History of the search for continuous melting

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The melting of crystals has resisted efforts to understand the microscopic process for more than a century. The course of the struggle has stimulated the development of quantum mechanics, concepts of long-range order, the role of dimensionality in condensed matter, surface physics, and more sensitive experimental techniques to test the theories. After years of probing the mechanism within the bulk material, we learn that the answer has been lying on the surface. [S0034-6861(99)00705-9]

CONTENTS

I. INTRODUCTION

Of all the phenomena exhibited by condensed matter, changes of state are among the most dramatic, and of these melting and freezing are especially striking. These phenomena helped to stimulate the development of classical thermodynamics in the nineteenth century. Liquid-solid phase changes are an important topic in modern undergraduate texts, yet they are rarely discussed in more detail in advanced courses. For many years a deeper understanding of first-order phase changes, in contrast to second-order transitions, did not advance much beyond the macroscopic level. This was not for lack of effort: the history of the search for a theory of melting stretches back more than 100 years. Consequently we have accumulated a great deal of information on the melting of many solids under various conditions [see, for example, Turnbull (1956) and Ubbelhode (1965)]. However, important aspects of the general phenomenon have been discovered quite recently and are still being explored. This review describes some of the significant events in this history.

II. ABRUPT AND CONTINUOUS MELTING

The question *How does a solid turn into a liquid?* can be answered on three levels.

The first level is dismissive. It points out that the melting of crystalline matter is a first-order phase change; it requires a finite latent heat. Liquid and solid can coexist; equilibrium occurs at a unique pressure for each corresponding temperature. Thus the transition is discontinuous. Since there are no intermediate equilibrium states it is hopeless to try to follow the progress of a melting transition.

The second level speculates that the phase change might be continuous or nearly so; given sufficient resolution it should be possible to track the breakdown of the solid throughout its transition to the liquid state. The concept of *one-phase melting* or *continuous melting* takes encouragement from several facts. Melting involves a relatively small increase in volume, typically about ten percent. The heat of fusion is much smaller than the heat of vaporization, so the cohesive energy between molecules is not very different in the two phases. The specific heat does not change greatly across the transition; hence the molecular motions are similar. Taken together, these changes suggest that the transition itself is a relatively mild and possibly gradual change of state. This promise has inspired many investigations and new directions of research in the properties of condensed matter. The history of this approach forms the major portion of this review.

Finally, the third level describes more recent studies, which show that continuous melting does indeed exist; it is typical of virtually all crystals. But rather than being a characteristic solely of the bulk materials, it is also a function of their boundaries.

The concept of continuous melting was inspired by the success of van der Waals' (1873) theory of the liquid-vapor critical point. The theory describes a substance in terms of two parameters: one for the strength of a long-range attraction between molecules, and the other for molecular size. With these fundamentals, vapor-liquid equilibrium can be treated by the methods of classical statistical mechanics. The two-phase system can be tracked into the neighborhood of the critical point,

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where the transition becomes continuous and where the intermediate regime can be studied in detail. Soon after van der Waals presented his thesis it was suggested that solid-liquid transitions might behave in a similar manner, so that a detailed study of the transformation process could be carried out at the end point of the melting line. In one of his earliest papers Max Planck (1882) tried to predict the possible coordinates of a critical point between ice and water. For many years experimentalists subjected a variety of materials to high pressures, extending the liquid-solid phase boundaries to high pressures and temperatures, in the hope of finding critical melting. The quest, which was one of the motivations for high-pressure research (Bridgman, 1952), led to the discovery of many new solid phases, but no solid-liquid end points were found.

III. A MELTING CRITERION

In 1910 Frederick Lindemann proposed a simple model of melting: solids liquefy when the amplitude of atomic thermal vibrations exceeds a fraction of the interatomic spacing. His quantitative model made use of Einstein's explanation of the low-temperature specific heats of solids, which proposed that the atoms vibrate as quantized harmonic oscillators. Einstein's (1907) theory had been published only three years earlier, and its adoption by Lindemann appears to be the first application of quantum theory to condensed matter after Einstein's own paper.

