

A Simple Dislocation Theory of Melting

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Abstract

The ratio of volume increment to energy for the introduction of a simple dislocation to a crystal is used in the Clausius–Clapeyron equation to determine the pressure dependence of the equilibrium phase boundary between a perfect crystal and a completely dislocated crystal. It yields the Lindemann melting formula, which is thermodynamically valid for materials with central atomic forces in which melting involves no gross changes in coordination. It is concluded that melting is properly described as the free proliferation of dislocations and that melting point is the temperature at which the free energies of dislocations vanish.

Introduction

The concept of crystal dislocations was originally developed to explain the fact that the shear strengths of solids are much lower than the theoretical strengths of ideal crystal lattices. Their existence is now extensively documented (see e.g. monographs by Cottrell 1953 and Friedel 1964) and is directly evident from electron micrographs. Since the normal mechanism for inelastic shear deformation of crystals is dislocation motion (glide) and the melting of a material means the complete disappearance of its shear strength (a ‘shear catastrophe’ in the words of Levy 1968), it is natural to suppose that the melting process is a spontaneous multiplication of dislocations. This means that in the liquid state a material is saturated with dislocation cores, which are continuously forming, disappearing and reforming in different microscopic arrangements. Their mobility is responsible for the fluidity of the material. In a liquid the atomic spacing is irregular, as is consistent with the atomic spacing in dislocation cores.

The basic idea of the dislocation theory of melting was mentioned by Mott (1952), but the essential idea for the present discussion arose from our study of a paper by Kuhlmann-Wilsdorf (1965), who suggested that melting point was the temperature at which the free energy of a dislocation vanished. However, she did not succeed in obtaining a simple or convenient melting law, such as that presented here. The idea of vanishing free energy neatly explains the sharpness of the melting points of simple materials, such as the elements. A sharp melting point T_M could not result from the proliferation of point defects, whose energies are not very many times kT_M , whereas dislocations, being extended linear defects, have energies which are many times kT_M and would have negligible Boltzmann probability of independent thermal excitation below the temperature of free energy balance.

The criterion of zero free energy is here applied simply by appealing to the Clausius–Clapeyron equation for the dependence of melting point T_M on pressure P :

$$T_M^{-1} dT_M/dP = \Delta V/L, \quad (1)$$

where ΔV and L are the volume change and latent heat of melting. This is a direct consequence of the assertion that at the melting point (at any pressure) the Gibbs free energies of the solid and liquid states must be equal. Thus we can apply the free energy condition to the dislocation theory of melting by calculating the ratio of the volume increment which a dislocation causes to its energy. This ratio gives the pressure dependence of the critical temperature for vanishing dislocation free energy by equation (1), and we identify this as the pressure dependence of the melting point. The result is the simple and familiar Lindemann melting law which we have shown in the previous paper to have a sound thermodynamic basis (Stacey and Irvine 1977; present issue pp. 631–40).

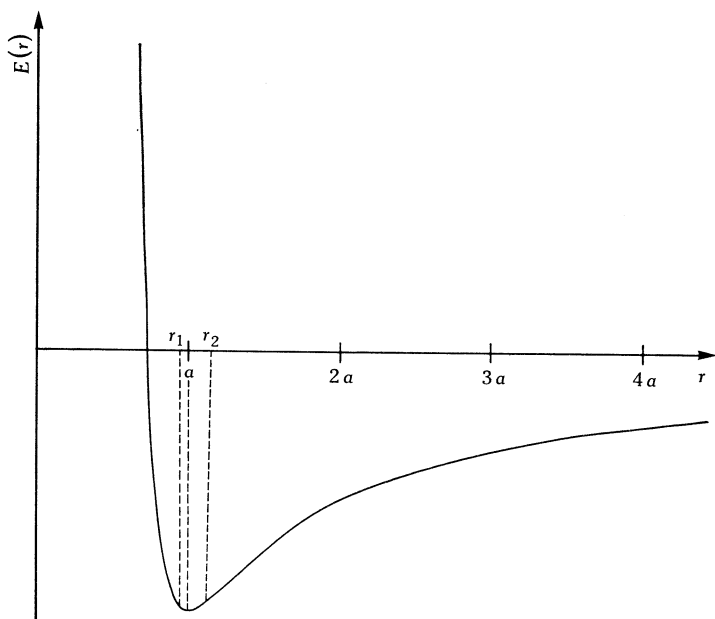


Fig. 1. Atomic potential function. Asymmetry of the potential well that binds neighbouring atoms is responsible for anharmonic effects, including the volume increase on melting of 'normal' materials.

