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PART I

Solid State Amorphization

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MOLECULAR DYNAMICS SIMULATION OF THE EFFECT OF INTERFACES IN MELTING AND SOLID-STATE AMORPHIZATION

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ABSTRACT

A newly developed molecular dynamics code was used to study the effect of free surfaces, grain boundaries and voids in the process of melting. It was found that conventional "thermodynamic melting" occurs via nucleation of the liquid at the extended defects with subsequent growth into the crystal. In the absence of interfaces, or when this transition is kinetically hindered, however, a second type of melting transition can be triggered by an elastic instability first described by Born ("mechanical melting"). It is suggested that the distinct characteristic features associated with the two types of melting are actually observed in solid-state amorphization experiments. A unified thermodynamics-based description, in the form of an extended phase diagram, of melting and solid-state amorphization is proposed which brings out the parallels between these two phenomena and suggests that their underlying causes are apparently the same. By investigating the effect of surface stresses on the structure and elastic behavior of free-standing thin films, we discuss how these concepts need to be modified in thin-film and small-grained materials.

1. INTRODUCTION

The crystalline-to-amorphous (C-A) phase transformation is currently receiving renewed attention due to new experimental evidence that amorphous alloys can be produced by a variety of irradiation-, chemically-, and mechanically-driven processes [1]. Given that the transformation can be induced by many different mechanisms, the question naturally arises as to what is the underlying nature of the transition that is common to all these processes. In the same context it can be asked what is the connection between melting and amorphization since both phenomena are concerned with the transition from an ordered to a disordered phase.

That amorphization is analogous to melting in certain respects has been recognized recently by a number of workers [1-5]. In particular, Cahn and Johnson [2] have pointed out parallels which exist in the processes involving the heterogeneous nucleation of disorder and Okamoto et al. [5] have discussed the similarity in the volume dependence of the shear modulus during irradiation-induced amorphization and heating-induced melting [6]. In the present work we suggest that the analogy between melting and amorphization may be taken further. By focussing on the role of the two thermodynamic state variables of temperature and volume in the destruction of crystalline order, we propose a unifying description which appears to be a natural extension of basic equilibrium thermodynamics. This representation brings out clearly the essential thermodynamic parallels between these two phenomena without being encumbered by specific mechanistic aspects. It also elucidates the important role played by self diffusion, a manifestation of the equilibrium

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dynamical behavior of a statistical-mechanical system. A more detailed and comprehensive account of this work has appeared recently [7].

2. MOLECULAR DYNAMICS SIMULATION OF MELTING

The fundamental concept of melting is based on the coexistence of the solid with the liquid when the free energies of the two phases are equal. It is implied that at temperatures above this coexistence the solid is unstable; but neither the mechanism of melting nor the kinetics of the process are considered in the thermodynamic definition. In reality, melting occurs in the presence of external or internal surfaces and over a finite time interval [8]. Despite a wealth of experimental data [9,10], it is not clear conceptually how the observed kinetic behavior is to be interpreted in the context of the thermodynamic basis of the transition.

Three basic physical scenarios of melting have been proposed. The first treats the phenomenon as a homogeneous, bulk process involving a lattice instability (see, for example, Refs. 11-13) in which the (temperature-dependent) normal modes of the lattice become unstable at sufficiently high temperature. The second involves a mechanical instability occurring when the concentration of intrinsic (i.e., thermally generated) defects reaches a critical concentration (see, for example, Ref. 14). The third, originating from experimental observation [8,10,15-18] describes melting as nucleating at extrinsic defects, such as free surfaces, grain boundaries, etc. Several recent experiments demonstrate that when the surface conditions are modified, the melting point can be depressed [15] or the solid can be substantially superheated [8,10,18,19]. The implications are that (a) melting is basically a heterogeneous process, and (b) the mechanism of nucleation at extrinsic defects generally determines the kinetics.

In any study of melting, knowledge of the thermodynamic melting point, T_m , is of primary importance. Hence, at the outset free-energy calculations should be performed for the crystalline and liquid phases to determine T_m . If this is not done, then one does not know the true melting point of the model system described by the particular interatomic interaction potential function adopted for the simulation. The interatomic potential used in the present work is an embedded-atom-method (EAM) potential [20] for copper parameterized for Cu/Ni alloys [21]. The zero-temperature equilibrium lattice parameter for this potential is $a_0 = 3.6208 \text{ \AA}$. An analysis of the free energies of the (undefected, perfect-crystal) solid phase and of the liquid phase then yields a coexistence temperature at zero pressure of $T_m = 1171 \pm 30 \text{ K}$. The details of that calculation have been described elsewhere [22].

