

Molecular Dynamics Study on Atomistic Details of the Melting of Solid Argon

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ABSTRACT

The atomic scale details of the melting of solid argon were monitored with the aid of molecular dynamics simulations. The potential energy distribution is substantially disturbed by an increase in the interatomic distance and the random offset distance from the lattice points, with increasing temperature. The potential energy barriers between the lattice points decrease in magnitude with the temperature. Eventually, at the melting point, these barriers can be overcome by atoms that are excited with the entropy gain acquired when the atoms obtain rotational freedom in their atomic motion, and the rotational freedom leads to the collapse of the crystal structure. Furthermore, it was found that the surface of crystals plays an important role in the melting process: the surface eliminates the barrier for the nucleation of the liquid phase and facilitates the melting process. Moreover, the atomic structure of the surface varies with increasing temperature, first via surface roughening and then, before the bulk melts, via surface melting.

Key words : Melting, Liquid, Molecular dynamics, Crystal, Surface

1. Introduction

Melting is a fundamental process by which a crystal changes from a solid phase to a liquid phase. Despite the common occurrence of this process, the task of understanding it remains a challenge. The various melting theories proposed during the past century³⁻⁸⁾ are reviewed in Ref. 1. The first theory on the melting mechanism of a crystal bulk was proposed by Lindemann,³⁾ who used the vibration of atoms in the crystal to explain the melting transition. Lindemann postulated that solids liquefy when the amplitude of their atomic thermal vibrations exceeds some fraction of the interatomic spacing. The average amplitude of the thermal vibrations increases when the temperature of the solid increases. The melting process is initiated at some point where the amplitude of the vibration becomes so large that the atoms start to invade and disturb the space occupied by their nearest neighbors.¹⁾

Another theory of bulk melting was suggested by Born in 1937.⁵⁾ The Born theory is based on the fact that a liquid differs from a crystal in that it has zero resistance to shear stress, that is 'loss of shear rigidity'. According to this theory, the distances between the atoms in a solid are increased by thermal expansion and, as a consequence of this expansion, the restoring forces between them are reduced. The decrease in the shear elastic moduli is there-

fore caused by the rise in temperature. The softening of the shear moduli reportedly leads to the mechanical instability of the solid structure and, eventually, to the collapse of the crystal lattice at a particular temperature.^{1,6)}

Previous models on the theory of melting⁷⁻¹⁰⁾ also include the notion of spontaneous thermal proliferation of intrinsic lattice defects (namely vacancies,⁸⁾ interstitials,⁸⁾ dislocations,⁹⁾ and disclinations¹⁰⁾ near the melting point, and this proliferation promotes the melting transition by breaking the long-range crystalline order. The formation of a lattice defect in a crystal requires the displacement of an atom (for point defects) or a group of atoms (for dislocations and disclinations) from its or their lattice sites and, thus, requires a certain activation energy of formation.¹⁾ According to these models, however, at temperatures close to the melting point, the defect formation energy can be greatly reduced, relative to the formation of isolated lattice defects, through the 'cooperative' formation of lattice defects. This kind of crystal disorder is subject to the condition that the appropriate sequence of neighboring sites be displaced cooperatively from the ideal lattice positions.¹⁾

For a solid at low temperature, the equilibrium concentration of the defects is quite small, which means the defects are isolated from each other. The cooperative effect is therefore negligible. However, this effect is amplified when the concentration of defects increases and, as a result, the insertion of more defects becomes easier as the temperature increases. At some critical concentration of defects, the lattice of the solid becomes unstable and collapses; that is, a mechanical melting transition occurs.¹⁾

However, most theoretical models of melting are phenom-

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enological in nature and rough in their description of the transition. Furthermore, the stability criteria say nothing about the final state toward which a structurally unstable system will evolve. Moreover, the theoretical models fail to clarify how the melting criterion can explain the presence of the latent heat and volume change associated with a first-order thermodynamic phase transition. Nonetheless, in spite of their shortcomings, these models are still used to estimate the melting temperature, due to the lack of a more precise melting theory.¹¹⁾

