e}_{(l)} a/2 \right) - f(\vec{x}) \right] / b$ and $\overline{\nabla}_{(l)} f(\vec{x}) = \left[f(\vec{x}) - f\left(\vec{x} - \vec{e}_{(l)} a/2 \right) \right] / b$, where b is the distance between the nearest neighbors. After some algebra calculation, the prefactors A, B, and C are related to the usual elastic constant of the crystal μ, λ and ξ defined by the continuum elastic energy

$$E = \mu \int d^3x \left[\sum_{i \neq j} u_{ij}^2 + \xi \sum_i u_{ii}^2 + \frac{\lambda}{2\mu} \left(\sum_i u_{ii} \right)^2 \right], \quad (4)$$

and can be expressed for fcc as follows:

$$A = \frac{\mu}{8}(2\xi - 1), \; B = \frac{\lambda + 2\mu(\xi - 1)}{8}, \; C = 1 - 8\frac{\xi - 1}{2\xi - 1}, \quad (5)$$

and for bcc as

$$A = \frac{3}{16}\mu\xi, \quad B = \frac{3}{16}(\lambda + \mu\xi - \mu), \quad C = \frac{2 - \xi}{\xi}, \quad (6)$$

For very low temperatures, the atomic positions deviate very little from those of an ideal crystal. It is therefore suggestive to use these small deviations for defining the displacement field. But this definition can be consistent only for a small time span. Due to fluctuations, thermals as well as quantum, the atoms are capable of exchanging positions with their neighbors and migrate, after a sufficiently long time, through the entire crystal. This process of self-diffusion makes it impossible to specify the displacement field uniquely. Thus, as a matter of principle, the displacement field is undetermined up to an arbitrary lattice vector, it is impossible to say whether an atom is displaced by $u_{(l)}(x)$ or by

$$u_{(l)}(\vec{x}) + bN_{(l)}(\vec{x})$$

where $N_{(l)}(\vec{x})$ is the jumping field with integer value. Because of this, we should introduce an extra sum over an integer-valued field $n_{(lm)}(x)$ with a gauge fixing term $\Phi[n_{(lm)}]$ in the corresponding partition function, thus the partition function of the defect melting model reads

$$Z = \sum_{n_{(lm)}} \prod_{x,i} \left[\int \frac{du_i(x)}{a} \right] \Phi[n_{(lm)}]$$
$$\times \exp\left\{ -\frac{a^3 A}{nk_B T} \sum_x \left[\frac{1}{2} \sum_{l<m} \Big(\nabla_{(l)} u_{(m)} + \nabla_{(m)} u_{(l)} \right.\right.$$
$$-b(n_{(lm)} + n_{(ml)}) \Big)^2 + C \sum_l \left(\nabla_{(l)} u_{(l)} - b n_{(ll)} \right)^2$$
$$+\frac{B}{2A} \Big(\sum_l [\nabla_{(l)} u_{(l)} (\vec{x} - \vec{e}_{(l)} \frac{a}{2})$$
$$\left.\left. -b n_{(ll)} (\vec{x} - \vec{e}_{(l)} \frac{a}{2})] \Big)^2 \right] \right\} \tag{7}$$

The partition function is invariant under the following defect gauge transformations

$$u_{(l)} \to u_{(l)}(x) + bN_{(l)}(x), \;\; n_{(lm)} \to n_{(lm)} + \nabla_{(l)} N_{(m)}(x).$$

This partition function can be expressed in terms of the stress field σ_{ij} by

$$Z = \left[8\xi^3 \left(1 + \frac{3\lambda}{2\mu\xi} \right) \right]^{-N/2} \left(\frac{1}{2\pi\beta} \right)^{3N} \prod_{x,i\le j} \left[\int d\sigma_{ij} \right]$$
$$\times \sum_{n_{(lm)}} \Phi[n_{(lm)}] \prod_{x,i} \left[\int \frac{du_i(x)}{a} \right] \exp\left\{ \frac{-1}{2\beta} \sum_x \left[\sum_{i<j} \sigma_{ij}^2 \right.\right.$$
$$\left.\left. + \frac{1}{2\xi} \sum_i \sigma_{ii}^2 - \frac{\lambda}{4\mu\xi^2 + 6\lambda\xi} \Big(\sum_i \sigma_{ii} \Big)^2 \right] \right\}$$
$$\times \exp\left[i\pi \sum_{x,l,m} \sigma_{(lm)} \Big(\nabla_{(l)} u_{(m)} + \nabla_{(m)} u_{(l)} - 2b n_{(lm)} \Big) \right], \tag{8}$$