The theory is quite simple. The average thermal vibrational energy is related to the temperature by the equipartition relation, which gives

$$m(2\pi\nu_E)^2(\delta x)^2=kT, \tag{1}$$

where m is the atomic mass, ν_E is the Einstein frequency, δx is the root-mean-square thermal average amplitude of vibration, k is Boltzmann's constant, and T is the absolute temperature. The frequency is related to Θ_E, the characteristic "Einstein temperature" of the low-temperature specific heat, by

$$h\nu_E=k\Theta_E, \tag{2}$$

where h is Planck's constant. Lindemann's basic assumption is that melting occurs when δx reaches a fraction of the nearest-neighbor spacing. The equations combine into a simple expression relating the melting point T_m to properties of the bulk solid: in its modern form.

$$\Theta_D=c[T_m/MV^{2/3}]^{1/2}, \tag{3}$$

where Θ_D is the Debye temperature of the specific heat, M is the molecular weight, and V is the molar volume. The empirical value of c for many simple solids indicates that melting occurs when the root-mean-square displacement reaches about 1/8 of the atomic spacing. But this reasonable and general result should not be allowed to obscure the serious defects of the model. It is based on harmonic forces, which never give way, whereas melting must involve bond breaking. The model describes melting as an individual atomic property, although a phase change is a cooperative process. Furthermore, the model describes melting in terms of the solid alone, although the transition must involve both solid and liquid phases. Nevertheless, the predictive success of the melting criterion lent support to the belief that melting could be a gradual process, beginning within the solid at temperatures below the melting point. Subsequent theories and numerous experiments helped to bolster the idea.

IV. EXPERIMENTAL SEARCHES FOR CONTINUOUS MELTING

A number of studies reported accelerating changes in properties such as heat capacity, density, compressibility, and electrical conductivity as the experimental samples were warmed toward the melting point, which could finally occur in a sharp transition. The gradual changes were attributed to a continuous precursor of the first-order phase change, termed *premonitory melting* (Ubbelhode, 1965). In some experiments there was no apparent discontinuity, so that melting occurred over an appreciable temperature interval. Such results have been interpreted at times as evidence of continuous melting. However, gradual changes near the melting point and broad melting transitions can be due to various forms of disorder. A common cause is dissolved impurities, which produce a progressive shifting of the melting point as the concentrations in the liquid and solid change along the phase boundary. Also, polycrystallinity can shift and spread a sharp transition, due to a combination of grain-boundary energy and size effects, whereas in typical studies of large and well-ordered single crystals the phase change is abrupt to within the experimental resolution.

However, the signals identified as premonitory melting may be due to the intrinsic disorder created by thermal excitations. There are several types, including vibrational modes, point defects such as vacancies and interstitials, dislocations, and, in the case of molecular crystals, orientational defects. Each type has a characteristic excitation energy governing an exponential increase with temperature. These increases cause changes in solid properties that may accelerate on the approach to the melting point, although the crystalline structure remains until the transition itself.

V. DISLOCATION MELTING

The type of thermal excitation most relevant to melting is dislocation, and detailed mechanisms of *dislocation-mediated melting* have been elaborated by many investigators. As described in reviews (Kuhlmann-Wilsdorf, 1965; Nabarro, 1967; Cotterill, 1979), the theory has several appealing features.

(i.) The free energy of a crystal containing a dense array of dislocations is comparable to the free energy of its melt liquid.

(ii.) The fluidity of a liquid can be attributed to the mobility of a dense array of dislocations.

(iii.) The total core energy of a solid saturated with dislocations is comparable to the latent heat of fusion.

(iv.) Pairs of dislocations of opposite sign can be thermally excited at temperatures within the range of typical solids.

(v.) The presence of dislocations lowers the energy of creation of additional dislocations; if the reduction is sufficiently strong it can lead to an avalanche of dislocations in a first-order transition.

A number of experiments and computer simulations have given some support for the theory, but the evidence is not clear enough to conclude that dislocation-mediated melting has been demonstrated. Beginning in the 1970s, hopes of seeing dislocation-mediated melting became focused on two-dimensional matter. Long before then, attention had been drawn to the effects of dimensionality on melting and other disordering transitions.