Most theoretical models also neglect the atomistic details of the phenomenon. There is no generally accepted picture of how solids melt at an atomistic level, even though it is a fundamental phenomenon in nature. The reason for this lack of understanding is that in experiments it is not yet feasible to directly observe the atomistic details of the process. Thus, the structural arrangements of the atoms and their characteristic motions before and during the melting process are still poorly perceived. The general understanding of the microscopic or atomic level processes of melting is incomplete, and atomistic models that describe the structure of the liquid state are unavailable. Molecular dynamics (MD) simulation enables the physical properties of atoms to be tracked not only as global averages but also locally. This capability is indispensable for exploring the correlation between the theories and the atomic-level mechanisms at the onset of melting.^{12,13)} Computer simulation is thus a very useful means of understanding the 'atomistic mechanism' of melting. For this reason, various computer simulation studies have been conducted on this topic.^{12,13)}

For a complete understanding of the melting process, however, all the relevant processes, including the arrangements of the atoms and their evolution during the melting process, should be explored comprehensively on an atomic scale. Furthermore, this data should eventually be coupled with macroscopic information for a better understanding of the thermodynamic behavior of the system. The aim of this study is therefore to provide the atomistic details of the melting process, to suggest a possible scenario of melting, and to explore the common structural features at the instant when melting begins.

2. Simulation

A model system composed of argon atoms that interact with each other via Lennard-Jones (LJ) pair potentials was chosen for this study. Various aspects of the argon-based system have been studied extensively.^{14,15)} As a consequence, the parameters for this simulation as well as comparisons with previous studies are readily available.

The LJ interatomic potential used in this simulation is characterized by a length, σ , of 3.405 Å and a minimum energy, ϵ , of 119.8 k_B (where k_B is the Boltzmann constant). These values, which were determined in Ref. 14, enable the

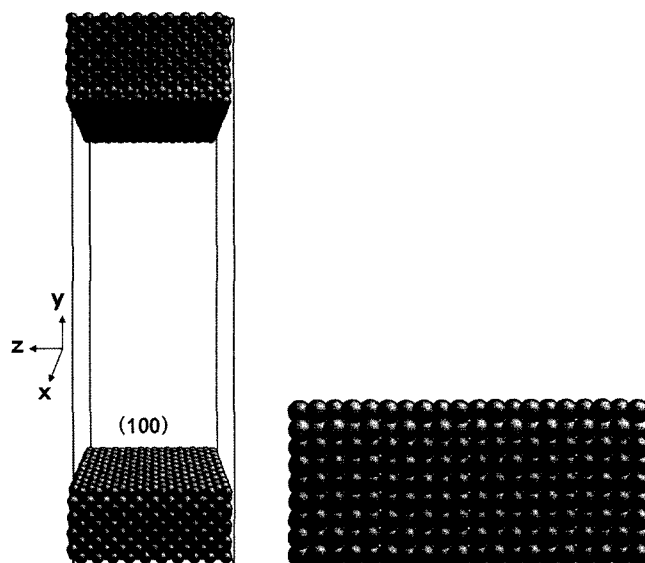


Fig. 1. Atomic arrangement of the simulation box used in this study. The three-dimensional view on the left of this figure clearly shows how the atoms are arranged, while the two-dimensional projection view on the right describes the perfectness of the arrangement in the box. The gray scale of the individual atoms in the figure represents their potential energy; hence the higher energy state of the surface atoms is easily recognized, as would be expected.

potential to fit the experimental properties. Furthermore, this potential has been used in many different simulations and is known to be quite reliable. A cut-off radius of 4.1σ was also applied.¹⁵⁾

The simulation was carried out on a rectangular block whose three-axes are parallel to the $\langle 100 \rangle$ crystallographic directions of a solid argon crystal. As shown in the simulation box in Fig. 1, the Ar atoms are arranged in a face-centered cubic (FCC) structure with a lattice parameter of 5.256 Å. The size of the block, which contains 4000 atoms, is $52.56 \text{ Å} \times 177.56 \text{ Å} \times 52.56 \text{ Å}$. Periodic boundary conditions were applied in all directions. The way the surface affects the melting was investigated by introducing the surfaces into the simulation block as follows: the block is divided into two pieces at its center through the plane parallel to the x - z plane, and the upper piece is shifted by as much as 125 Å along the y -axis.