where $\sigma_{(lm)} = (\sqrt{3}/16) e^i_{(l)} e^j_{(m)} \sigma_{ij}$ for bcc lattice and $\sigma_{(lm)} = (\sqrt{2}/16) e^i_{(l)} e^j_{(m)} \sigma_{ij}$ for fcc lattice, and $\beta = (a^3\mu)/(nk_B T (2\pi)^2)$. In the calculation process from (7) to (8), the corresponding expressions of A, B, C and $e^i_{(l)}$ are used. In spite of the tedious intermediate calculation, the prefactors in the partition functions (8) are the same for all cubic lattices.

For the-lowest order approximation, we need only to investigate the system in low-temperature and high-temperature limits. It has been shown in the textbook [3] (see Fig. 12.1 on p. 1084) that the intersection of the free energies of the two limiting curves yields good estimates for the melting temperatures in simple-cubic lattices.

For $T \to 0$, the defect configuration is completely frozen out, and the partition function has a classical limit. From the lattice energy (1) we obtain the classical partition function of cubic lattice

$$Z_{\rm cl} = \prod_{x,i} \left[\int \frac{du_i(x)}{a} \right] e^{-E/k_B T} = \sqrt{\frac{2\pi nk_B T}{Aa^3}}^{3N} e^{-N\frac{1}{2}\ell},$$

where the dimensionless parameter ℓ is defined by the trace log

$$\ell = \int\limits_{-2\pi/a}^{2\pi/a} \frac{d^3 k a^3}{(4\pi)^3} {\rm tr} \log \mathbf{M}, \tag{9}$$

and $\mathbf{M}$ denotes the matrix

$$M_{ij} = 4\delta_{ij} a^2 \sum_m \overline{K}_{(m)} K_{(m)} + 2(C-1) a^2 \sum_l e^i_{(l)} K_{(l)} \overline{K}_{(l)} e^j_{(l)}$$
$$+ \left(\frac{B}{A} + 1 \right) a^2 \sum_{l,n} e^i_{(l)} K_{(l)} \overline{K}_{(n)} e^j_{(n)} \tag{10}$$

and $K_{(l)}$ and $\overline{K}_{(l)}$ are lattice momenta, for fcc

$$K_{(l)} = \frac{\sqrt{2}}{ai} (e^{i\vec{k}\cdot\vec{e}_{(l)}\frac{a}{2}} - 1), \;\; \overline{K}_{(l)} = \frac{\sqrt{2}}{ai} (1 - e^{-i\vec{k}\cdot\vec{e}_{(l)}\frac{a}{2}}), \tag{11}$$

and for bcc

$$K_{(l)} = \frac{2i}{\sqrt{3}a} (1 - e^{i\vec{k}\cdot\vec{e}_{(l)}\frac{a}{2}}), \overline{K}_{(l)} = \frac{2i}{\sqrt{3}a} (e^{-i\vec{k}\cdot\vec{e}_{(l)}\frac{a}{2}} - 1). \tag{12}$$

Thus we find the free energy density of the fcc and bcc lattices in the low-temperature limit

$$-\frac{f^{T\to 0}}{k_B T} = \frac{3}{2} \log \left(\frac{2\pi nk_B T}{\mu a^3} \right) + \frac{3}{2} \log \frac{\mu}{A} - \frac{1}{2} \ell. \tag{13}$$

In the opposite limit of high temperature, the defects are prolific and the sum over $n_{(lm)}$ can be approximated by integral enforcing $\sigma_{ij} \equiv 0$. Then the partition function (8) yields the free energy density

$$-\frac{f^{T\to\infty}}{k_B T} = 3 \log \left(\frac{2\pi nk_B T}{\mu a^3} \right) - \frac{1}{2} \log \left[8\xi^3 \left(1 + \frac{3\lambda}{2\mu\xi} \right) \right]. \tag{14}$$

