

A Molecular-Dynamics Model for Thermal Failure of the BCC Crystal.

II. Structure

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Abstract – The structure of a stable and a superheated sodium crystal (including a failing one) is studied in a molecular-dynamics model. The radial distribution function of the bcc crystal differs in shape only insignificantly from that of liquid sodium. Variations in the structure of the crystal with increasing temperature are analyzed using the statistical distributions of Voronoi polyhedra and of their elements. Both the bimodal angle distribution of the nearest geometrical neighbors and the abrupt decrease in the number of polyhedra of the cuboctahedron-type point to a complete disorder in the bcc crystal.

INTRODUCTION

Melting is a phase transition of the first order. The crystal can exist above its melting point, T_m , in a superheated state. At the disordering temperature, T^* , the symmetry of the crystal changes stepwise, and the thermodynamic variables experience discontinuity. In any solid there exist shear modes, whereas in a sufficiently large volume of liquid they cannot propagate. The shear modulus μ is directly related to the velocity u of long-wave transverse acoustic phonons, $u^2 = \mu / \rho$, where ρ is the density of the solid.

Part I of this study [1] shows how the elastic properties of the bcc crystal change in the disorder region. Part II deals with structural changes in the same model. The object of study is the sodium crystal. Our goal is, above all, to investigate the physical properties of the superheated crystal and to gain insight into the disordering mechanism. To this end, we use the additive pair interparticle interaction potential [2]. The basic cell consists of 128 particles. The influence of the surface is counteracted by the use of periodic boundary conditions.

The two-dimensional case offers a better grasp of the disorder in the crystal. Melting in “two dimensions” is initiated [3] by the thermal generation of topological defects in the lattice. However, not only do fundamental differences exist between a three-dimensional and a two-dimensional solid, the mechanism by which disorder occurs in the crystal is also different. Melting is related to the loss of order resulting from the short-wavelength fluctuations of atomic displacements. Therefore, studying the short-range variations of atomic packing in the crystal-to-liquid transition region is important. Computer “experiments” offer a way to critically appraise the information that coherent X-ray and neutron scattering experiments yield about the structure of solids.

THE STATISTICAL GEOMETRY METHOD AND THE METRIC PROPERTIES OF VORONOI POLYHEDRA

The point where order gives way to disorder in the crystal is established by a detailed study of the three-dimensional structure using the statistical geometry method based on the construction of Voronoi polyhedra (VP). To each particle (atom) there corresponds a polyhedron which characterizes the particle's environment. The number of faces in the polyhedron is equal to the number of nearest geometric neighbors. The polyhedra tightly pack the space occupied by the particles. We construct VP for the particle configurations averaged at a time interval of $1000\Delta t$, where $\Delta t = 2 \times 10^{-15}$ s, or ~ 3 to 6 periods of oscillation of the atoms [4].

The Voronoi polyhedron of an ideal bcc lattice has the shape of a cuboctahedron. Each vertex of a cuboctahedron is formed by the intersection of three planes. These are standard vertices [5]. A nonstandard vertex of a VP, that is, a vertex formed by the intersection of four or more planes, readily splits into two standard vertices owing to the thermal motion of particles. The shape of the VP also changes owing to the appearance of new elements: fine faces and edges. A VP of the cuboctahedron type is highly stable towards thermal fluctuations (small displacements of particles). Up to a temperature of 354 K the structure of the crystal being modelled is characterized by one type of Voronoi polyhedron – the cuboctahedron (see Fig. 1a). Not until a temperature of 398 K is reached do other types of VP come about. The typical VP corresponding to a bcc crystal in the disorder region has (see Fig. 1b), like the cuboctahedron, 14 faces, each of which differ from each other in size and shape, and the number of edges in a face ranges from 3 to 7. In contrast, a cuboctahedron consists of 6 tetragons and 8 hexagons.

Statistically, the analysis of VP and their elements proceeds in terms of metric and topological features.

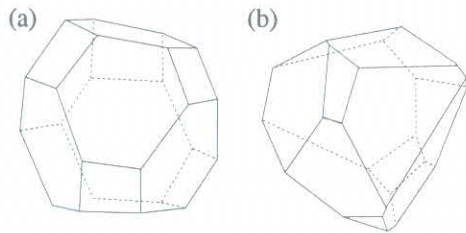


Fig. 1. Voronoi polyhedra of the bcc sodium crystal at $T = 354$ K (a) and $T = 470$ K (b).