The atoms in the block are then simulated under the constraint of an NPT ensemble (constant pressure and constant temperature) for several nano seconds (ns) with the IMD molecular dynamics simulation package*. The molecular dynamics simulations were done while the crystal was heated at a constant pressure. The temperature was controlled by a rescaling of the velocities of the atoms. For this purpose, a Verlet algorithm was used with a time step of

*IMD (The ITAP Molecular Dynamics Program), <http://www.itap.physik.uni-stuttgart.de/~imd/>

0.002 ps (pico seconds) under an external pressure of 1 atm. The heating from 0 K to 130 K was done in a step-by-step procedure. The heating rate was 10^{-4} K per MD step, which is equivalent to a heating rate of 50 K/ns.

3. Results and Discussion

Given that the key features of melting are the presence of latent heat and a change in volume, the variations in the potential energy per atom and the atomic volume were monitored, as shown in Figs. 2(a) and 2(b), in relation to the increasing temperature. The first-order melting transition manifests itself at a melting temperature at which both the average potential energy per atom and the mean atomic volume undergo sudden upward jumps, as noted in Figs. 2(a) and 2(b), regardless of the presence of the surface.

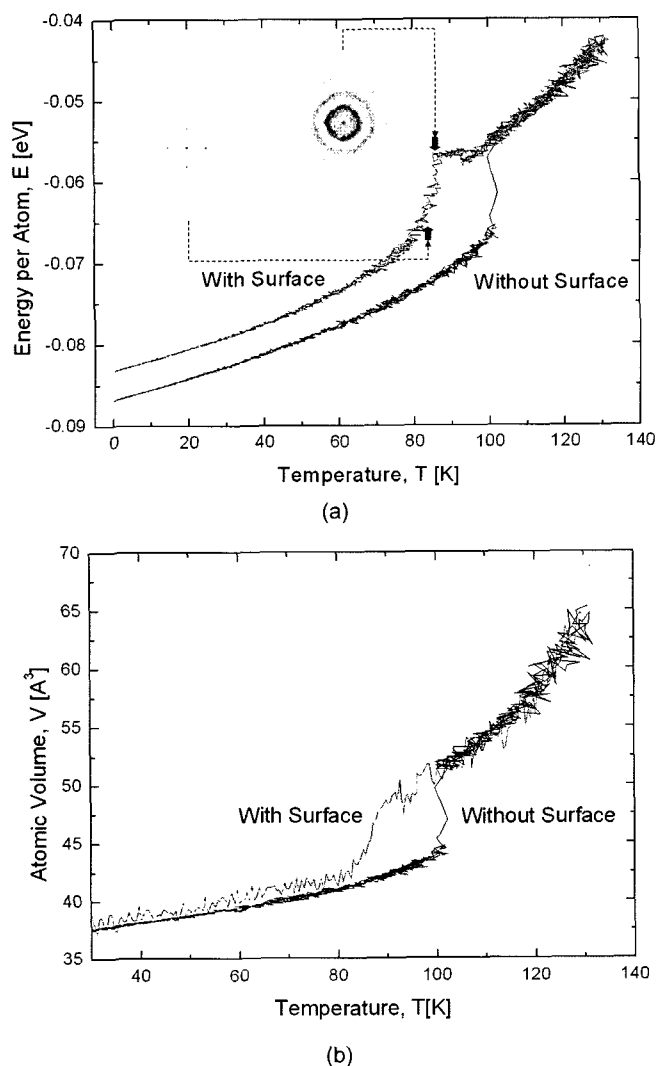


Fig. 2. Variations of the (a) potential energy per atom and (b) atomic volume with temperature for crystals of finite size (with surface) and of infinite size (without surface).

