



HAL
open science

ORDER-DISORDER TRANSITION PRODUCED BY DISLOCATIONS IN AN FCC LENNARD-JONES SOLID

E. Jensen, W. Damgaard Kristensen, M. Cotterill

► **To cite this version:**

E. Jensen, W. Damgaard Kristensen, M. Cotterill. ORDER-DISORDER TRANSITION PRODUCED BY DISLOCATIONS IN AN FCC LENNARD-JONES SOLID. *Journal de Physique Colloques*, 1975, 36 (C2), pp.C2-49-C2-54. 10.1051/jphyscol:1975209 . jpa-00216256

HAL Id: jpa-00216256

<https://hal.science/jpa-00216256>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ORDER-DISORDER TRANSITION PRODUCED BY DISLOCATIONS IN AN FCC LENNARD-JONES SOLID

E. J. JENSEN, W. DAMGAARD KRISTENSEN, and R. M. J. COTTERILL

Department of Structural Properties of Materials
The Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark

Résumé. — On a étudié les changements structuraux et thermodynamiques accompagnant une transition ordre-désordre donnée grâce à un modèle pseudostatique calculé par ordinateur.

Les déplacements atomiques entraînés par l'insertion de dislocations parfaites réparties et orientées au hasard ont été répétés jusqu'à saturation. Chaque dislocation résultait de la solution élastique du champ de déformation et on procédait ensuite à une relaxation du système par une technique modifiée de dynamique moléculaire.

La configuration atomique désordonnée obtenue s'apparente à celle d'un liquide.

Une simulation complètement dynamique de la fusion a été ensuite menée à bien au cours de laquelle on a observé la formation de petites boucles partielles de dislocation de type Shockley. La concentration des dislocations va en augmentant lorsque le processus de fusion progresse.

Ces 2 modèles de simulation pseudostatique et totalement dynamique présentent chacun des caractéristiques favorables à une théorie de la fusion faisant appel aux dislocations.

Abstract. — A pseudostatic computational model has been used to study the structural and thermodynamic changes associated with an imposed order-disorder transition. Atomic displacement operations corresponding to the insertion of randomly situated and oriented perfect dislocations were repeatedly performed until saturation was observed. Each dislocation was generated according to the elastic solution for the displacement field and subsequently the system was permitted to relax using a modified molecular dynamics technique. The resulting disordered atomic configuration was found to display a liquid-like structure. In a fully dynamical simulation of the melting process the formation of small partial dislocation loops of the Shockly type was observed. The concentration of dislocations was found to increase as the melting process progressed. Both the pseudostatic and the fully dynamical simulation thus exhibit features which support the dislocation theory of melting.

1. Introduction. — Many different phase transitions exist in nature. Crystals transform from the solid into the liquid and gaseous states, liquids into gases, crystals from one lattice structure into another. Ferromagnets become paramagnetic at a characteristic temperature, etc. The transition solid-liquid is, however, unique among phenomena usually classified as nucleation and growth processes, since the existence of a metastable solid phase is apparently impossible if the stable phase is a liquid. The theory of homogeneous nucleation cannot explain this; it predicts that the rate of formation of liquid nuclei should not become appreciable until the solid is superheated by an amount comparable to the supercooling needed to freeze the liquid. There are two possible explanations for the impossibility of superheating a solid. The first one utilizes the conventional theory of heterogeneous nucleation, and the second one is based on the various lattice theories of liquids which assume a near continuity of state between solid and liquid.

In the heterogeneous nucleation approach it is assumed that under normal conditions melting always begins at the surface of the solid which is able to act

as its own heterogeneous nucleating agent. A liquid droplet formed on the surface will have free energy terms corresponding to the liquid-solid and liquid-vapor interfaces. If the sum of these is less than the free energy of the original solid surface, there is no activation energy for nucleation. The condition for this is that the liquid wets the solid in the presence of the vapor, a condition that is satisfied for most liquids in contact with solid of the same composition. The nucleation theory implies that it should be possible to superheat the solid if liquid can be prevented from forming at the free surface.