2.1 Thermodynamic Melting

In order to investigate the role of extrinsic defects on melting, we have investigated the high-temperature behavior of a bicrystal containing a symmetrical grain boundary (GB). Far from the interface in the direction of the GB normal the GB is embedded in perfect-crystal blocks which are allowed to slide parallel and perpendicular to the interface plane, thus enabling both GB migration and a volume expansion at the boundary. Details of this 2-d periodic simulation model are given elsewhere [23].

The particular GB we have studied is the so-called $\Sigma 29$ (001) twist GB. This GB is created by rotating one half of the bicrystal about the $\langle 001 \rangle$ axis by an angle of 43.60° relative to

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the other half. The resulting GB is periodic in the (001) plane with a square planar unit cell containing $\Sigma=29$ atoms, and with sides of length $3.808 a_0$ at zero temperature. This boundary was chosen because of (i) the large interplanar spacing of the (001) planes compared to the vibrational amplitudes of the atoms and (ii) its relatively large planar unit cell. The latter allows us to consider this a "generic" high-angle boundary as opposed to boundaries with small planar unit cells, such as symmetric tilt GBs, for which the GB energy is known to be unusually sensitive to relative translations of the two halves of the bicrystal [24]. The simulation cell contains 32 (001) planes, 16 in each half of the bicrystal, with a total of 928 atoms.

To investigate the breakdown of crystalline order upon melting, we define the squared magnitude of the static structure factor, $S(\mathbf{k})$, which for brevity we denote simply as $S(\mathbf{k})$,

$$S(\mathbf{k}) = [1/N \sum_i \cos(\mathbf{k} \cdot \mathbf{q}_i)]^2 + [1/N \sum_i \sin(\mathbf{k} \cdot \mathbf{q}_i)]^2 \quad (1)$$

where \mathbf{q}_i is the position of atom i . For the overall $S(\mathbf{k})$, all atoms in the simulation cell are included in the sums in Eq.(1), whereas for the *planar* structure factor, $S_p(\mathbf{k})$, only atoms in a given lattice plane are considered. For an ideal-crystal lattice at zero temperature, $S_p(\mathbf{k})$ then equals unity for any wave vector, \mathbf{k} , which is a reciprocal lattice vector in that plane. By contrast, in the liquid state, without long-range order in the plane, $S_p(\mathbf{k})$ fluctuates near zero.

For the twist GB considered here, the two halves of the bicrystal are rotated relative to one another. A reciprocal-lattice vector lying in a (001) plane in one half of the bicrystal is not a reciprocal-lattice vector in the other half. Two different wave vectors, \mathbf{k}_1 and \mathbf{k}_2 , are thus required to monitor planar order in the two halves. They are related by the relative rotation of the two halves of the bicrystal. For a well-defined lattice plane, say in crystal 1, $S_p(\mathbf{k}_1)$ then fluctuates about a finite value, somewhat less than unity, which is appropriate for the temperature of the crystal, while $S_p(\mathbf{k}_2)$ fluctuates about a value that is essentially zero. In the interface region, due to local disorder, one expects somewhat lower values of $S_p(\mathbf{k}_1)$. By monitoring $S_p(\mathbf{k}_1)$ and $S_p(\mathbf{k}_2)$, every plane may be characterized as (a) belonging to crystal 1 (if $S_p(\mathbf{k}_1)$ is near unity and $S_p(\mathbf{k}_2)$ near zero), (b) belonging to crystal 2 (if $S_p(\mathbf{k}_1)$ is near zero and $S_p(\mathbf{k}_2)$ is near unity), or (c) disordered (if $S_p(\mathbf{k}_1)$ and $S_p(\mathbf{k}_2)$ are both near zero). The vectors \mathbf{k}_1 and \mathbf{k}_2 were chosen, in the present case, to be reciprocal-lattice vectors in the $\langle 100 \rangle$ directions.