However, as expected, the presence of the surface greatly influences the melting behavior of the crystal. The melting temperature of a finite size crystal, T_m (which is the actual melting temperature or the so-called thermodynamic melting temperature), was estimated to be 85 K. This temperature is fairly close to the experimental melting point of 83.8 K. In contrast, the melting temperature of an infinite crystal, T_b , which is called the bulk melting temperature, was estimated to be 101 K. These results confirm that the surface can promote melting and trigger the melting process earlier. The surface lowers the melting temperature by as much as 16 K, that is, from 101 K to 85 K. The results also highlight the importance of the surface in initiating or nucleating melting, as well as the possibility that it may cause the crystal to become disordered (or lose its long-range order) at temperatures below the bulk melting point.

The melting of crystals begins at the surface because the activation energy for the formation of a liquid phase is lower at the surface than in the bulk.^{16,17} The liquid layer at the surface eliminates the barrier for the nucleation of the liquid phase and, thus, no meta-stability effects (superheating) exist.^{16,17} It has been reported¹⁸⁻²⁰ that this thermodynamic melting process can be suppressed experimentally if the surface is eliminated; for example, by coating one material with another one with a higher melting point. In this way, silver coated with gold was superheated by 25 K above its T_m . Because bulk melting models consider melting as a process that occurs homogeneously throughout the crystal, they usually overestimate the melting temperature. Real crystals, which are finite and always have boundaries, start to melt from the surface at a temperature that is lower than the temperature predicted by the theories of bulk melting.

The diffraction patterns at 84 K and 86 K, inserted in Fig. 2, show that the long-range order of the crystal vanishes at 85 K and, as a consequence, the melting transition occurs at this temperature, which is exactly coincident with the sudden jump in the potential energy and volume. The diffraction patterns were computationally generated by a Fourier transform of the atomic arrangements obtained at each temperature. On the other hand, the difference in potential energy, as shown between the two lines in Fig. 2(a), is attributed to the excess energy of the atoms in the surface region.

Fig. 3 shows the radial distribution of the atoms; that is, the radial distribution functions calculated from the atomic arrangements just before and after melting. Further evidence of melting can be found in the clear observation that the long-range order (peaks at long distances) vanishes. For the purpose of comparison with the experimental properties of melting, the volume change and the latent heat of fusion were calculated from the magnitudes of the relevant jumps observed in Fig. 2 and estimated to be 18.7% and 1084 J/mol, respectively. These values are very close to the experimentally determined values, namely 15.2%²¹ and 1180 J/mol.²²

The thermodynamic parameters which characterize the

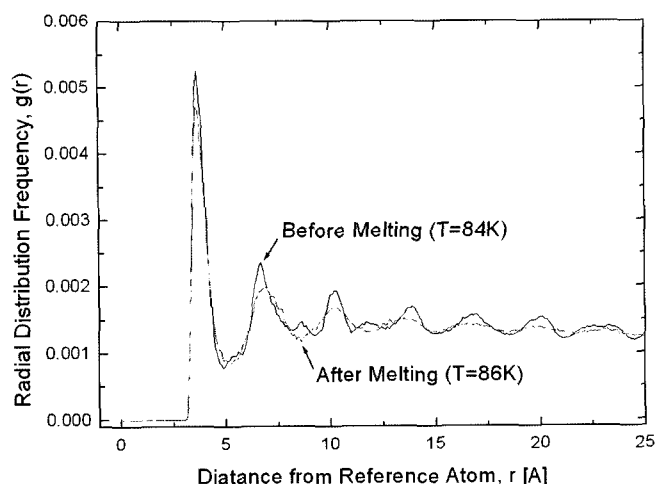


Fig. 3. The radial distribution function, $g(r)$, as calculated from the atomic arrangements of the simulation blocks before melting ($T=84$ K) and after melting ($T=86$ K).