VI. LONG-RANGE ORDER AND DIMENSIONALITY

A prediction of continuous melting in lower-dimensional systems originated with Rudolf Peierls (1935), who treated the disorder produced by thermal vibrations in one-dimensional (1D) and three-dimensional (3D) lattices. A simple model of a 1D crystal is a regular chain of identical masses connected by identical elastic bonds. The classical array is perfectly motionless at zero temperature. The location of each atom is exact, the nth atom being located at nd, no matter how distant. But at finite temperature, the thermal motion causes a diffuseness in the location of neighbors that increases with distance. To quantify the deviations, consider the separation between two atoms some distance apart; define their instantaneous displacements from the ideal lattice positions by $u_n = x_n - nd$ and $u_m = x_m - md$. The deviation of their separation $\delta_{nm} = (u_n - u_m)$, and a gauge of the average deviation is given by its mean-squared thermal average:

$$\langle \delta_{nm}^2 \rangle = (n-m)^2 d^2 kT/mv^2, \tag{4}$$

where v is the speed of elastic waves. Equation (4) predicts that at finite temperature the precision of position decays monotonically with separation. In the thermodynamic limit *long-range positional order* is destroyed by thermal vibrations as soon as T rises above absolute zero.

In the corresponding 3D model long-range order persists at finite temperature: the displacement does not increase with distance, even as T increases without limit. Furthermore, if the 3D result is combined with the Lindemann hypothesis, which states that melting occurs when the mean-squared displacement reaches a fraction of a lattice spacing, the analysis leads to the original melting criterion. This result answers one of the objections to Lindemann's formulation, since in Peierls's theory the motions are collective.

The two-dimensional case is intermediate: long-range order is destroyed by thermal motion, but much more gradually than in 1D (Frenkel, 1946; Jancovici, 1967; Dash and Bretz, 1972). In 2D the mean-squared displacement grows as the logarithm of the separation distance.

The trend seen in the lattice models of crystals was found to have broader scope: thermal excitations destroy other forms of long-range order in lower-dimensional systems. Peierls's theory was actually anticipated a few years earlier; an analysis of ferromagnetism by Felix Bloch (1930) showed that spin waves destroy long-range ferromagnetic order in a 2D system above zero temperature. Similar results were obtained for long-range momentum order in a 2D Bose gas (Osborne, 1949; Ziman, 1953; Goble and Trainor, 1965) and superfluidity in a 2D Bose liquid (Hohenberg, 1967; Chester *et al.*, 1969).

The predictions of the general effect of dimensionality on various forms of long-range order stimulated strong and continuing interest in models of 2D matter and their physical realizations. With respect to melting in particular, the theory seemed to predict that a 2D crystal would begin to break down at low temperature and would melt continuously until no trace of the structure remained. An extreme view was expressed by Landau (1937), who said that Peierls had shown that one- and two-dimensional crystals could not exist. Frenkel (1946) scoffed, pointing out that long periodic chainlike molecules and large regular sheets of molecules are stable to quite elevated temperatures. Nevertheless, the work inspired the hope of finding continuous melting in lower-dimensional systems. The main question was whether physical realizations of 2D matter existed and, if so, whether they would be amenable to experiment.

VII. PHASE TRANSITIONS IN SURFACE FILMS

Laboratory approximations of 2D matter had been studied since the nineteenth century as monomolecular films floating on water (Pockels, 1891; Gaines, 1966). In these films certain types of rodlike molecules are bound to the water-air interface but are free to move about on the surface. Many exhibit changes from low density to condensed states, analogous to the condensation of ordinary gases to liquids. Some films exhibit structural and orientational transitions, but clear examples of melting transitions have not been observed (Rice, 1985; Dutta, 1991).