Figures 1(a) and (b) show the instantaneous planar structure-factor profile for the GB at 1300 K after 5000 and 10,000 time steps, respectively. At zero time steps, immediately after the temperature has been raised from 1200 to 1300 K, the GB is sharply defined by the crossing of $S_p(\mathbf{k}_1)$ and $S_p(\mathbf{k}_2)$. The intrinsic disorder due to the GB is evidenced by the lower values of the structure factors in the GB region. As time progresses, it is clear from Figs. 1(a) and (b) that a region of disorder forms at the GB and spreads outward. From the linear increase with time of the mean-square displacement of atoms within the disordered region, the diffusion constant is determined to be $4.1 \times 10^{-9} \text{ m}^2/\text{s}$; this value is typical of a molten metal and agrees with the value obtained from an independent simulation of the liquid at that temperature. Further evidence of melting is the overall volume expansion when the entire system becomes disordered. This was investigated at 1400 K. Upon complete disordering, the time-averaged overall volume is found to be $26.69 a_0^3$. This compares well with the value of $26.75 a_0^3$ for a liquid at this temperature, simulated by ordinary 3-d borders, and is significantly greater than the volume of the defect-free ideal crystal at 1400 K ($25.29 a_0^3$).

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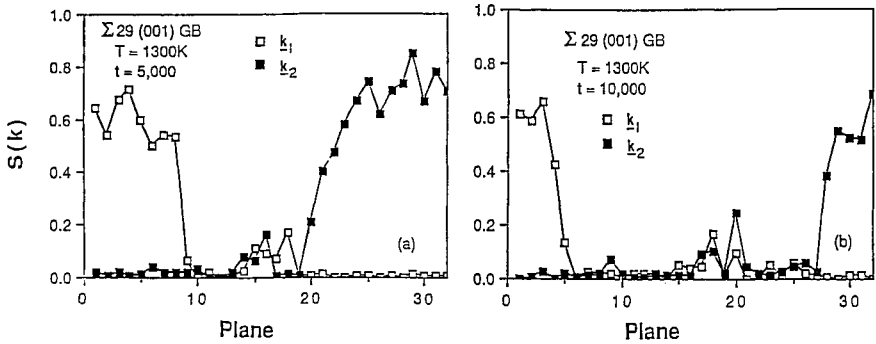


Figure 1. Instantaneous values of $S_p^2(k_1)$ and $S_p^2(k_2)$ defined in Eq. (1) for the 32 slices parallel to the (001) $\Sigma 29$ twist GB (a) after 5000 time steps and (b) after 10,000 time steps at 1300 K.

From this evidence we conclude that above T_m a GB can nucleate the liquid phase which then propagates through the crystal. One might ask whether other extended defects can also act as nucleation centers. To investigate this question, we have studied the effects of voids of various sizes and of a free (001) surface. As discussed in more detail in Ref. 22, both the insertion of a 13-atom void into the simulation cell and the simulation of a thin slab terminated by free (001) surfaces yields the same behavior, namely, the nucleation at temperatures above T_m of the liquid phase at the extended defect, with subsequent spreading of the solid-liquid interface through the crystal. A planar 5-atom void was also investigated, with the result, however, that the void broke up into highly mobile mono- and divacancies without inducing melting during a 20,000 time-step MD run [22].

From the results of our simulations at several temperatures above T_m , propagation velocities for the spreading of the solid-liquid interfaces into the crystalline regions, v , can be extracted. In Fig. 2 these velocities are plotted as function of temperature for the case of the $\Sigma 29$ GB. (Similar plots are obtained for our void and free-surface simulations [22].) Extrapolation of these temperature-dependent velocities to zero velocity should yield an estimate of the coexistence temperature, T_m . The temperature so obtained from Fig. 2 is 1179 ± 20 K, in remarkable

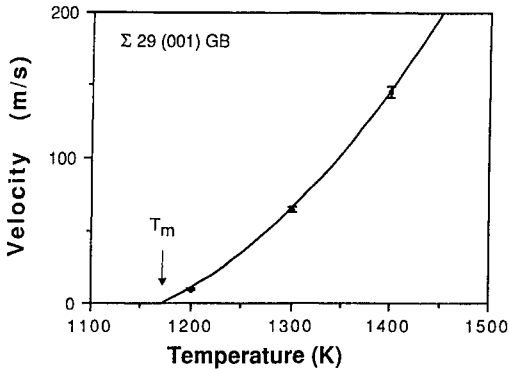


Figure 2. Velocity of propagation of the two crystal-liquid interfaces nucleated at the GB as function of temperature above the thermodynamic coexistence temperature T_m . The solid line shows a quadratic fit to the data points [7,22]. The data obtained for the free surface and the 13-atom void fall on the same curve [22].

agreement with the temperature of 1171 ± 30 K obtained from the free-energy analysis [22]. Equally good agreement was obtained from our simulation involving nucleation of the liquid at the free surface or at the 13-atom void. The time required for nucleation of the liquid at the free surface was found to be much longer, however, than at the GB and at the void [22].