melting process (ΔH_{fusion} , ΔS_{fusion} , ΔV_{fusion} , and so on) have been well established for most monatomic and diatomic sol-

ids.¹⁹⁾ Detailed discussions of the thermodynamics of melting are available,²³⁾ along with some improvements of the thermodynamic data.²⁴⁾ However, the kinetics of melting, or the mechanism by which the melting interface moves into the bulk of the solid, has been investigated to a much lesser extent.

The atomic arrangements were monitored in relation to the increasing temperature for the purpose of investigating the kinetics or mechanisms of melting. Figs. 4(a) to 4(d) show the results of the monitoring. Each of these figures includes both a three-dimensional view of the entire simulation block on its left side and a two-dimensional projected and magnified view of the lower portion of the block on its right-hand side. As can be seen, the arrangement of the surface atoms is already disturbed at the low temperature of 48 K. The atomic structure of the surface seems to start its transition from smooth to rough arrangements, and this tendency becomes greater as the temperature increases, as seen in Fig. 4(b), where the surface structure is quite rough in terms of its atomic arrangement. Furthermore, the vaporization of argon starts even at temperatures well below its melting point, for example 73 K, which does not

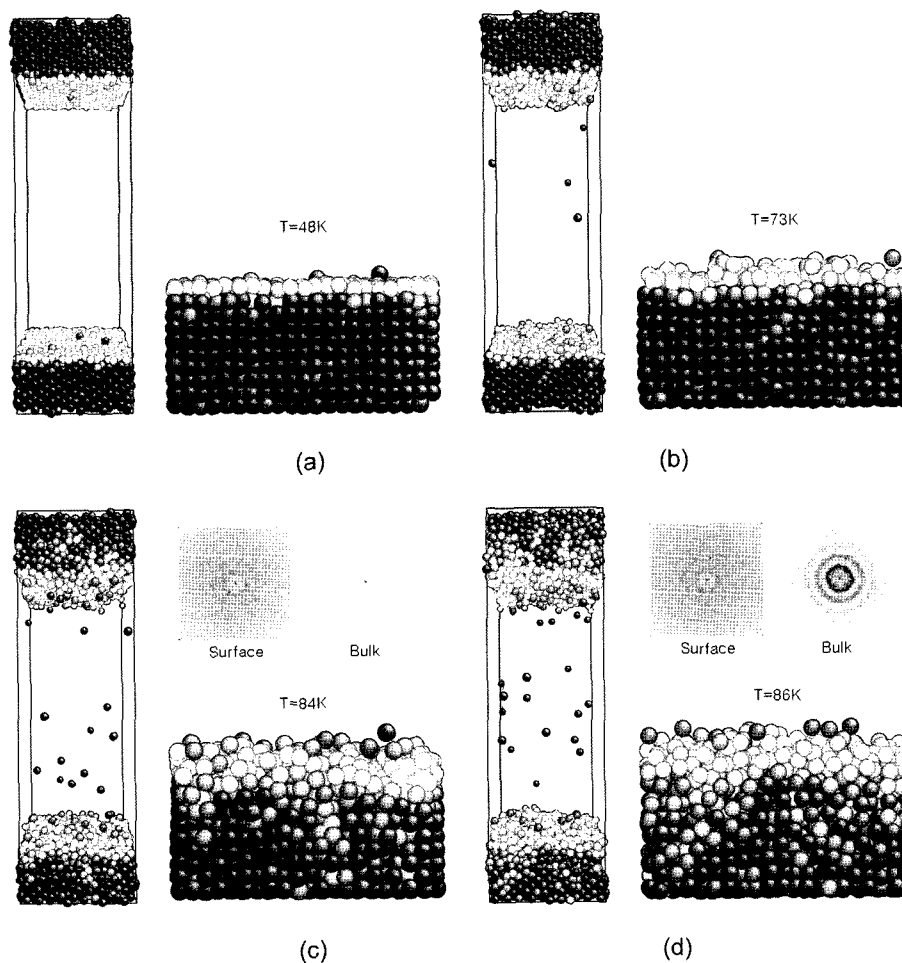


Fig. 4. A three-dimensional view of the entire simulation block and a two-dimensional projected view of the lower part of the block, at various temperatures designated in the respective figures. The diffraction patterns for the surface and the bulk regions of the simulation block are included for the block (c) just before and (d) just after melting.

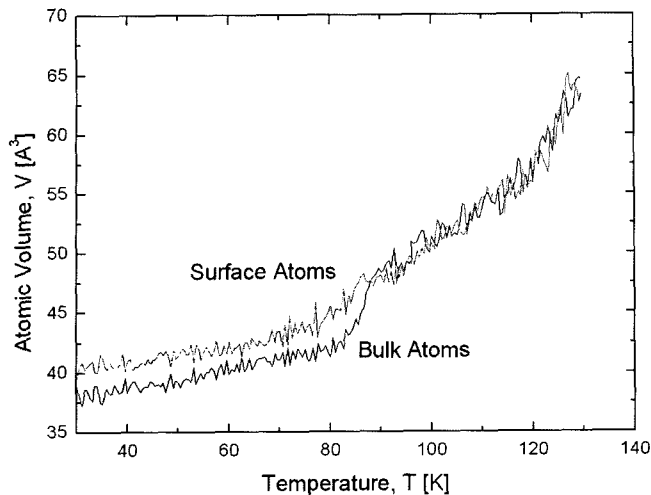


Fig. 5. Variations of atomic volume with increasing temperature for surface atoms and bulk atoms.

conflict with nature. Note that some water molecules vaporize at room temperature under ambient conditions.