In practice grain boundaries and dislocations might be almost equally effective as heterogeneous nucleation sites, so that nearly perfect single crystals are also required.

Various workers [1-6] describe experiments designed to explore this possibility but more convincing demonstrations of the existence of superheating would be necessary in order to reject the prevailing continuity theories and support the theory of heterogeneous nucleation.

The second explanation for the impossibility of

superheating a solid is based on a detailed knowledge of the structure of the solid. At the melting point the long-range order of the lattice is assumed to break down spontaneously at all parts of the solid, so that melting is effectively a homogeneous process without the need for thermally activated nucleation. Theories of this kind fall into three groups, vibrational theories of melting [7-9], mechanical theories of melting [10-12], and order-disorder theories of melting [13-17]. They all suffer from the same drawback, namely that they predict a limit to the stability of the solid regardless of the nature of the phase into which the solid transforms on fusion in contrast to the two-phase theory of melting imposed by thermodynamics. These one-phase theories are thus based on the idea that there is a limit to how much thermal agitation a regular crystal structure can tolerate. The most promising of these theories seems to be the order-disorder theory based on dislocations [18] and the present paper deals with two of the major questions in connection with the dislocation theory of melting; can the liquid structure be produced by a suitable arrangement of dislocations and can dislocations be observed during the melting transition?

2. Models and computational procedures. — In order to answer the first question, the model shown in figure 1 was constructed. An fcc crystal, oriented as

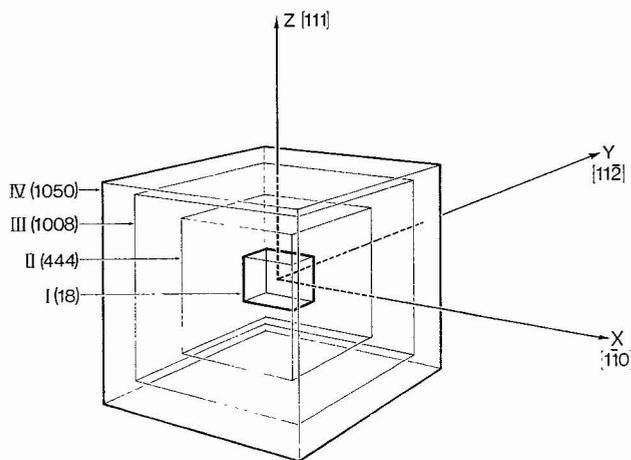


FIG. 1. — Schematic view of the four computational regions of the pseudostatic model system, showing the crystalline axes and the number of atoms in each region.

indicated by the lattice directions of the coordinate axes, was divided into four regions, regions I and II forming the computational cell and regions III and IV forming the boundary. The number of atoms in the different regions are indicated on the figure giving a total number of atoms of 2 520. The atoms interacted through a Lennard-Jones pair potential truncated midway between the second and third nearest neighbor distances. By randomly selecting one of the twelve perfect Burgers vectors of the fcc system ($a/2 < 110 >$,

where a is the lattice parameter) as well as a random direction defining the direction of the dislocation line, and finally selecting at random a point within the computational cell defining the site of the dislocation, a dislocation was generated by imposing the atomic displacements given by the elastic solution [19]. Using a modified molecular dynamics technique, maintaining the neighbor sets obtained from the unrelaxed configuration [20, 21], the atoms of regions I, II and III were relaxed after the insertion of a dislocation, while the atoms of region IV formed an unrelaxed, fixed boundary. As is apparent, region III is a buffer region introduced in order to minimize the effect of the fixed boundary on the computational cell. By repeating the insertion/relaxation procedure, systems with extremely high dislocation concentrations can be realized, since the maintenance of the unrelaxed neighbor sets has a restrictive influence on dislocation splitting and dislocation reactions. For various dislocation concentrations, the model was used to calculate the pair distribution functions at different temperatures and zero pressure. The atoms of region I were used as datum points in the pair distribution function calculation and the pressure was adjusted by linear scaling of the dimensions of the model.