From these results we draw the conclusion that thermodynamic melting of a "real" crystal (i.e., one containing extended defects) occurs via nucleation of disorder at the extrinsic defects with subsequent thermally-activated [7,8,25,26] growth of the liquid phase into the crystal. For a typical propagation velocity of 100 m/s at ~ 150 K above the melting point (see Fig. 2), a single crystal 1mm in diameter, bordered by free surfaces, would thus require a time of the order of 10^{-5} s to melt completely.

2.2 Mechanical Melting

In order to induce the melting transition, some degree of superheating into a range of metastability is obviously needed to drive the phase transformation at finite rate, because exactly at the thermodynamic melting point a solid-liquid interface, nucleated at the extended defects, cannot propagate. With both the nucleation and growth of the liquid phase requiring mobile atoms near extended defects, however, thermodynamic melting may be hindered by either eliminating the nucleation centers or lowering the atomic mobility. The latter may be achieved by lowering T_m , for example, through a hydrostatic expansion of the crystal. As discussed in more detail in Sec. 3, this kinetic hindrance of thermodynamic melting appears to play an important role in solid-state amorphization.

In computer simulations thermodynamic melting is easily suppressed by elimination of extended defects, i.e., by the simulation of a perfect crystal with 3-d periodic borders [11]. Experimentally superheating is extremely difficult even in the most favorable cases due to the presence of dislocations [8,10,18,19]. Over half a century ago Born [12] pointed out the existence of an absolute limit to superheating for any crystalline structure. By considering the volume dependence of the normal modes of a crystal lattice he demonstrated the existence of a phonon instability at a certain critical volume expansion, V_s . By couching the discussion in terms of the elastic response of a crystal lattice under isotropic tension, Born's phonon instability can be shown to correspond to an elastic instability in the minimal shear constant, C' , defined by (for cubic crystals)

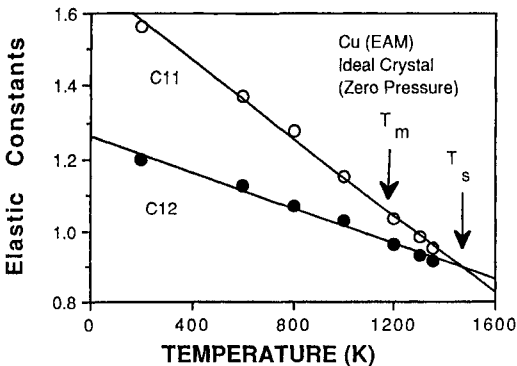


Figure 3. Elastic constants C_{11} and C_{12} (in 10^{12} dyn/cm²) vs. temperature for a perfect crystal containing no extended defects. The solid lines are straight-line fits to the data points. The "stability temperature" is denoted by T_s .

$$C' = (C_{11} - C_{12})/2 \quad (2)$$

i.e., C_{44} expressed in a coordinate system with z axis parallel to $\langle 001 \rangle$ and the x - y axes parallel to the $\langle 110 \rangle$ and $\langle \bar{1}\bar{1}0 \rangle$ directions in which C_{44} assumes its smallest value for any cubic crystal. Born's criterion, when applied to a superheated crystal lattice, establishes the existence of a maximum volume, V_s , coupled with a maximum superheating temperature, T_s , above which the crystal becomes mechanically unstable and therefore has to undergo some kind of phase transformation (to the liquid state or some other crystal structure). The temperature associated with the maximum thermal expansion is referred to as the mechanical melting point, T_s .

Figure 3 illustrates a method for determining T_s from the elastic constants of a superheated perfect crystal. From a least-squares fit to the decrease of the elastic constants C_{11} and C_{12} with increasing temperature, a value of $T_s = 1432 \pm 12$ K is obtained, which is about 260 K higher than the thermodynamic melting point, $T_m = 1171 \pm 30$ K, obtained for the Cu(EAM) potential. The elastic constants in Fig. 3 were obtained from constant-pressure molecular dynamics simulations [27] with evaluation of both the Born and fluctuation contributions [28].