Besides the surface roughening with the increasing temperature, the surface starts melting before the melting of the bulk. Fig. 4(c) shows the atomic arrangement of the block and the diffraction patterns for both the surface and bulk at 84 K, which is below the melting point. According to the diffraction patterns, the surface atoms (namely the atoms within 25 Å or approximately five atomic layers from the surface) lose their long-range order, whereas the atoms in the bulk still possess their long-range order. This result indicates that the melting starts at the surface (or is triggered by the surface) and that the melting temperature at the surface is much lower than the thermodynamic melting point. Up to the melting point, the crystal seems to be coated with a very thin liquid layer composed of several atomic layers. This speculation is also confirmed by the variations in the atomic volume with the increasing temperature for the surface atoms and bulk atoms. As shown in Fig. 5, the transition (or sudden jump) of the atomic volume for the surface atoms occurs at a lower temperature than that for the bulk atoms, which means that the surface atoms experience melting at a lower temperature than the bulk atoms.

For a crystal of infinite size (crystal without a surface), melting inevitably occurs homogeneously throughout the crystal. Such homogeneous, simultaneous melting throughout the crystal is usually called mechanical melting (or bulk melting). Fig. 6 shows the atomic distributions time-averaged over 10000 MD steps (20 ps) and the corresponding diffraction patterns of the crystals at 98 K and 102 K. These results indicate that bulk melting occurs simultaneously throughout the crystal at 101 K. However, a question still remains. How does the infinite perfect crystal melt? Although the melting of the crystal is unreal, it first needs to be understood so that the actual mechanism of melting can be determined.