From the intersection of this with the low-temperature approximation (13), we obtain the melting relation for the fcc and bcc lattices

$$\frac{a^3 \mu \xi}{2\pi nk_B T_{\rm melt}} = \frac{A}{\mu} \frac{1}{8^{1/3}} \left(1 + \frac{3\lambda}{2\xi\mu} \right)^{-1/3} e^{\ell/3} \quad . \tag{15}$$

The formula is structurally very similar to the Lindemann rule $L = $ const., but *predicts*, in addition, the size of L to be averagely of the order of 126. Moreover, from our expression, one can recognize clearly that the melting temperature will be zero when the anisotropic parameter ξ equals to zero, this is in contrast to recent phenomenological theories of melting by other authors [24]. The novelty of this formula with respect to a similar formula in Ref. [3] [see Eq. (12.13) on p. 1079] lies in a determination of trace log term ℓ for bcc and fcc lattices. The resulting melting temperatures from Eq. (15) are shown in Table 1, where they are compared with experimental numbers and with the results found from Lindemann's rule where the Lindemann number is initially undetermined and must be extracted from the average over all materials. Our lowest-order theory has an average precision of about 12%, which is better by a factor 2 than the 22% of the numbers from derived Lindemann's rule.

Element	μ	λ	ξ	$T_{m,\mathrm{theor.}}$	$T_{m,\mathrm{exp.}}$	$\kappa(\%)$	$\delta(\%)$
Ag (fcc)	51.10	97.30	0.335	1246.5	1234.0	1	24
Au (fcc)	45.40	169.70	0.351	1201.4	1336.2	-10	6
Ba (bcc)	9.50	8.00	0.242	875.4	998.0	-12	22
Ca (fcc)	16.30	18.20	0.294	889.0	1112.0	-20	-14
Co (fcc)	128.00	160.00	0.320	1892.7	1765.0	7	-2
Cu (fcc)	81.80	124.90	0.314	1299.8	1356.0	-4	16
Li (bcc)	10.80	12.50	0.110	450.2	454.0	-1	-14
Nb (bcc)	28.70	134.00	1.951	2778.2	2741.0	1	-39
Ni (fcc)	124.70	147.30	0.398	2034.9	1726.0	17	16
Pb (fcc)	14.40	39.20	0.222	507.4	600.6	-15	26
Pd (fcc)	71.20	176.10	0.407	1723.0	1825.0	-6	7
Pt (fcc)	76.50	250.70	0.627	2527.3	2042.0	23	29
Sr (fcc)	9.90	10.30	0.253	868.0	1045.0	-17	11
Ta (bcc)	81.80	157.40	0.627	3879.0	3271.0	18	-32
Th (fcc)	47.80	48.90	0.278	1882.8	2024.0	-7	43
Tl (bcc)	11.00	34.00	0.309	609.9	576.0	5	8
V (bcc)	46.00	119.40	1.228	2444.3	2178.0	12	-15
W (bcc)	163.10	204.90	1.005	3497.4	3653.0	-4	3

Table 1. Theoretical results of melting temperatures (units in K) derived from the elastic constants of cubic crystals (units in GPa, gotten from [31]) compared with the experimental data (units in K, gotten from [17]). The second-last column shows the relative error $\kappa = (T_{m,\mathrm{theor}}/T_{m,\mathrm{exp}} - 1) \cdot 100$ of our theory, which is by a factor 2 lower than the relative error $\delta = (T_{m,\mathrm{Lind}}/T_{m,\mathrm{exp}} - 1) \cdot 100$ found from Lindemann's rule. The Lindemann melting temperatures $T_{m,\mathrm{Lind}}$ are from Ref. [32].

There is no problem, in principle, to calculate systematic improvements to formula (15) by including defect excitations into the low-temperature approximation (13) and stress corrections into the high-temperature approximation (14). This was done in Ref. [3] for the unphysical simple cubic lattices, and will be done for bcc and fcc lattices in future work.

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