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Statistical mechanics of melting mediated by two types of defects

Kejia Liu *, Huifen Chen

Department of Material Science, Shanghai Institute of Technology, 200233 Shanghai, China

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Abstract

We propose a defect-mediated melting theory based on the statistics of two types of lattice defects, the point defects and dislocation pairs. The model predicts a first-order phase transition. Based on the model, phase transition temperature, latent heat and other thermodynamic functions are derived. Melting occurs due to discontinuous growth of point defects into dislocation pairs. The calculated phase transition temperature for five alkali metallic crystals are in fair agreement with measured melting temperatures, and the Richards' rule is derived by the model also.

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1. Introduction

Solid–liquid phase transition is one of the fundamental topics in condensed matter physics. The very first theory of melting was proposed by Lindemann nearly 100 years ago [1], and the idea of a proliferation of dislocations being associated with melting dates back to Mott more than 50 years ago [2]. It was in the 1970s that a formal dislocation-mediated melting theory was proposed by Kosterlitz and Thouless (KT) [3], which suggested that the phase transition occurs via an unbinding dislocation pairs (DP) in the crystals. Subsequently, the dislocation mediated melting was studied for elemental crystals covering more than half of the elements in the Periodic Table and some empirical rules for melting have been established [4].

However, despite of the effort of many researchers, the melting process has not been fully understood. Even though many theories on melting have been proposed, some of them cannot predict the melting temperature correctly, while others fail to predict the correct order of the phase transitions. For example, second-order phase transition was predicted for crystals based on the KT theory, but first-order phase transition was observed experimentally for all of the melting transition. Some of the existing melting theories are based on the mechanism of one-phase melting or continuous melting, i.e., the phase transition is derived from one phase. Since first-order phase transition deal with two phases, such theories cannot be expected to correctly describe a first-order phase transition. Therefore, how a solid melts has been a longstanding question.

In the present work, we study melting of crystals mediated by two types of defects: point defects and dislocation pairs, and develop a defect mediated melting theory. Different types of defects are allowed to transform from one to the other, and this transformation may lead to the first-order of phase transition of a crystal.

Many quantities character a melting process. Besides the melting temperature T_m, the latent heat of fusion is another one. Based on the model proposed in this Letter, theoretical predictions for both quantities are verified by experimental data.

2. Theory of melting

We first consider a dislocation pair (DP) which consists of two parallel line dislocations with opposite Burgers vectors. The interact energy per unit length for a screw dislocation pair

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* Corresponding author.
E-mail address: kjliu@sit.edu.cn (K. Liu).

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can be written as [5]

$$U(r) = j \ln\left(\frac{r}{r_0}\right) + 2\varepsilon_c, \tag{1}$$

where j is the coupling constant per unit length which is related to the elastic interaction between two dislocations in the DP, r is the distance between two dislocations of the pair, and r_0 is the radius of the cylindrical dislocation core region. The energy per unit length inside the core region for a single dislocation is taken to be a constant, ε_c. Only screw dislocation pair will be considered in the present study for reason given below. The interaction energy given in Eq. (1) is the same as that of a two-dimensional (2D) dipolar Coulomb gas which has been studied by many researchers [6–8]. However, we provide an alternate and simpler approach in the present work.

The coupling constant j per unit length can be obtained from the dislocation theory. For screw dislocation, j is given by [9]

$$j = \frac{\mu}{2\pi} b^2, \tag{2}$$

where μ is the shear modulus and b is the modulus of the Burgers vector. Although the core cutoff r_0 cannot be obtained from the elastic theory, it can be estimated using the Periels–Nabbaro model [9] of dislocation. According to this model, the radius r_0 of the dislocation can be expressed as

$$r_0 = b/\alpha, \tag{3}$$

where α is called the core parameter which has the value 3–4 for nonmetal crystals and 1–2 for metals [9]. To simplify our discussion, we shall only discuss the metal case through out this Letter.