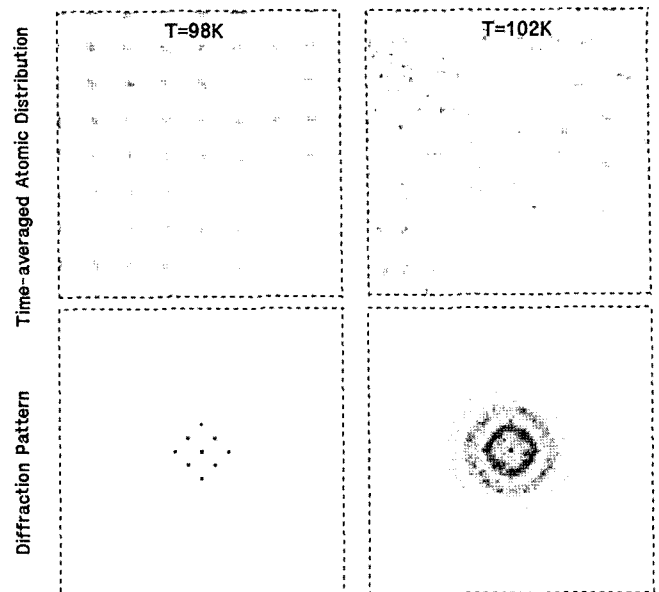


Fig. 6. Atomic positions averaged over 10000 MD steps (20 ps) before bulk melting ($T=98$ K) and after bulk melting ($T=102$ K), and their respective diffraction patterns.

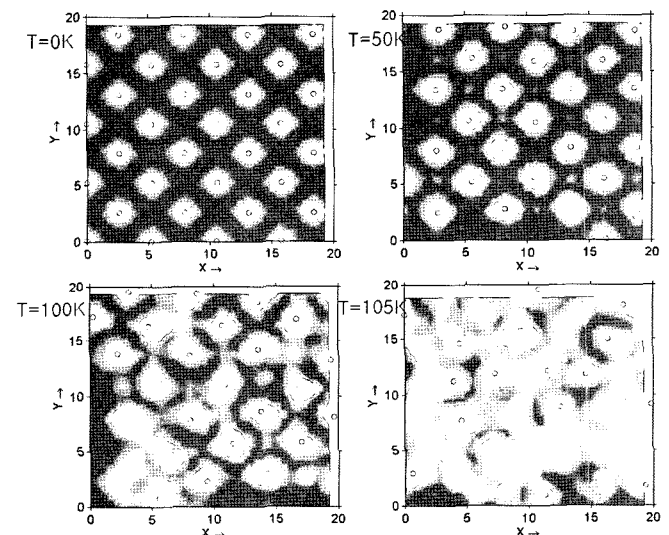


Fig. 7. Spatial distributions of potential for atoms over the whole space of the crystal and the resultant atomic arrangements at 0 K, 50 K, 100 K, and 105 K, where the marker 'o' represents the atoms.

The plots in Fig. 7 are the spatial distributions of the potential (energy) for the atoms over the space of the crystal and the resultant atomic arrangements at 0 K, 50 K, 100 K, and 105 K, respectively. The darker the gray scale, the higher the potential. Note that the potential is a 'functional' of the atomic arrangement; that is, the potential at a point is determined by the atomic arrangement around the reference point and the atomic arrangement is again determined by the distribution of the potential around the point, as a consequence of the mutual determinations (or interactions) between them. Hence, the potential variation is quite sensi-

tive to the atomic environment around the point of concern, and vice versa.

At low temperatures, for example 0 K or 50 K, the potential barriers between the atoms are periodic and quite large in terms of their height; thus, the atoms that reside at each potential well are confined to vibrating at their lattice points. However, as the temperature increases, the anharmonicity of the lattice vibration causes the interatomic distance to become longer and the resultant effect on the potential and its distribution cannot be neglected. The ensuing appreciable increase in both the interatomic distance and the random offset distance of the vibrating atoms from their equilibrium lattice points produces substantial disturbances in the potential distribution.

At a quite high temperature but below the melting point, for example 100 K, the potential distribution, as seen in Fig. 7, is remarkably disturbed by the thermal vibration of the atoms. As a result, the height of the barrier for atomic displacement, which involves the deviation of the atoms from their lattice points, becomes smaller. Furthermore, because the potential energy of an atom at a point is the sum of the interactions with all other atoms in the system, the increase of the average interatomic distance with increasing temperature and the resultant weak interaction give rise to a shallow potential energy well. Even though the potential distribution is substantially disturbed, however, the potential barrier is still present between atoms arranged in a regular and periodic fashion. Thus, the periodicity in the atomic arrangement remains intact at this temperature.