In order to investigate the possibility of observing dislocations during melting a fully dynamical simulation of the melting process was performed. The model consisted of a computational cell containing 336 atoms with imposed periodic boundary conditions. The computational cell, originally arranged in the fcc structure, had the dimensions 7 , $4\sqrt{3}$ and $2\sqrt{6}$ in units of the nearest neighbor distance in the crystal directions $[1\bar{1}0]$, $[11\bar{2}]$ and $[111]$ respectively. The atoms again interacted through the Lennard-Jones potential but in this case the truncation was chosen to be midway between the fourth and fifth neighbor shells. The model was heated to a temperature slightly below the melting point and taken through the melting transition by successive addition of small amounts of kinetic energy. The rate of addition of energy was mainly determined by the requirement of reasonable computing time. The entire experiment was thus accomplished within 1 000 computational cycles corresponding roughly to ten atomic vibrational periods. The atomic configurations obtained during the melting transition were analyzed with respect to the dislocation content and pair distribution functions were calculated. The experiment was carried out under zero pressure conditions, obtained through a successive expansion of the model. The calculations were performed in units of 12ϵ , r_0 , m and k_B , where ϵ and r_0 are the depth and the position of the minimum of the Lennard-Jones potential, m is the atomic mass, and k_B is the Boltzmann constant. The results from both models are presented in these units and for details of the calculations reference is made to the series of papers entitled *Molecular Dynamics Studies of Melting I, II and III* [20, 21, 24].

3. **Results from the pseudostatic model.** — The calculated pair distribution functions for the dislocated crystal is shown in figures 2 and 3. The zero temperature results are shown in figure 2 for increasing dislocation concentration going from bottom to top. A particularly striking feature is that the second peak disappears as the dislocation density is increased.

The same effect is seen in figure 3, showing the results for the same dislocated crystals heated to about half the melting temperature. The effect of the thermal vibrations is thus of a smoothening character, resulting in a decrease of the peak maxima, increase of the peak widths, and a depression of the ripples observed in figure 2.

It was found that the pair distribution functions were not affected by a further increase in the dislocation concentration when this concentration had reached a value of 0.15. As can be seen in figure 4,

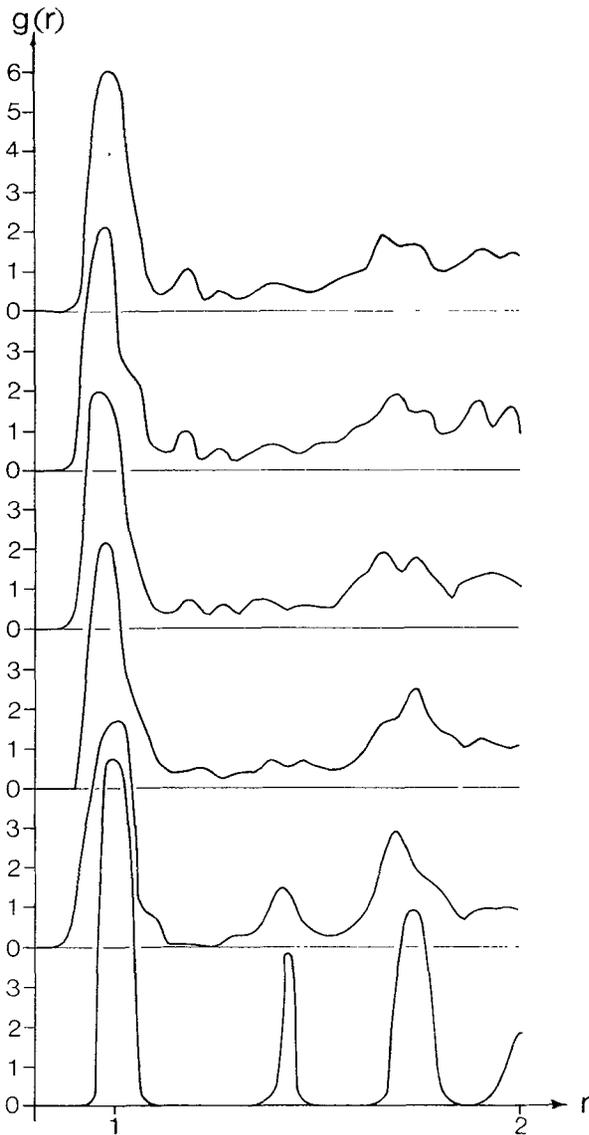


FIG. 2. — The pair distribution functions calculated at zero temperature for the dislocation densities 0.021, 0.073, 0.118, 0.142, 0.163 and 0.185 (reduced units) going from bottom to top.