The statistical system we study is a three-dimensional crystal containing N lattice sites in its surface, where $N (= \text{even})$ is assumed to be the order of Avogadro's number. We further assume that there are n pairs of dislocations in the system, and all of dislocation lines are perpendicular to the surface. As a DP involves at lest two lattice sites, we thus have $0 < n < N/2$. Let r_i denotes the distance between the two dislocations in the ith $(0 \leqslant i \leqslant n)$ DP. The interaction energy of each pair is expressed by Eq. (1). To simplify the calculation, the pair–pair interaction will be neglected through out this Letter, so that the partition function for the system containing n DP, denoted by z_n is given by

$$z_n = \sum_{i=1}^{n} \sum_{\text{all config}} \exp\bigl(-\beta U(r_i)\bigr), \tag{4}$$

where $\beta = (k_B T)^{-1}$ with k_B being the Boltzmann's constant and T the temperature. The first summation on the right-hand side of Eq. (4) is over all n DPs, and the second summation is over all configurations of the ith pair. The simplest but non-trivial case of Eq. (4) is $n = 1$. Based on the continuous media model of solid, it is

$$z_1 = \sum_{\text{all config}} \exp\bigl(-\beta U(r)\bigr) = \frac{1}{2}\frac{N}{A} \iint_R \exp\bigl(-\beta U(r)\bigr) r\, dr\, d\theta. \tag{5}$$

The factor N in Eq. (5) comes from the fact that each dislocation of the DP can be located at each of the N lattice sites. The factor of $1/2$ is due to double counting of the configurations resulting from exchange of the two dislocations of the DP. The domain of the integration, R, is over the entire 2D area, i.e., $b < r < \infty$ and $0 < \theta < 2\pi$. The symbol, A, in Eq. (5) denotes the area of the primitive lattice cell such that $R = NA$, or $A = \pi(b/2)^2$ in the continuous media model. The integration in Eq. (5) can be carried out exactly. Inserting Eq. (1) into Eq. (5), one has

$$z_1 = \frac{N}{2} \frac{4\alpha^{-j/k_B T}}{J/k_B T - 2} \xi \quad (\text{for } j/k_B T > 2),$$

where ξ is given by

$$\xi \equiv \exp(-2\beta\varepsilon_c).$$

For more general case ($n > 1$), if the pair–pair interaction is neglected, the partition function z_n can be written as

$$z_n = \binom{N/2}{n} \left(\frac{4\alpha^{-j\beta}}{j\beta - 2}\xi\right)^n,$$

where $\binom{N}{i} = \frac{N!}{i!(N-i)!}$ is the binomial coefficient and $N!$ denotes the factorial of N.

The dislocation pairs in the system can be treated like non-distinguishable particles. The number of such particles n varies in the range $(0 \leqslant n \leqslant N/2)$ because the particles can be thermally excited at finite temperature. It is noted that chemical potential does not appear in the partition function. This is because the number of particles n is a non-conservative number, similar to the number of phonons in solid.

The grand partition function, $Z(T)$, can be expressed as

$$Z(T) = \sum_{i=0}^{N/2} z_i = \sum_{i=0}^{N/2} \binom{N/2}{i} \left(\frac{4\alpha^{-j\beta}}{j\beta - 2}\xi\right)^i = \left(1 + \frac{4\alpha^{-j\beta}}{j\beta - 2}\xi\right)^{N/2}. \tag{6}$$

Thus, the thermodynamic grand potential $\Omega(T)$ is given by

$$\Omega(T) = -k_B T \ln Z(T) = -\frac{N k_B T}{2} \ln\left(1 + \frac{4\alpha^{-j\beta}\xi}{j\beta - 2}\right). \tag{7}$$

Next, we consider the statistical mechanics of point defects. In order to compare the statistical results of the point defects with those of the dislocation pairs, the point defect model should be compatible to that of the DP. Therefore, the DP and point defect must have the same origin, so that one defect system can transform to the other under certain conditions.

A point defect in a 2D crystal can be expressed in terms of a minimum dislocation pair. The energy of a point defect, U_p, can be given by the extreme case with $b = r_0$ in Eq. (1), i.e.,

$$U_p = j \ln(\alpha) + 2\varepsilon_c. \tag{8}$$

This model of point defect is similar to that of a lattice gas, except that our model is derived based on the minimum screw dislocation pair. The geometrical structure of such a defect is an