One of the limitations of these systems is their restricted temperature range. In the 1950s research on another type of monolayer film, which escapes this limitation, began to show promising features. Gas adsorption on solid substrates had been in use for many years in studies of powders and porous materials (Steele, 1974; Dash, 1975). A common technique was the measurement of adsorption isotherms, whereby the adsorbent is exposed to increasing amounts of gas. With most substrates and gases at moderate temperature the initial quantity of gas is strongly adsorbed, after which adsorption becomes progressively weaker. The initial stage is due to the formation of a strongly bound monolayer. With most substrates the isotherms have no other distinctive features, a smoothness attributed to surface heterogeneity. What was new was the development of more homogeneous substrates that could better approximate the uniform planar surfaces of the theoretical models. One of the most uniform was found to be graphite. A series of studies in the 1960s showed certain features in the course of adsorption of molecular gases on graphite suggesting that the first layer progressed, as the gas quantity increased, through 2D gas, liquid, and solid phases (Thomy and Duval, 1969). To study the two-dimensional nature of these systems in more detail would require methods such as calorimetry that are more sensitive to the thermodynamics within the layer. Using this technique, Goodstein *et al.* (1965, 1968) found that adsorbed monolayers of He^3 and He^4 had low-T heat capacities varying as T^2, the thermal signature of 2D solids (Band, 1955; Dash, 1975; Dash *et al.*, 1993). When heated these films displayed pronounced specific-heat maxima, suggesting broad 2D melting transitions. These results were a surprise (Peierls, 1968, 1979) because it had been thought that a 2D solid would disorder so gradually that there would be no thermal signal. It was then realized that another form of long-range order, the breakdown of which is more relevant to melting, could persist in 2D matter at finite temperatures.

VIII. TOPOLOGICAL ORDER AND TWO-DIMENSIONAL MELTING

David Mermin (1968) analyzed thermal distortions of a harmonic 2D lattice by the directions of bonds between an atom and its neighbors. The *orientational order* of the lattice is treated by considering a closed path along the bonds, enclosing an area of the lattice. As the temperature is raised the path stretches and distorts, but as long as the bonds do not break the path remains closed: the topology is constant. Thus, although thermal motion destroys long-range positional order at $T>0$, long-range orientational order persists. In physical terms the two types of order are related to two distinct qualities: crystal structure and elasticity. The loss of positional order can be seen in the weakening of x-ray diffraction lines as the crystal is heated, but the solid does not melt as long as the network is intact. Melting requires ruptures, so that the atoms can be rearranged: a liquid can be *stirred*.

Soon after, Michael Kosterlitz and David Thouless (1972, 1973) proposed a fundamental theory of the thermal breakdown of long-range topological order and related their basic theory to the transitions of two-dimensional crystals, superfluids, and magnets. Their theory of melting treated Mermin's description of orientational order with more realistic interactions, permitting dislocations. Thus the theories of dislocation melting and concepts of lower-dimensional order were brought together. A disruption of the closed path occurs when the area encloses a dislocation. At low temperature there are no isolated dislocations, but they can be created as the temperature rises, by the dissociation of oppositely directed bound dislocation pairs. This occurs at an estimated critical temperature

$$T_c = \nu b^2(1+\tau)/4\pi k_B \,, \tag{5}$$

where ν and τ are the two-dimensional rigidity modulus and Poisson's ratio, respectively. A similar theory was proposed independently by Richard Feynman (1972) but was never published.

The transition temperature given by Eq. (5) is an upper limit because it ignores the effect of other dislocations in the system. These other pairs will relax in the strain field of the first pair, thereby renormalizing the rigidity modulus downward and consequently reducing the critical temperature. Kosterlitz and Thouless found that a mean-field model yielded a very weak singularity.

The theory was greatly extended and detailed by Halperin and Nelson (1978) and Young (1979), who predicted that the complete transition from solid to liquid could take place in two steps. Dissociation of dislocation pairs could drive a crystal with long-range orientational order into a "liquid-crystal" phase that retains finite-range orientational order. A second transition at higher temperature would complete the transition to an isotropic liquid. The theory gave detailed predictions of the behavior of the specific heat, the structure factor, and elastic constants. The theory was also extended to the case of melting on structured substrates. The theory and its applications are discussed in several reviews (Nelson, 1983; Morf, 1984; Strandburg, 1988; Glaser and Clarke, 1993; Gulacsi and Gulacsi, 1998).