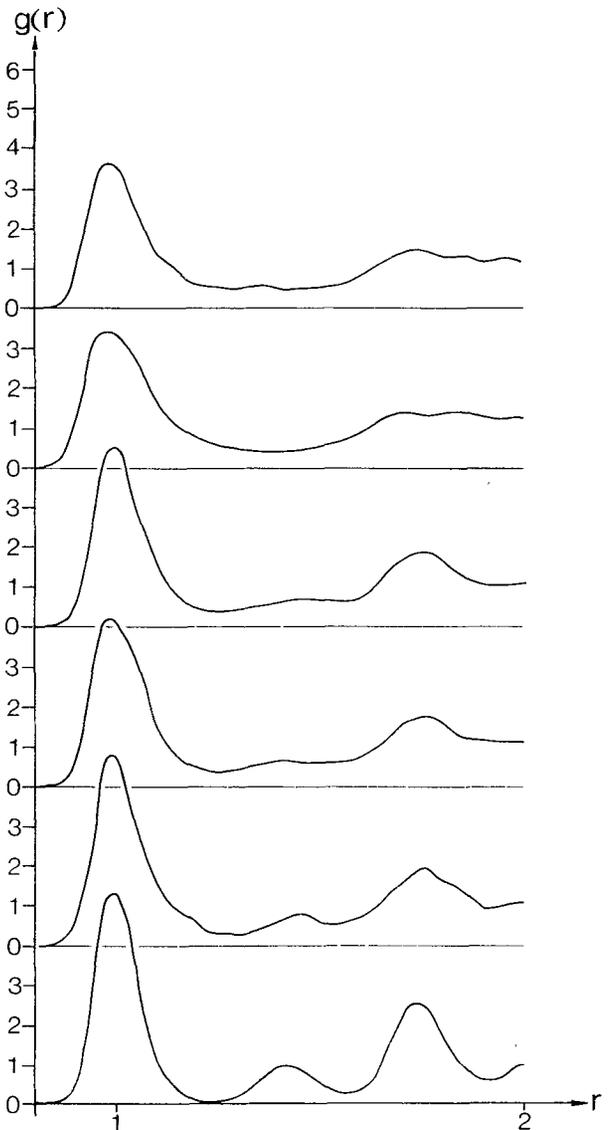


FIG. 3. — The pair distribution functions of figure 2, calculated at the temperature 0.03, corresponding approximately to half the melting temperature. The thermal vibrations have only a smoothening effect on the curves.

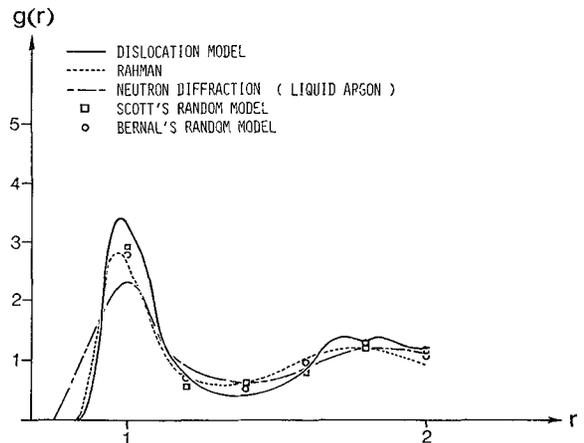


FIG. 4. — The calculated pair distribution function for the temperature 0.03 and the dislocation density 0.163, compared with experimental and theoretical results for comparable systems.

where one of the calculated pair distribution functions is compared with Scott's [22] and Bernal's [22] random packing of hard spheres, with the molecular dynamics result of Rahman [24] and with a neutron scattering experiment [22] on liquid argon, reasonable agreement exists with these comparable systems. From this comparison it transpires that a liquid-like structure is obtained for a sufficiently high dislocation concentration even at low temperatures. Part of the discrepancy observed in figure 4 is probably due to the fact that the pair distribution function is calculated at only half the melting temperature. The reason why higher temperatures were not considered was that the occurrence of self-diffusion would make the dislocation concentration indeterminate.