In practice it is very difficult, even in simulations, to reach the maximum superheating temperature, T_s , because of statistical fluctuations in the volume and temperature of the sample. By gradually stepping up the simulation temperature, we were able to superheat a perfect crystal (with the same unit-cell geometry as that used above, however without the GB) to within about 80 K of T_s ; beyond this temperature the crystal could not be stabilized. Figure 4 illustrates how rapidly a perfect crystal melts above T_s . After a step increase of the simulation temperature above T_s to 1700 K, only about 500 MD time steps (or about 10-20 lattice vibration periods) are required to destroy the long-range order within the (001) planes. This evidence suggests that the liquid phase is formed *homogeneously*, as one would expect from a phonon or elastic instability.

In the above discussion we have emphasized the role of the lattice instability in establishing a maximum superheating temperature, T_s , at zero external pressure (see Fig. 3). Because of the thermal expansion accompanying any temperature change, this temperature is related to a maximum volume, $V_s(T_s)$, above which the crystal cannot exist. To see the variation with volume alone, in Fig. 5 the results of Fig. 3 are replotted accordingly, from which the critical stability volume, $V_s(T_s)$, can be extracted. As expected, this volume expansion exceeds that associated with the thermodynamic melting point, $V_m(T_m)$.

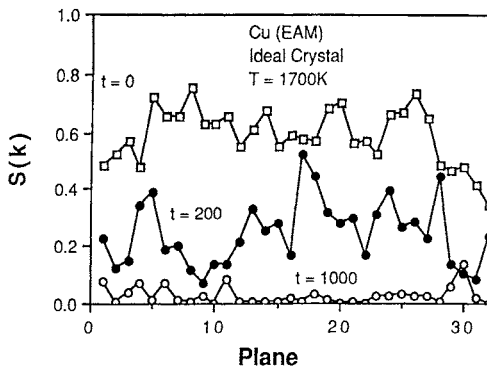


Figure 4. Mechanical melting of a perfect crystal, simulated by use of 3-d periodic borders, after suddenly increasing the temperature from 1300 to 1700 K. The three instantaneous slice-by-slice profiles of the planar static structure factor after 0, 200, and 1000 time steps show that planar order is lost simultaneously in all parts of the crystal.

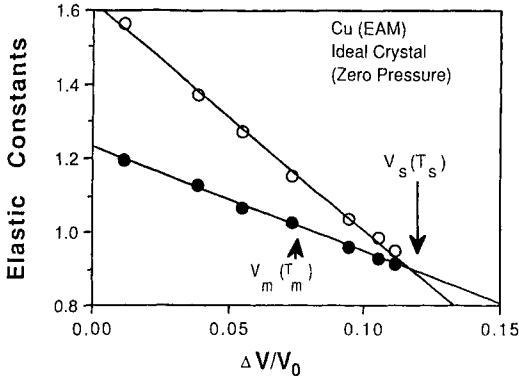


Figure 5. Elastic constants of Fig. 3 replotted vs. relative volume change, $\Delta V/V_0$ [with $V_0=V(T=0)$]. $V_s(T_s)$ is the maximum volume up to which, at $T=T_s$, crystalline order can be sustained. This volume exceeds that associated with the thermodynamic melting point, $V_m(T_m)$.

2.3 Comparison of the Characteristics of Thermodynamic and Mechanical Melting

The above simulations illustrate that every crystal, in principle, has two melting points, T_m and T_s . Conceptually the two transitions have distinct physical origins: whereas thermodynamic melting is governed by the free energies of the liquid and the solid phases, mechanical melting is triggered by a phonon instability. Since the volume expansion required for mechanical melting is always larger than that associated with thermodynamic melting [29], the free energy always favors thermodynamic over mechanical melting; i.e., $T_m < T_s$. However, as illustrated above, the former requires thermally activated atomic mobility and therefore may be kinetically hindered by slow atomic diffusion in the liquid phase. If a crystal is melted under atmospheric conditions (i.e., by conventional heating to melting), the thermodynamic state variables usually will be such that high atom mobility in the liquid enables the nucleation and growth of the liquid phase at extended defects. However, if a crystal is disordered at lower temperature (for example, by uniformly expanding the crystal), the consideration of limited atom mobility as a possible hindrance to phase change by thermodynamic processes may be of significant importance, particularly because atomic mobilities decrease *exponentially* with decreasing temperature but increase only approximately *linearly* with increasing volume. The crystal may therefore not be able to disorder at the volume specified by equilibrium thermodynamics until a larger volume is reached. The largest possible volume is the instability volume, V_s , associated with the ultimate ("mechanical") stability limit, where the crystal structure breaks down without change in volume.