On the other hand, every natural system always tries to increase its entropy by allowing atoms to gain freedom in their motion, for the purpose of minimizing its free energy. The available motions of the atoms in a system include translation, rotation, and vibration relative to other atoms. However, due to interactions between atoms, there is a restriction in the atomic motion and in the resultant maximization of the entropy. The structure of a potential energy well that is formed as a consequence of such interactions limits the atomic motion to vibration in a crystalline state. It has been geometrically demonstrated²⁹⁾ that an additional homogeneous volume expansion, with the exception of thermal expansion, is required for the rotational freedom of atomic motions in the crystalline state, though this demands a huge amount of energy to be expended and thus cannot be realized at low temperature. However, as the temperature increases, the energy that needs to be expended (ΔU) is reduced due to the anharmonic vibration of the atoms, as pointed out in the previous paragraph; in contrast, the entropy gain ($T\Delta S$) upon the acquisition of rotational freedom grows, as would be expected.

Once the energy expense can be compensated by the entropy gain ($T\Delta S$), the atoms in the system come to be thermodynamically more stable in the state that possesses rotational freedom than in the crystalline state. The sudden jump in volume at the moment of melting, as shown in Fig. 2(b), is attributed to the additional volume expansion that

accompanies the acquisition of this rotational freedom, as mentioned above. Due to this newly found rotational freedom, the atoms lose their periodic atomic arrangement, though their interatomic distance remains close to that in the crystalline state; that is, the crystal structure collapses and then melting occurs. This phenomenon is the reason why a liquid has a similar density to that of its solid form despite having a random structure in terms of its atomic arrangement. Furthermore, atoms that possess such freedom may reach anywhere in the system by successive rotational motion relative to the others. This mechanism seems to be the basis of the atomic movement in a liquid and the reason for its fluidity. In the last plot in Fig. 7, which shows the potential distribution at a temperature above the melting point, such as 105 K, the barrier for atomic movement vanishes, thereby yielding a random structure in terms of the atomic arrangement.

4. Conclusion

The atomistic simulation study confirms that the melting of the crystal is caused by the collapse of the crystal structure, which occurs when, with increasing temperature, the entropy gain ($T\Delta S$) acquired upon obtaining rotational freedom in atomic motion exceeds the energy expense (ΔU) needed for such rotational freedom. The rotational motion of atoms relative to other atoms requires a volume expansion equivalent to a certain fraction of the interatomic distance. This amount of volume expansion, however, is not attainable by thermal expansion at low temperatures and needs an additional increase of the interatomic distance, which gives rise to an energy expense. This energy expense ensures the stability of the crystal structure at low temperature.

With increasing temperature, the energy expense becomes smaller due to the lowering of the potential energy barrier for atomic displacements, which is caused by the anharmonicity of the lattice vibrations. At the same time, there is an increase in the entropy gain when the rotational freedom is obtained. At a critical point, namely the melting temperature, the entropy gain exceeds the energy expense and then melting occurs. Once the obstacles to the atomic displacements, which confine atoms to their lattice points, are removed, the atoms lose their rotational symmetry. The atoms can then reach anywhere inside the system, and fluidity is consequently attained. This phenomenon is why melting occurs instantly at T_m with an abrupt volume change.

Furthermore, the results highlight the importance of surface in the process of melting. The melting of the surface-free crystal is suppressed and superheating by as much as 16 K is required for the melting of the surface-free solid argon. The surface is believed to eliminate the barrier to nucleation of the liquid phase and facilitate the process of

melting. On the other hand, the atomic structure of the surface varies with the temperature, first via surface roughening and then via surface melting.

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