The influence of the dislocations on the thermodynamic properties of the system was investigated by calculating the potential energy, the vibrational entropy and the expansion caused by the inserted dislocations. In figure 5 the potential energy as a function of the inserted dislocation concentration is shown.

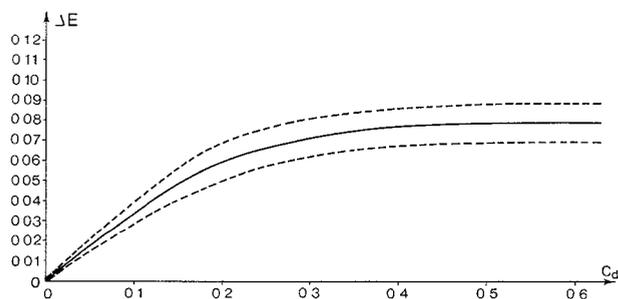


FIG. 5. — The zero temperature potential energy per atom, ΔE , versus inserted dislocation concentration C_d . The saturation value agrees closely with the experimental latent heats of melting of the noble gases. The broken lines indicate the limits of the scatter of 90 measuring points.

The energy is seen to saturate at high dislocation concentrations at a value of 0.0812, which agrees within 2.5% with the experimental latent heats of melting of the noble gases (1). Keeping zero pressure the dilatation as a function of dislocation density can be calculated as shown in figure 6, where the linear expansion of the system is given. The volume expansion saturates at a value of 10.8% which is comparable with the experimental volume change of melting for the noble gases which is close to 15%.

From the results of a harmonic approximation calculation of the vibrational entropy shown in figure 7 and an estimation of the configurational and communal entropy of disordered systems the entropy difference between a crystal saturated with dislocations in which diffusion is allowed and a perfect crystal was found

(1) When referring to experimental results for the noble gases, an average value has been taken for the values for argon, krypton and xenon [25].

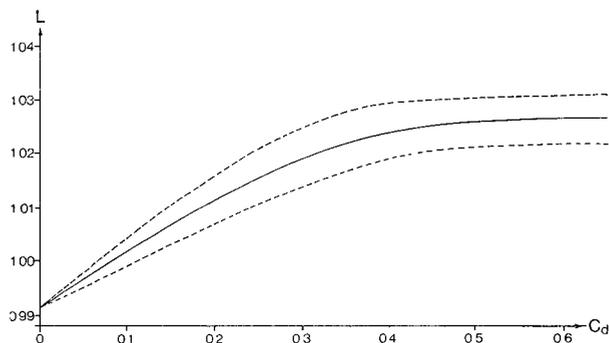


FIG. 6. — Average distance L between nearest neighbors as a function of inserted dislocation concentration C_d . The limits of the scatter is indicated by the broken lines.

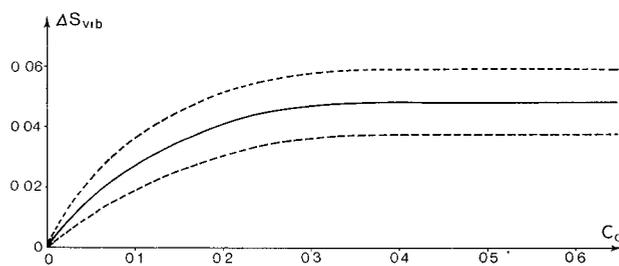


FIG. 7. — The harmonic approximation result for the vibrational entropy per atom ΔS as a function of the inserted dislocation concentration C_d .