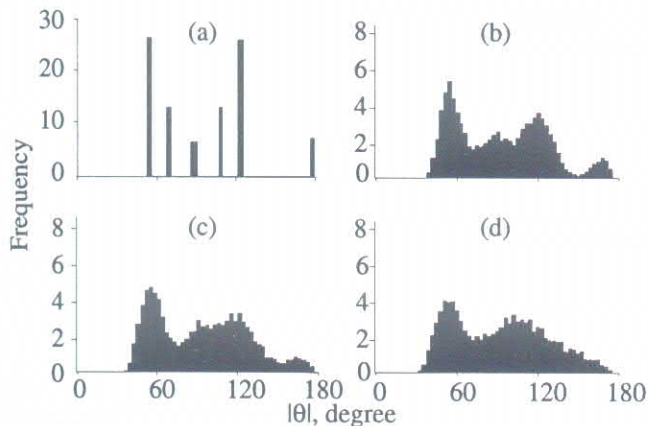


Fig. 2. Angle distributions of nearest geometrical neighbors for crystalline sodium at $T = 354$ K (a), 398 K (b), 453 K (c), and 460 K (d).

The former include the length of an edge; the area of a face; the volume of a VP; the angle formed by any pair of nearest geometrical neighbors, with the corner at the center of the VP. The topological features of polyhedra characterize the distribution of VP by the number n of faces, the distribution of faces by the number m of edges (corners), and the distribution of VP by types which are classified on the basis of topological indices. Furthermore, mixed distributions can be analyzed [6], such as the n - and m -distributions, if the fine VP edges are excluded, or the m -distributions of fine faces. Exclusion of small-scale thermal fluctuations in the form of fine faces and edges makes possible the analysis of the averaged structure of liquid in the model. Of the purely metric and topological characteristics, special mention can be made of the angle distribution of the nearest geometric neighbors and the distribution of VP types specified by topological indices. The structure of the crystal in the model is most precisely identified by means of such distributions. The angles θ made by pairs of nearest geometric neighbors with the central particle, that is, the particle around whose center a VP is constructed, are distributed in the interval $[0, 180^\circ]$. We consider the absolute values of these angles. Up to a temperature of 354 K inclusive, the θ -distributions of the bcc crystal (Fig. 2) are represented by six well-resolved peaks. The first to broaden is the peak at 90° (see Fig. 2a). At a temperature of 398 K (see Fig. 2b) the number of peaks, q , in the θ -distribution decreases to 4. The four peaks are

preserved even at $T_m \approx 423$ K [1], but they are smeared still more. The smeared peaks indicate that the bcc lattice of the crystal suffers distortion due to the thermal motion of atoms. The 90° and 120° peaks almost merge into one at $T = 453$ K (Fig. 2c). The θ -distribution for that temperature of the crystal has only three strongly smeared peaks. This is a distinguishing feature of a superheated crystal. Finally, at the disordering temperature ($T = 460$ K), the θ -distribution takes on the shape of the θ -histogram corresponding to a liquid. This histogram has only two smeared peaks located at 54° and 112° . To the metastable states of the crystal in Fig. 2 there correspond histograms with $q = 3$. The number q for a superheated crystal takes on a value which stands midway between those for a stable crystal and liquid.

DESCRIPTION OF CRYSTAL STRUCTURE IN TERMS OF TOPOLOGICAL INDICES

The type of a Voronoi polyhedron can be defined with topological indices [5]. Each index, n_m , is the number of m -gonal faces in a VP. For example, n_3, n_4, n_5 are the numbers of trigonal, tetragonal, pentagonal, etc. faces in a given polyhedron. Any VP is characterized by a set of topological indices $(n_3, n_4, n_5, \dots, n_j, \dots)$, and

the total number of faces in a VP is $n = \sum_{j=3}^{\infty} n_j$. Statis-

tical analysis of configurations in this case reduces to determining the frequency of the occurrence of a specified list of indices. Figure 3 gives the histograms showing the frequencies of occurrence of sets of topological VP indices for the bcc crystal. They are arranged in increasing order of the probability of occurrence for a VP of a given type. The lists of topological indices are given immediately below the histograms, and the lowest line gives the total number n of VP faces.