IX. EXPERIMENTS AND COMPUTER SIMULATIONS

The novel and detailed predictions of the theory stimulated experimental tests and computer simulations in laboratories all over the world. In the years since the 1960s the quality of substrates had improved, so that adsorbed monolayer films could more closely approximate the two-dimensional matter of the theoretical models. With these substrates it was also possible to apply many of the experimental probes used in studies of bulk condensed matter to the adsorbed films and other forms of quasi-two-dimensional matter. It was found that some special systems, especially electrons on the surface of liquid helium, liquid-crystal films, and some computer models, display aspects of dislocation-mediated melting, either by continuous transitions or by gradual changes of structure followed by a first-order transition (Morf, 1979; Guo *et al.*, 1983; Toxvaerd, 1984; Glattli *et al.*, 1988; Murray *et al.*, 1990; Simon *et al.*, 1992; Bagchi *et al.*, 1996; Chao, 1997; Sikes and Schwartz, 1997; Somer *et al.*, 1997). The clearest case of two-stage melting to date was exhibited in a film of paramagnetic colloidal particles (Zahn, 1999).

But melting in many other experimental systems and computer simulations is first order (Abraham, 1981; Broughton *et al.*, 1981; Phillips *et al.*, 1981; Bruch *et al.*, 1997; Thouless, 1998). The reason seems to be that the first-order phase change preempts the continuous transition. Most molecular systems and some computer models include physical properties, such as anharmonicities and vacancies, that may be absent or unimportant in simpler or more specialized systems and that can lead to mechanisms that circumvent continuous melting. One such mechanism is grain-boundary melting, which was proposed many years earlier in the dislocation theory of melting of bulk matter (Mott, 1939). Since a grain boundary consists of an array of dislocations, grain-boundary excitation depends on the energy of dislocations. Chui (1982, 1983) and Saito (1982) found that melting could be either continuous or first order depending on the size of the dislocation core energy relative to the elastic constants. A continuous dislocation-mediated transition requires a low density of dislocations, which presumes a relatively high core energy. If it is too low, the dislocation density will rise dramatically, leading to an avalanche. The liquid state can also intervene when the dislocation energy is too large. As the crystal is heated its free energy increases until it crosses the trajectory of the free energy of the liquid, so that continuous melting is preempted by the first-order phase change.

However, a completely different kind of continuous melting can occur in both two-dimensional and three-dimensional matter. Indeed, it appears to be the principal mode of melting for virtually all crystalline materials, as described below.

X. SURFACE MELTING

The importance of the surface in melting was suggested by Tammann (1910) in the same year that Lindemann proposed his criterion. *Surface melting* was deduced by Stranski (1942) from the absence of superheating in melting. In general, superheating or supercooling in a transition is associated with the birth of the new phase, due to the interfacial energy between the new phase and its parent. This requires the temporary excursion of temperature, pressure, or other thermodynamic variable to initiate condensation from the vapor, boiling of a liquid, or crystallization from the melt. But in contrast to these transitions, melting requires no superheating. Frenkel (1946) reasoned that the liquid begins early:

> It is well known that under ordinary circumstances an overheating (of a crystal), similar to the overheating of a liquid, is impossible. This peculiarity is connected with the fact that the melting of a crystal, which is kept at a homogeneous temperature, always begins on its free surface. The role of the latter must, accordingly, consist in lowering the activation energy, which is necessary for the formation of the liquid phase, i.e., of a thin liquid layer, down to zero (Frenkel, 1946).