to be 1.45. From the equilibrium condition of zero free energy difference between coexisting liquid and solid states

$$\Delta G = \Delta E - T \Delta S \equiv 0$$

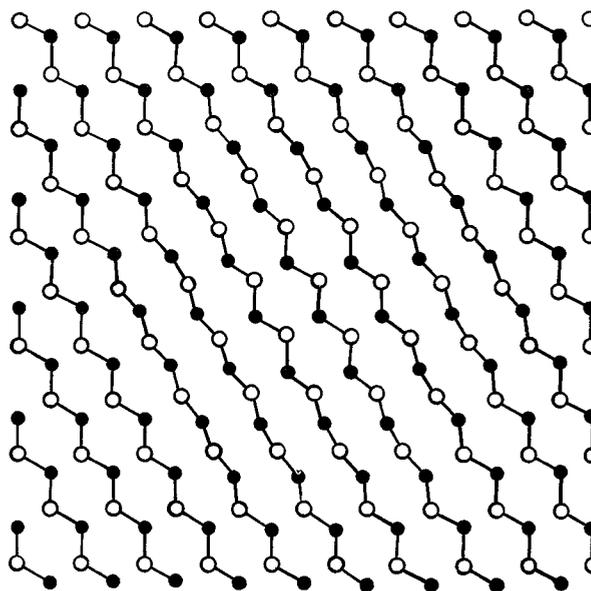


FIG. 8. — Two adjacent close-packed planes (open and closed circles, respectively) containing a Shockley partial dislocation loop encircling a stacking-faulted area. The faulted area is characterized by a shift in the pattern of the introduced linkages.

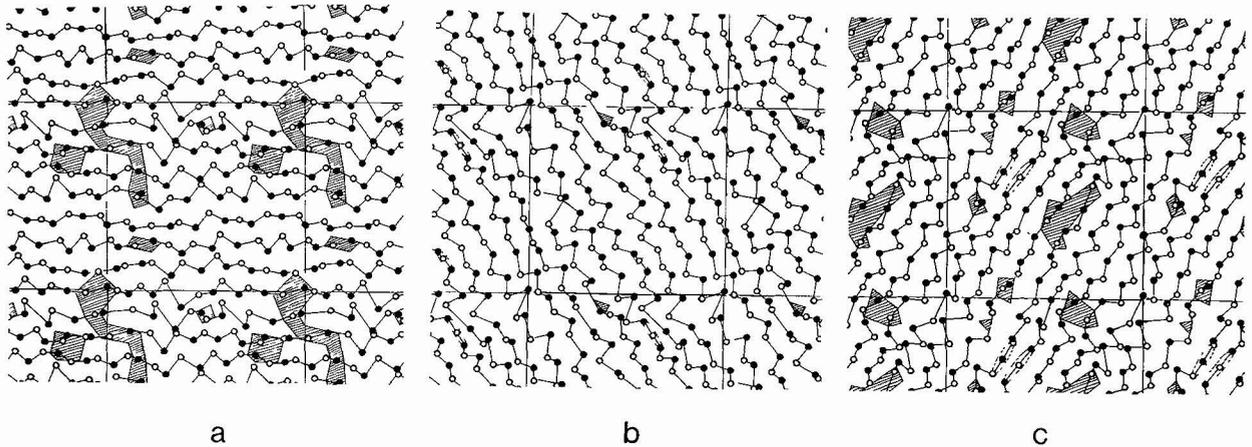


FIG. 9. — Two close-packed neighbor planes analyzed for dislocations in the three possible directions of the Shockley partial Burgers vector. The situation corresponds to an advanced state of melting. The shaded areas are stacking fault areas, revealing numerous dislocation loops.

the transition temperature can be estimated, giving $T_M = 0.056$ which is 12.5 % higher than the melting points of the noble gases. It should be noted that the dislocations inserted in the model fcc crystal all were perfect dislocations. The results extracted from the model suggested that insertion of partial dislocations might result in even better agreement with the experimental data quoted.

Instead of investigating such a model, however, the dynamical simulation of the melting process was performed, since this experiment should also permit one to differentiate between possible defect mechanisms and thus to reveal which defect is in fact responsible for the transition.