In the temperature range from 17 to 354 K inclusive (Fig. 3a), only one type of polyhedron, $(0\ 6\ 0\ 8\ 0)$, that is, a cuboctahedron, occurs. At 398 K, however, other VP types (Fig. 3b) appear, but the cuboctahedron still occurs rather frequently ($\sim 75\%$ of all VP are the $(0\ 6\ 0\ 8\ 0)$ type). As the temperature of the superheated crystal is raised, the number of VP types increases. The structure of the bcc crystal at $T = 453$ K (see Fig. 3c) is dominated by the $(0\ 4\ 4\ 6\ 0)$ type, which accounts for $\sim 32\%$ of all VP modifications. Next in probability of occurrence ($\sim 17\%$) is the $(0\ 6\ 0\ 8\ 0)$ type. Polyhedra of the $(0\ 4\ 4\ 6\ 0)$ type are likewise more probable [7] in the distorted fcc structure that is formed in the MD model. When used alone to identify the structure, the topological indices are unable to distinguish between the fcc and bcc lattices strongly distorted by thermal motion. Both the rhombic dodecahedron, $(0\ 12\ 0\ 0\ 0)$, in the case of the fcc lattice, and the cuboctahedron, in the case of the bcc lattice, are readily reducible topologically to a polyhedron of the $(0\ 4\ 4\ 6\ 0)$ type. The proportion of type $(0\ 6\ 0\ 8\ 0)$ VP decreases with the increasing temperature of the crystal, and at 460 K they

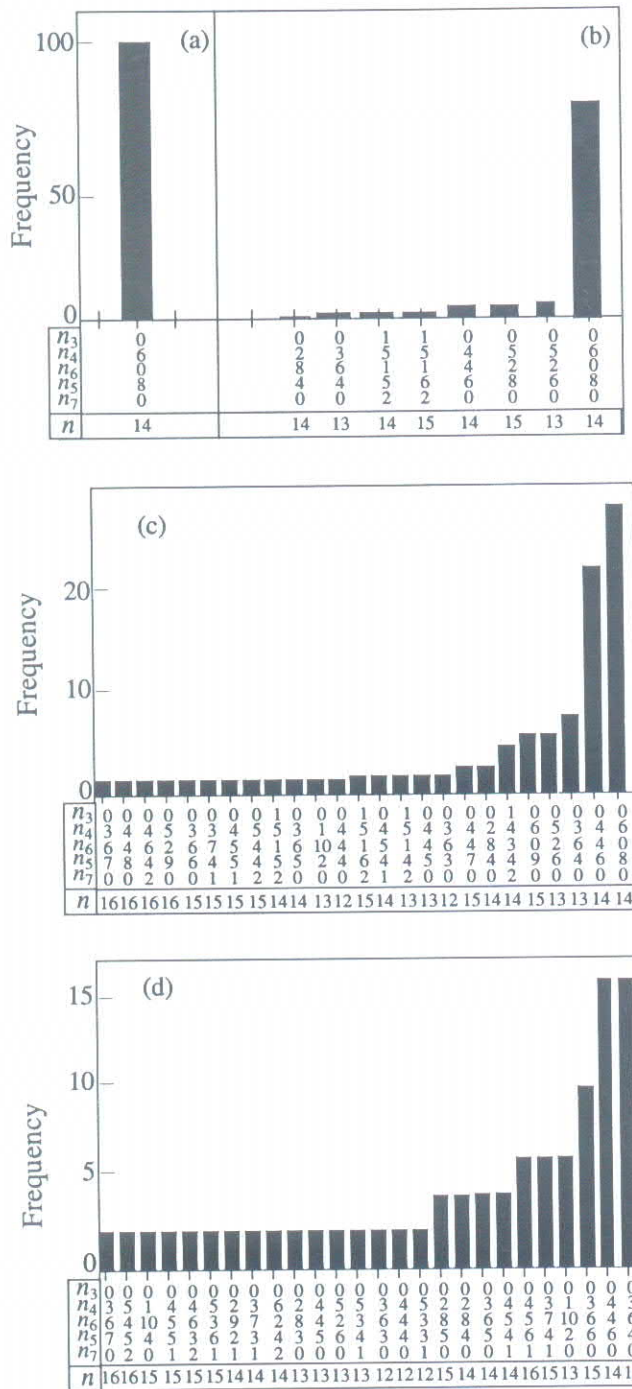


Fig. 3. Frequency of occurrence of VP classified in terms of topological indices in the MD model of the sodium crystal. The temperatures corresponding to (a), (b), (c), (d) are the same as in Fig. 2.

are completely absent (Fig. 3d). Fragments of the bcc structure are not preserved in liquid sodium. The simple liquid, of which molten sodium is an example, shows a certain structural similarity to the Bernal model of irregularly packed solid spheres [8] and does not correspond to the model of a liquid containing paracrystalline microdomains [9]. Up to 30% of the VP occurring upon failure of the crystal are polyhedra of two types:

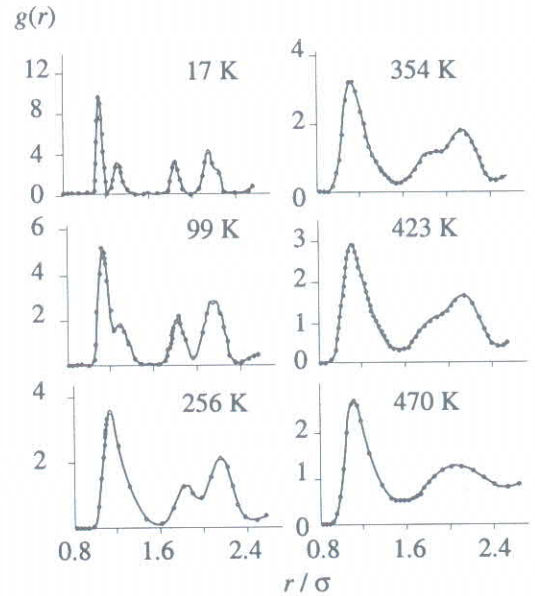


Fig. 4. Radial distribution functions for crystalline sodium.

(0 4 4 6 0) and (0 3 6 4 0). The third most common polyhedron is the pentadecahedron of the (0 3 6 6 0) type; it accounts for not more than 10% of the total number of VP occurring upon failure.

THE RADIAL DISTRIBUTION FUNCTION

The ability of the crystal to scatter X-rays and neutrons in a coherent way is assessed in terms of the structure factor, which can readily be reduced to the radial distribution function $g(r)$ by taking its Fourier transform. Each value of the radial distribution function for a one-component system is given by an expression of the form [10]

$$g(r) = \frac{2v}{4\pi r_k^2 \Delta r N} \sum_{j>i} U([r_i - r_j]^2 - r_k), \quad (1)$$

where $v = V/N$ is the volume per particle, r_k is the radius of the k -th spherical layer described around the center of the i -th particle, Δr is the thickness of the layer, and U is the inverse linear interpolation function

$$U(\xi) = \begin{cases} 1 - |\xi|/\Delta r^2, & |\xi| < \Delta r^2 \\ 0, & |\xi| \geq \Delta r^2. \end{cases} \quad (2)$$

The inverse linear interpolation over particles j is carried out on a grid of concentric spherical cells with a center at the i -th particle.

The calculated $g(r)$ for the bcc crystal, with the exception of the curves corresponding to $T = 181, 423,$ and 460 K, are shown in Fig. 4. Even at 17 K the thermal motion noticeably hinders the identification of the structure. The first four peaks of $g(r)$ are as yet well-defined, but the fifth peak formed by the eight particles of the next coordination shell of radius $R_n = 3^{1/2}a$ (where a is the lattice constant) shows up only as a sub-

peak in the 4th maximum of the radial distribution function. At 99 K, this subpeak disappears completely. Furthermore, the second peak, which reflects the arrangement of six neighbors on the sphere of radius a , appears merely as a subpeak of the first peak. At 181 K, the remainder of this subpeak is but a small "shoulder" which in turn disappears at 256 K. The last of the remaining three peaks merge into one with the next rise in temperature ($T = 354$ K) and form the left-hand shoulder of the last peak. The shoulder is still clearly visible at 398 K and 423 K, becomes very faint at 453 K, and disappears completely at 470 K. The last state of the system is a liquid state. That the second peak of $g(r)$ shows no singularity at this temperature reflects complete irregularity in the arrangement of atoms in the model. In its shape, the radial distribution function near T_m corresponds to the $g(r)$ of a liquid rather than of a crystal.

In summary, the traditional method of structure identification in the model with the aid of $g(r)$ is not as accurate as the statistical geometry method based on the construction of Voronoi polyhedra. The one-dimensional function $g(r)$ inadequately reflects the structural changes that occur in the bcc crystal in the high temperature region.

CONCLUSIONS

The joint statistical analysis of the metric and topological properties of Voronoi polyhedra gives a detailed view of the structural changes that occur during a crystal-to-liquid transition. In the case of the bcc crystal, the radial distribution function, when used alone, does not distinguish unambiguously between the superheated crystal and liquid states. The failure point of the crystal can conveniently be determined from the shape of the angle distribution of the nearest geometric neighbors. The θ -distribution corresponding to the liquid state has 2 peaks ($q = 2$), that of the stable bcc sodium crystal has $4 \leq q \leq 6$, and that of the metastable crystal, $q = 3$. The increase in the superheating of the bcc crystal is accompanied by a decrease in the probability of occurrence for VP of the (0 6 0 8 0) type, this being the basic structural element of the stable sodium single crystal.

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