The deduction seemed plausible, but it remained untested until techniques became adequate to prepare well-ordered crystal surfaces and to detect extremely thin layers of the incipient liquid. Surface melting has now been observed in many classes of solids. Several reviews discuss the theory, experiments, and computer simulations.[1]

Surface melting is a consequence of the wetting of a solid by its melt liquid, which occurs when the surface energy of the combined solid-liquid-vapor interface is lower than that of the ‘‘dry’’ solid. The reduced surface energy makes it advantageous for a thin layer of the solid to *premelt* at temperatures lower than the bulk transition. Not all facets are wetted by the melt liquid (Pluis *et al.*, 1987), but since typical crystals have some facets that are wetted, premelting is the general rule (Metois and Heyraud, 1989). Premelting can also occur at boundaries between the solid and the vapor (‘‘surface melting’’), between two materials (‘‘interfacial melting’’), and between crystallites of the same substance (‘‘grain-boundary melting’’). Most experiments have been carried out near equilibrium. But even when a solid is heated suddenly, melting still tends to be initiated at the surface (Häkkinen and Landman, 1993). Under some conditions it is possible to force the solid to break down internally, but then the melting will tend to begin at internal interfaces such as grain boundaries.

Theoretical aspects of surface melting have been studied by classical phonon theory, lattice models, phenomenological Landau theories, and a Kosterlitz-Thouless approach. Density-functional theory (Löwen, 1994; Ohnesorge *et al.*, 1994) and computer simulations (Abraham, 1982; Phillips, 1990; Häkkinen and Manninen, 1992; Landa *et al.*, 1995) are particularly revealing of interfacial features. They show that, as surface melting proceeds, the short-range structure of the interface evolves gradually from the crystalline order to liquidlike disorder. As the melting point is neared, the melted layer grows into a thick film, which in its upper layers is indistinguishable from the liquid phase but which retains some solidlike order within a few molecular distances of the solid interface. The transitional zone has been explored experimentally by measurements of the heat capacity during melting of adsorbed rare-gas multilayers (Zhu *et al.*, 1988), showing that the latent heat of melting evolves gradually with distance from the solid interface. The results are in general agreement that solidlike order extends into the melt to distances of several molecular diameters.

Theory predicts that the temperature at which premelting begins and the temperature dependence of the film thickness are controlled by the interactions within the system. In van der Waals solids, premelting typically begins at a reduced temperature $t=(T_m-T)/T_m<0.1$, and the film thickness increases as $t^{-1/3}$ close to T_m. The power law has been confirmed by experiments on rare-gas films (Zhu and Dash, 1986). In many metals the thickness typically varies as $|\log(t)|$, which is the tem-

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[1] See, for example, Nenow (1986); van der Veen *et al.* (1988); Dash (1989); Oxtoby (1990, 1998); Schick (1990); Bienfait (1992); Dash *et al.* (1995); Wettlaufer (1999).

perature dependence characteristic of short-range interactions (Frenken and van der Veen, 1985).

Surface melting has a lower-dimensional analog, called *edge melting*. In a number of experiments and computer studies, the melting of a 2D solid was found to begin gradually, at its boundaries (Abraham, 1981; Shechter *et al.*, 1990; Feenstra *et al.*, 1992; Pengra and Dash, 1992). The physics of edge melting is essentially the same as that of surface melting, except for changes of critical exponents due to dimensionality. Similarly, lower-dimensional equivalents of interfacial and grain-boundary melting should occur. Indeed, grain-boundary melting has been shown to produce a first-order transition in 2D matter whenever the grain boundary is coupled to a density change (Chui, 1982, 1983).

The story of surface melting is not yet complete. Still to be explored is the evolution of lateral structure. In the layer nearest to the solid there is considerable epitaxy, where the crystal structure of the solid is impressed on the layer. The density and structure of further layers must evolve stepwise toward that of the liquid. One possible way is through the development of two-dimensional domains of epitaxial structure, separated by disordered grain boundaries of increasing thickness. Such an evolution can be inferred from some computer simulations and perhaps someday might be seen in experiments on real matter.

XI. CONCLUSIONS

The effort to understand the microscopic mechanism of melting has intrigued scientists since the late nineteenth century. Although major progress has been made quite recently, the long struggle has helped to bring about many of the developments in modern condensed matter and statistical physics. Collective phenomena and phase transitions, crystal growth, surface physics, and computational techniques have all benefited from the challenges to understand and to test the theories. We are now able to use all of these fields to probe deeper into the question. But although a gradual microscopic change from solid to liquid has finally been found in surface melting, significant details of the transition are still incompletely known. We can expect that the struggle to complete the picture will continue to stimulate the further development of physical science.

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