Linear Dislocation Model

Consider two linear chains of atoms which are held together by a general anharmonic force law, with arbitrary atomic potential energy $E(r)$ between neighbours at spacing r (Fig. 1). The two chains are locked together at their ends, but we suppose at this stage of the argument that there are no cross-linkages to be considered. In the equilibrium state the two chains each have equal numbers n of lattice spacings r_e and we treat the externally applied pressure p_0 as balancing the atomic force over an area r_e^2 . Thus we have

$$p_0 = -r_e^{-2} (dE/dr)_{r=r_e} \equiv -r_e^{-2} E'(r_e). \quad (2)$$

Now we introduce what we shall call a 'linear edge dislocation' by withdrawing one atom from one of the chains and reconnecting the chain so that it now has $n-1$ lattice spacings, as in Fig. 2. This chain contracts, compressing the other one but, if pressure along the chain is maintained constant, the lattice spacing r_1 of the compressed chain differs from the equilibrium spacing r_e by less than does the lattice spacing r_2 of the shortened chain and the result is an increase in the volume per atom. This volume increment is one of the parameters we need to calculate for use in equation (1). However, it is easier to avoid error by increasing the pressure to maintain constant volume per atom and relating the necessary pressure increment to the volume change which would have occurred at constant pressure, in terms of the bulk modulus of the material.

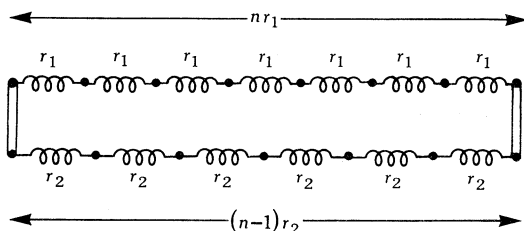


Fig. 2. Elementary model of an edge dislocation. Two linear atomic chains, locked together at their ends, have unequal numbers of atoms. The upper chain is in compression and the lower one is in extension. But extensions are greater than compressions, by virtue of the asymmetric atomic potential function $E(r)$, thus causing an increase in the average volume per atom.

A constant average atomic volume gives

$$nr_1 = (n-1)r_2 = \frac{1}{2}(2n-1)r_e, \quad (3)$$

so that

$$r_1 - r_e = -r_e/2n, \quad r_2 - r_e = r_e/2(n-1). \quad (4)$$

The necessary pressure increment, taken as the average longitudinal force per unit area over both chains together, is

$$\Delta P = -r_e^{-2} \left\{ \frac{1}{2} (E'(r_1) + E'(r_2)) - E'(r_e) \right\}. \quad (5)$$

We consider the condition $n \gg 1$, so that $r_1 - r_e$ and $r_2 - r_e$ are small compared with r_e , and then use Taylor expansions for $E'(r_1)$ and $E'(r_2)$ about r_e to $E'''(r_e)$, giving

$$\begin{aligned} \Delta P = & -\frac{1}{2}r_e^{-2} \left\{ (r_1 - r_e)E''(r_e) + \frac{1}{2}(r_1 - r_e)^2 E'''(r_e) + \dots \right. \\ & \left. + (r_2 - r_e)E''(r_e) + \frac{1}{2}(r_2 - r_e)^2 E'''(r_e) + \dots \right\}. \end{aligned} \quad (6)$$

Substituting for $r_1 - r_e$ and $r_2 - r_e$ by equations (4), representing ΔP as a power series in n^{-1} and truncating the expansion at the term in n^{-2} we are left with

$$\Delta P = -\frac{1}{8}n^{-2} \{ 2r_e^{-1} E''(r_e) + E'''(r_e) \}, \quad (7)$$

The volume change per atom ($V = r_e^3$) corresponding to this pressure increment is

$$\Delta V = \frac{V \Delta P}{3K} = \frac{r_e^3 \Delta P}{3K} = -\frac{2r_e^2 E''(r_e) + r_e^3 E'''(r_e)}{24n^2 K}, \quad (8)$$

where K is the bulk modulus. Note that the factor 3 with K arises because we are considering compression of the chains along one axis whereas the definition of K refers to the volume change resulting from compression along all three axes. Also the negative sign appearing in the definition $K = -V dP/dV$ is here reversed because the ΔV in equation (8) is the volume increment which results from release of the pressure increment ΔP .

The energy increment per atom resulting from the introduction of the dislocation is

$$\Delta E = \frac{nE(r_1) + (n-1)E(r_2)}{2n-1} - E(r_e). \quad (9)$$

Using a Taylor expansion to $E'''(r_e)$, substituting for $r_1 - r_e$ and $r_2 - r_e$, expressing the result as a power series in n^{-1} and terminating the expansion at n^{-2} , as for ΔP , we find that the energy increment reduces to a single term:

$$\begin{aligned} \Delta E &= \frac{n}{2n-1} \left((r_1 - r_e)E'(r_e) + \frac{1}{2}(r_1 - r_e)^2 E''(r_e) + \frac{1}{6}(r_1 - r_e)^3 E'''(r_e) + \dots \right) \\ &\quad + \frac{n-1}{2n-1} \left((r_2 - r_e)E'(r_e) + \frac{1}{2}(r_2 - r_e)^2 E''(r_e) + \frac{1}{6}(r_2 - r_e)^3 E'''(r_e) + \dots \right) \\ &= \frac{1}{3} n^{-2} r_e^2 E''(r_e). \end{aligned} \quad (10)$$