4. Results of the dynamic model. — During the dynamical simulation of the melting process the model was analyzed with respect to the occurrence of dislocations. The method applied is illustrated in figure 8, showing two adjacent close packed planes (open and closed circles respectively) in the $[111]$ projection, containing a stacking fault area encircled by a Shockley partial dislocation (Burgers vector of the type $a/6 < 112 >$). By connecting adjacent atoms as illustrated, the faulted area reveals itself by a shift in the characteristic zig-zag pattern. This technique therefore enables one to define the position of the dislocation line. By carrying out this type of analysis in the three possible $< 110 >$ directions in the close packed planes for all the six pairs of adjacent close packed planes of the model, the dislocation concentration was measured at different stages of the melting process. A typical result for a single pair of planes, representing an advanced stage of melting, is shown in figure 9. The shaded areas indicate the stacking fault areas. The atomic configuration was obtained as an average over 50 consecutive computational cycles. A similar analysis with averaging periods of 200 cycles was carried out, and the dislocation concentrations at various stages of the melting process were measured

from these plots. The results are shown in figure 10, where the dislocation concentration against cycle number is plotted. The upper curve gives the results of the 50 cycles averaging period and the lower one corresponds to the 200 cycles averaging period, for which only two average configurations were analyzed. A closer inspection of the 50 cycle averaging plots revealed that very small dislocation loops (point dislocations) frequently formed and disappeared. The difference in dislocation concentration for different averaging periods, as apparent in figure 10, shows that the lifetime of the point dislocation is close to the atomic vibration period (roughly 100 cycles). The increasing slope of the dislocation concentration curve, taken together with the constant energy input rate during the melting process, suggest the dislocation formation mechanism to be of a cooperative nature.

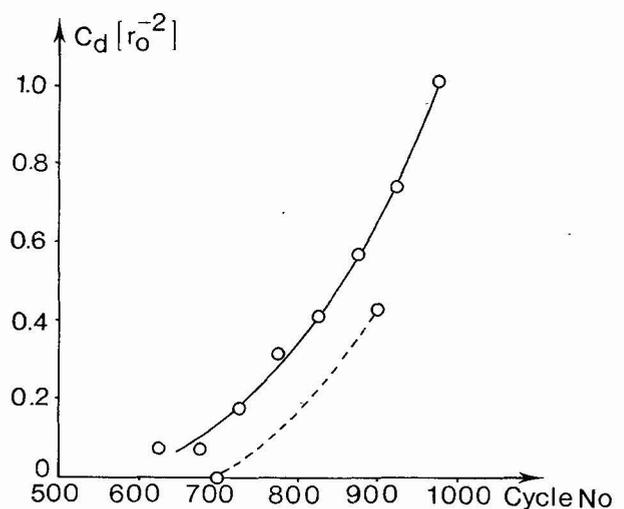


FIG. 10. — The dislocation density as observed during the melting experiment. The solid curve represents average atomic configurations taken over 50 computational cycles, while the broken curve is a suggested connection between the two 200-cycle averaging configurations.

The curve of figure 11, giving the area-to-length ratio as a function of the perimeter length of the dislocation loop, shows that the larger loops develop into a dipolar shape. The average width of a dipole, which can be calculated from the saturation value of the curve, is found to be of the order of twice the Burgers vector. This means that the long-range strain field cancels and that only the core energy contributes to the energy of formation of a dislocation loop. Since the core energy is only a small fraction of the long range strain field energy the narrow dipolar character

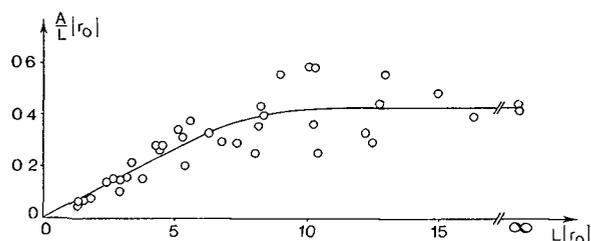


FIG. 11. — The area-to-length ratio for the observed loops as a function of loop-perimeter length. The two points marked « ∞ » represent loops repeating into themselves across the periodic boundaries of the computational cell. For small loop lengths only part of the observed loops are plotted.

of the loops offers an explanation why thermal formation of dislocations can occur at all and thus why dislocations are involved in the melting process.