To conclude, we summarize the four main distinguishing characteristics of thermodynamic and mechanical melting.

(a) Whereas thermodynamic melting, characterized by (T_m, V_m) , is based on the free energies of both the crystalline and liquid states, mechanical melting is triggered by a phonon instability in the crystal lattice at a critical volume, V_s , associated with T_s .

(b) Thermodynamic melting requires the existence of extended defects at which the liquid phase can nucleate. By contrast, mechanical melting can occur with and without the presence of such defects, although one would expect that the combination T_s, V_s of thermodynamic state variables needed to trigger the phonon instability depends somewhat on whether or not the system contains extended defects and on the nature of these defects.

(c) The growth of the liquid phase into the crystal (by propagation of solid-liquid interfaces) requires thermally-activated diffusion in the liquid. Mechanical melting, by contrast, is caused by a

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phonon instability, and therefore happens typically within a few dozen lattice vibration periods; i.e., typically within about 10^{-12} sec, without requiring thermal atom mobility.

(d) As a consequence of (c), thermodynamic melting involves relatively slow kinetic processes in contrast to mechanical melting. Also, thermodynamic melting is a *heterogeneous* process, involving nucleation and growth of the liquid phase, whereas mechanical melting takes place *homogeneously*, without the need for the presence of lattice defects.

3. THE T-V PHASE DIAGRAM AND ITS LOW-TEMPERATURE EXTENSIONS

We can summarize our discussion of thermodynamic and mechanical melting by referring to a typical phase diagram of a monatomic system in the T-V plane as shown in Fig. 6. The phase-diagram representation is useful not only for expressing the relation between the thermodynamic variables at the two melting transitions, but also for discussing the underlying thermodynamic basis of the connection between melting and solid-state amorphization.

In Fig. 6 we have drawn the usual phase boundaries delineating the single-phase regions of crystal (C), liquid (L), and vapor (Vap) which, with one exception, require little comment. The condition for thermodynamic melting is expressed by the melting curve, $T_m(V)$, which terminates at the triple-point temperature, T_t . This is the lowest temperature, according to equilibrium thermodynamics, at which the crystal, at a volume V_t^C , can coexist with the liquid (and also with the vapor). The freezing curve, $T_f(V)$, which is in near-coincidence with the mechanical stability curve, $T_s(V)$, and lying more or less parallel to the melting curve, also terminates at T_t , where the liquid has a volume V_t^L .

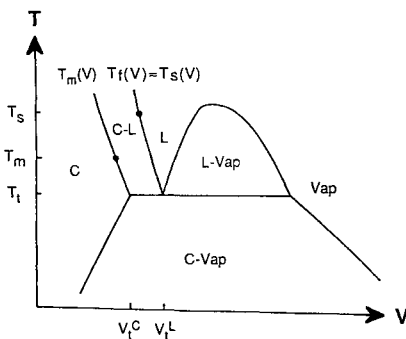


Fig. 6. Schematic temperature-volume phase diagram of a monatomic substance showing the single-phase regions of crystal (C), liquid (L), and vapor (Vap), and the various two-phase regions. On the horizontal triple line, at temperature T_t , the crystal (at volume V_t^C) and the liquid (at volume V_t^L) coexist with the vapor. The points on the thermodynamic melting line, $T_m(V)$, and the freezing curve, $T_f(V)$, indicate conditions of ambient pressure. To a good approximation, the freezing curve and the mechanical-stability line, $T_s(V)$, coincide.

While it is not clear whether the stability and freezing curves, $T_s(V)$ and $T_f(V)$, are the same, we believe they should lie rather close to each other. There also exists experimental evidence pointing to similar values for V_s and V_f [6]. Since in the present discussion it is not necessary to differentiate between the stability and freezing curves, we assume throughout that the two curves coincide.

It has been noted by Tallon [6] that an empirical expression for the variation of C' with volume change, ΔV , for isobaric heating can be written as