Combining equations (8) and (10), we have

$$\frac{\Delta V}{\Delta E} = -\frac{1}{3K} \left(2 + r_e \frac{E'''(r_e)}{E''(r_e)} \right). \quad (11)$$

Now we wish to relate $E''(r_e)$ and $E'''(r_e)$ to the bulk properties of the material. Inverting equations for P , K and $dK/dP \equiv K'$ given by Stacey (1977, p. 175), we have

$$E'' = r_e(3K - 2P), \quad E''' = -9KK' + 9K - 2P, \quad (12)$$

so that

$$\frac{\Delta V}{\Delta E} = \frac{1}{K} \left(\frac{K' - \frac{5}{3} + \frac{2}{3} P/K}{1 - \frac{2}{3} P/K} \right) = \frac{1}{K} \left(\frac{K' - 1 + \frac{2}{9} P/K}{1 - \frac{2}{3} P/K} - \frac{2}{3} \right). \quad (13)$$

The second version of equation (13) has been written in a form which facilitates comparison with the thermodynamic Grüneisen parameter γ . For a three-dimensional lattice with central atomic forces the Vashchenko-Zubarev relationship applies (Irvine and Stacey 1975), namely

$$\gamma_{VZ} = \frac{1}{2} \left(\frac{K' - \frac{5}{3} + \frac{4}{9} P/K}{1 - \frac{4}{3} P/K} \right), \quad (14)$$

but the thermal expansion of a linear chain is represented by the Dugdale-MacDonald expression (Irvine and Stacey 1975)

$$\gamma_{DM} = \frac{1}{2} \left(\frac{K' - 1 + \frac{2}{9} P/K}{1 - \frac{2}{3} P/K} \right). \quad (15)$$

For comparison with the linear-chain problem considered here, γ_{DM} is appropriate. Thus

$$\Delta V/\Delta E = K^{-1} (2\gamma_{DM} - \frac{2}{3}). \quad (16)$$

Generalization to Three Dimensions

The foregoing calculation simply gives the ratio of change of volume to energy due to balanced extensions and compressions of atomic bonds in one dimension. The introduction of extensions and compressions of cross linkages in perpendicular directions, to make real crystal dislocations, yields volume and energy changes which at first sight would appear to be in the same ratio but on closer examination are seen to have a subtle but important difference. The forces between atoms due to displacements in three mutually perpendicular directions are independent in the harmonic approximation but not when anharmonicity is allowed for. As pointed out by Irvine and Stacey (1975), this is the reason for the difference between the Dugdale-MacDonald and Vashchenko-Zubarev formulations of γ (equations 15 and 14). The error in γ_{DM} is that it assumes mutual independence of the bond forces in perpendicular directions when atoms are displaced by thermal agitation and therefore that the expansion coefficient can be calculated from bond forces in a single direction. The mutual dependence is allowed for in γ_{VZ} . Similarly in generalizing the linear dislocation to dislocations in a three-dimensional analysis we must replace γ_{DM} by γ_{VZ} . But γ_{VZ} is identified as the thermodynamic Grüneisen ratio for materials with purely central atomic forces (Irvine and Stacey 1975) so that we can drop the subscript and write quite generally

$$\Delta V/\Delta E = 2K^{-1}(\gamma - \frac{1}{3}). \quad (17)$$

Now we identify the spontaneous generation of dislocations with melting, so that the ratio given by equation (17) can be used in equation (1):

$$T_M^{-1} dT_M/dP = 2K^{-1}(\gamma - \frac{1}{3}). \quad (18)$$

This is the familiar Lindemann melting law.

Discussion

We previously concluded that equation (18) applies to the melting of materials with central atomic forces in which the atomic coordinations are similar in the solid and liquid phases (Stacey and Irvine 1977). Although this appears to be a very restrictive condition, there are many materials which follow Lindemann's law quite closely (Vaidya and Gopal 1967), particularly those with close-packed crystal structures. Further we can see now more clearly why others do not.

A significance of the dislocation approach presented here is that it offers the prospect of a more general melting theory which may be applied to materials with rigid molecular bonds or to those which undergo gross coordination changes on melting. The original derivation of Lindemann's law in terms of atomic vibration amplitudes is empirical and unsatisfying, so that it is important for it to have a sound thermodynamic basis. Accepting that this is so, agreement of the thermodynamic and dislocation approaches gives very strong justification for an interpretation of melting in terms of the proliferation of dislocations, and so provides a sound microscopic picture of the melting process. We can therefore hope to interpret in terms of dislocations the melting of theoretically more difficult or complicated materials which will not yield to a thermodynamic approach. It may also be useful to recognize the directness of the connection between dislocation mobility and fluid viscosity.

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