5. Conclusion. — It has been shown that insertion of randomly oriented dislocations in an otherwise perfect fcc crystal results in a saturated configuration having a liquid-like structure. Using this structure it was possible to calculate melting parameters in reasonable agreement with experimental data for the noble gases.

The dislocation theory of melting has been given further support through the results of the dynamical simulation of the melting process. The results show that the melting process occurring in fcc materials are initiated by thermal generation of Shockley partial dislocation loops. The melting process proceeds both by growth of existing dislocations yielding larger loops with dipole character and by a continuous formation of small loops.

Acknowledgments. — One of the authors (WDK) acknowledges financial support from the Danish Technical Science Research Council (Statens Teknisk-Videnskabelige Forskningsråd).

References

- [1] KHAIKIN, S. E. and BENET, H. P., *Dokl. Akad. Nauk. SSSR* **23** (1939) 31.
- [2] CHALMERS, B., *Proc. R. Soc. A* **175** (1940) 100.
- [3] CHAUDRON, B., LACOMBE, P. and YANNAQUIS, N., *C. R. Hebd. Séan. Acad. Sci.* **226** (1948) 1372.
- [4] PUMPHREY, W. I. and LYONS, J. V., *Nature (Lond.)* **163** (1951) 960.
- [5] SHEWMON, P., *Acta Met.* **5** (1957) 335.
- [6] WEINBERG, F. and TEGHTSOONIAN, E., *Acta Met.* **5** (1957) 455.
- [7] LINDEMANN, L. A., *Z. Phys.* **11** (1910) 609.
- [8] ROSS, M., *Phys. Rev.* **184** (1969) 233.
- [9] IDA, Y., *Phys. Rev.* **187** (1969) 915.
- [10] BORN, M., *J. Chem. Phys.* **7** (1939) 591.
- [11] UBBELOHDE, A. R., *Annual Reports Chem. Soc.* **36** (1940) 167; **37** (1941) 150.
- [12] SIOL, M., *Z. Phys.* **164** (1961) 93.
- [13] FRENKEL, J., *Kinetic Theory of Liquids* (Dover, New York) 1955.
- [14] LENNARD-JONES, J. E. and DEVONSHIRE, A. F., *Proc. R. Soc. A* **169** (1931) 317; **A 170** (1931) 464.
- [15] MORI, H., OKAMOTO, H. and ISA, S., *Progress of Theoretical Physics* **47** (1972) 1087; **48** (1972) 731; **48** (1972) 1474; **50** (1973) 1248.
- [16] MIZUSHIMA, S., *J. Phys. Soc. Japan* **15** (1960) 70.
- [17] KÜHLMANN-WILSDORF, D., *Phys. Rev.* **140** (1965) A 1599.
- [18] COTTERILL, R. M. J., JENSEN, E. J. and DAMGAARD KRISTENSEN, W., *Anharmonic Lattices, Structural Transitions and Melting*, ed. T. Riste (Noordhoff, Leiden) 1974 p. 405.
- [19] HIRTH, J. P. and LOTHE, J., *Theory of Dislocations* (McGraw-Hill) 1968 chap. 3.
- [20] JENSEN, E. J., DAMGAARD KRISTENSEN, W. and COTTERILL, R. M. J., *Phil. Mag.* **27** (1973) 623.
- [21] DAMGAARD KRISTENSEN, W., JENSEN, E. J. and COTTERILL, R. M. J., *Phil. Mag.* **30** (1974) 229.
- [22] BERNAL, J. D., *Liquids: Structure, Properties, Solid Interactions*, ed. T. J. Hughel (New York: Elsevier) 1965 p. 25.
- [23] RAHMAN, A., *Phys. Rev.* **136** (1964) A 405.
- [24] COTTERILL, R. M. J., DAMGAARD KRISTENSEN, W. and JENSEN, E. J., *Phil. Mag.* **30** (1974) 245.
- [25] POLLACK, G. L., *Rev. Mod. Phys.* **36** (1964) 748.